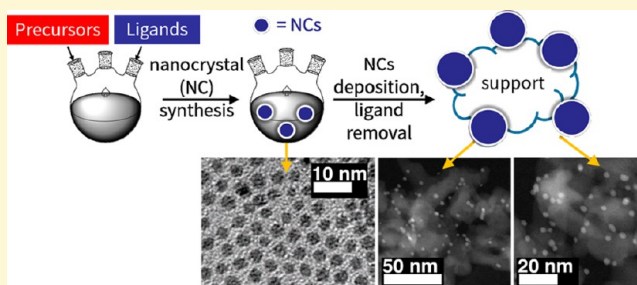


# Colloidal Nanocrystals as Building Blocks for Well-Defined Heterogeneous Catalysts<sup>†</sup>

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**ABSTRACT:** The goal of this perspective is to highlight the use of colloidal nanocrystals in the preparation of heterogeneous catalysts of well-defined structures with the objective to advance catalytic science. Colloidal nanocrystals are prepared with control over size, shape, and composition and are used as precursors to provide supported systems of interest in different areas of catalysis. Advances in the preparation of this class of catalysts are discussed, as well as their use to understand the effect of size, shape, composition, and support chemistry in catalyzed reactions. The use of these materials for microscopy and spectroscopy studies, especially in the investigation of structural changes that occur to catalytic materials, is also highlighted. Finally, challenges and opportunities in the field are discussed to underline prospects and limitations of this approach. It is expected that this area will grow in interest in the future and that these materials will help elucidate several aspects of catalytic science through a systematic approach introduced by using controlled colloidal nanocrystals.



## 1. WHY DO WE NEED WELL-DEFINED HETEROGENEOUS CATALYSTS?

Catalysis has grown in the last decades to become a prominent research area with applications expanding into several different aspects of thermal, photo-, and electro-catalysis. The importance of catalysis is reflected by the fact that much of the chemical industry relies on some catalytic process—indeed, it is estimated that about 90% of the products contain at least one catalytic step in their production, whether it is using a heterogeneous or a homogeneous catalyst. The last few decades also witnessed the growth of catalysis as a science, with the advent of surface science techniques to explore the role of crystallographic facets and atomic scale features on catalytic mechanisms.<sup>1,2</sup> The importance of this progress was highlighted by the Nobel Prize in chemistry attributed to Gerhard Ertl in 2007 for his pioneering work in the area.<sup>3</sup> The idea of building knowledge to design catalytic materials and the huge shift created by the development of computational techniques,<sup>4</sup> allowed us to steer away from trial-and-error approaches that dominated most of the initial progress in the field, at least from an industrial standpoint. An additional change that contributed to this shift in the last two decades is the development of synthesis techniques that allow to prepare materials with much better defined structures than what was available in the past. Zeolites have certainly been the most notable example of this change in paradigm very early on (at least since the 1960s), and their introduction in the petrochemical industry marked a dramatic change in the way we think about catalytic processes at the atomic scale.<sup>5–7</sup>

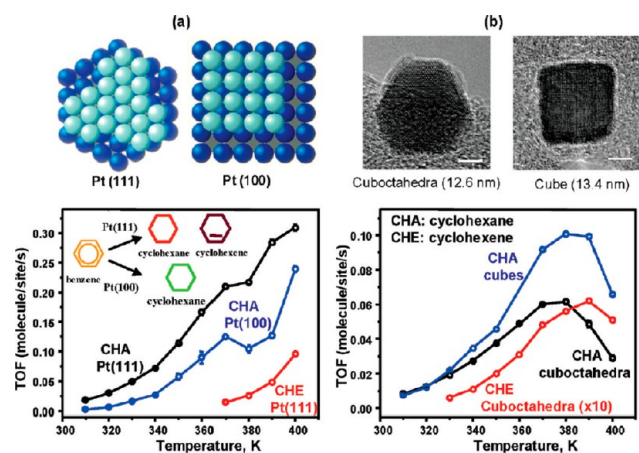
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Tremendous advances in the science of impregnation techniques provided a much more rational approach to develop supported catalysts with better control than previously available.<sup>8–10</sup> In parallel to these efforts, techniques for the preparation of size- and shape-controlled nanomaterials have evolved at a fast pace since the 1990s, with the introduction of synthetic techniques and concurrent fundamental knowledge to control the growth of nanocrystalline materials in aqueous and nonaqueous conditions,<sup>11–23</sup> which opened up opportunities in several areas of science and technology.<sup>24</sup> These synthetic techniques are nowadays so advanced that certain systems can be prepared with precise control over the number of atoms present in clusters and nanoparticles, as in the exemplary case of Au structures.<sup>25–29</sup> The control over size and shape distributions of these nanoparticles and nanocrystals with the aid of surfactants and organic ligands opened up an entire new area of research in catalysis, where single crystalline surfaces are translated into high surface area, supported nanocrystal phases that could be operated under more realistic reaction conditions (Figure 1).<sup>1,30,31</sup> These materials not only demonstrated catalytic performance on par with their conventional counterparts but also improved properties especially when selectivity is concerned, to the point that industry started to commercialize colloidal catalysts for hydrogenation reactions.<sup>32,33</sup> There is clear potential in this area to increase basic knowledge in structure–property relationship studies and in being able to affect catalytic processes at scale.

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**Figure 1.** Catalytic properties of well-defined, nanocrystal-based heterogeneous catalysts are similar to corresponding single crystals, but they can be used under more realistic conditions. (a) Turnover frequency of cyclohexane ( $C_6H_{12}$ , CHA) and cyclohexene ( $C_6H_{10}$ , CHE) formation under benzene hydrogenation on Pt(100) and Pt(111) single crystals. (b) Supported cubic and cuboctahedral Pt nanocrystals tested for the same reaction under 10 Torr of benzene, 100 Torr of hydrogen, and 650 Torr of argon. Reprinted with permission from ref 1. Copyright 2009 American Chemical Society.

Despite the increased interest and potential in using well-defined nanostructures in catalytic processes, there is however, the need for a better focus on what these materials can provide in terms of knowledge and performance compared to those prepared through conventional impregnation routes. There can be indeed the tendency to produce highly sophisticated nanostructures and to rely on simple catalytic tests to demonstrate the usefulness of these structures. However, the focus should be on what questions can be addressed with these materials and how these materials can play a role in shedding light on some poorly understood aspects of catalytic mechanisms, rather than using catalysis as a mere tool to demonstrate the potential applicability of a nanomaterial. It needs to be kept in mind that fabricating complicated nanostructures for large-scale applications, such as almost any catalytic process is, may not be a valuable route since cost of production must be compensated by a large improvement in performance. The scalability of some of these approaches therefore has to be taken into account if one wants to justify their potential comparison with standard impregnation catalysts. It is the goal of this perspective to highlight these aspects and provide the reader with the idea of how well-defined, controlled nanostructures prepared by colloidal approaches can help us answer open questions in the community and potentially form the basis for improved catalysts that can be used at the industrial scale in the near future.

## 2. WHY ARE COLLOIDAL MATERIALS INTERESTING PRECURSORS FOR HETEROGENEOUS CATALYSTS?

The need for synthesis methods that provide higher precision in the preparation of catalytic materials is not new. Entire conferences and books have been dedicated to discussing this topic. Advances have been tremendous, especially in conjunction with improvements in characterization methods such that the structure of catalytic materials could be investigated in much better detail. Impressive advances in the synthesis of supported systems, whether it is metals or

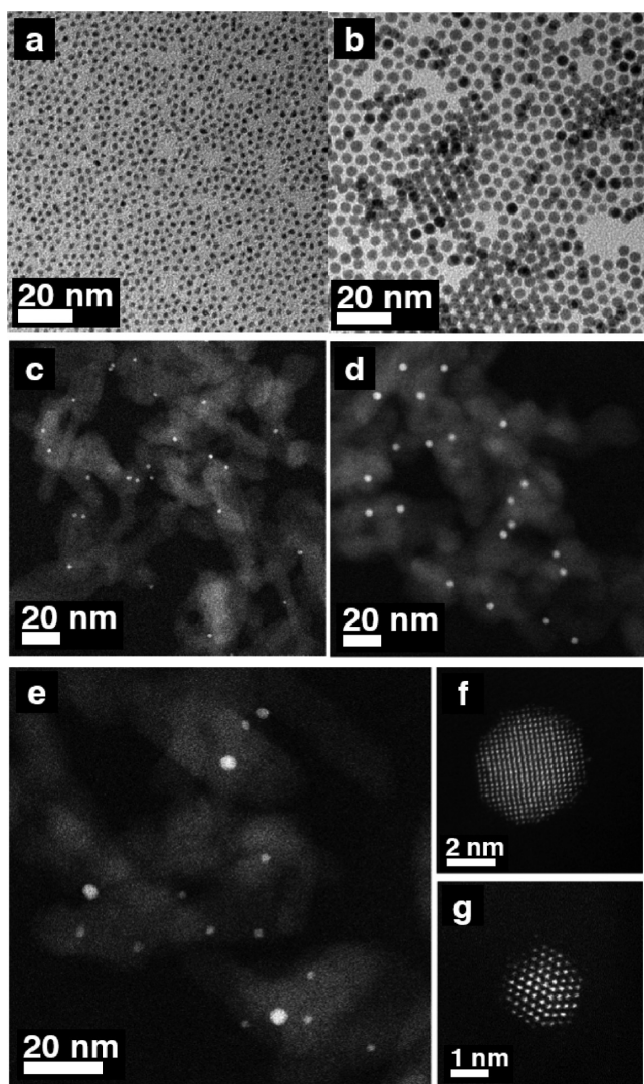
metal oxides, have emerged, with precision of some approaches that does not necessarily compromise their scalability.<sup>8–10,34</sup>

However, catalysts prepared by conventional impregnation methods still lack control over multiple parameters of the synthesis at once, which is one of the advantages of using colloidal nanocrystals. Despite that these methods may achieve control over one or a selected few parameters, it is usually impossible to vary one parameter without affecting others. For example, when preparing a catalyst by conventional impregnation, by varying the support it is rather usual to observe differences in particle size, particle size distribution, and/or shape because of the different interactions between the support and the atomic precursors used during deposition or precipitation. In another often encountered example, changing the metal weight loading usually causes a variation in the average particle size. These effects limit the capability to systematically investigate a single given parameter in heterogeneous catalysts. One of the most appealing impregnation methods to prepare supported systems with well-defined structures is selective electrostatic adsorption, which takes advantage of the electrostatic interaction between charged metal oxide support surfaces (at specific pH values) and charged precursors.<sup>8,10,35</sup> These methods have now been extended to supported bimetallic particles,<sup>9</sup> with precision and scalability that make them very promising for a large range of catalytic reactions. These advances are important, yet even better precision and tunability in the synthesis of nanostructured materials can be useful to further explore a larger parameter space in catalysis. Another relevant issue with conventional impregnation approaches is the fact that, for each precursor/support combination, an optimization study is required in order to be able to tightly control size and size distribution of the supported phases.

One of the main advantages of colloidal nanocrystal methods stands in the ability to independently control the properties of the supported phase and in the ability to tune and engineer it in solution before the impregnation step (Figure 2).<sup>36</sup> This feature allows to independently study how specific parameters affect reactivity, helping disentangle effects that would otherwise become convoluted in conventional materials.<sup>37–39</sup> It is also possible to vary the properties of supported phases while at the same time being able to vary the properties of the support independently. This feature allowed many researchers to use colloidal methods to prepare catalysts for several different applications, including thermal, electro-, and photocatalysts, where supports with different characteristics need to be used (e.g., oxides, carbons, semiconductors). This high degree of flexibility is very appealing to achieve a fundamental understanding of parameters affecting catalytic properties and to improve our knowledge of important elements playing a role in the development of improved catalysts for a variety of reactions.

## 3. HOW CAN CATALYSTS BE PREPARED USING COLLOIDAL BUILDING BLOCKS?

The synthesis of colloidal nanocrystals has been reviewed in many excellent papers.<sup>20,40,41</sup> These materials are soluble in a variety of common organic solvents depending on the choice of ligands and protecting agents for the synthesis. Aqueous-based conditions with water-soluble surfactants or glycol-based systems provide colloidal nanocrystals soluble in polar solvents.<sup>42–44</sup> When using hydrophobic ligands such as amines, carboxylic acids, and phosphines with long alkyl chains, the



**Figure 2.** Colloidal nanocrystals are useful building blocks to prepare uniform and well-defined heterogeneous catalysts. Their synthesis allows control of several parameters including size (e.g.,  $2.2 \pm 0.4$  and  $4.4 \pm 0.2$  nm Pt nanocrystals, TEM images reported in a and b). Once deposited onto high surface area supports such as  $\text{Al}_2\text{O}_3$  (high angle annular dark field-scanning transmission electron microscopy, HAADF-STEM, images in c and d, respectively), they offer the opportunity to independently control several of the catalyst parameters, including obtaining “artificial” bimodal particle size distributions by “mixing and matching” nanocrystal precursors (e) to answer fundamental questions about activity and stability of these systems (f and g are high magnification images of individual 4.4 and 2.2 nm nanocrystals, respectively). Reprinted with permission from ref 36. Copyright 2016 Elsevier.

materials are usually hydrophobic<sup>19,20</sup> and can be manipulated to be made soluble in more polar solvents if needed.<sup>45,46</sup> Because of their properties, colloidal nanocrystals can be treated as molecular precursors for the preparation of catalysts similarly to how salts are used for conventional impregnation processes and can be deposited onto arbitrary supports. The interaction between the colloidal nanocrystals and the support is very important to determine their deposition, as it has been observed that nanocrystal–nanocrystal interactions can drive their aggregation instead of resulting in a homogeneous dispersion on high-surface area supports.<sup>47</sup>

There have been early attempts to use preformed metal nanoparticles for impregnation onto support materials. However, the particles are usually mixed with the support powder and the dispersion evaporated to force the particles to deposit onto the support surface.<sup>48,49</sup> Using this process, an optimal dispersion may not be achieved and preferential deposition of nanocrystals in few regions of the support may occur. Deposition methods that instead rely on specific interactions between nanocrystals and support surface are preferable; however, these interactions can be tricky to understand and control. Zheng and Stucky hypothesized that Coulombic interactions are crucial and proposed the use of aprotic solvents.<sup>50</sup> If protic solvents were used, it was claimed, hydrogen bonding interactions between solvent molecules and hydroxyls on the oxide surface could displace the nanocrystals, thus leading to particle desorption. In chloroform, instead, Au nanocrystals of several sizes up to 6.3 nm could be readily impregnated, leaving a clear supernatant indicating the successful and complete deposition of the nanocrystals on different oxide materials (Figure 3). It must be kept in mind though that this process highly depends on the nanocrystal and support composition.



**Figure 3.** Deposition of 6.3 nm Au nanocrystals capped with dodecanethiol (vials on the left) on several oxide supports in chloroform. The powders settle at the bottom of each vial leaving a colorless supernatant and indicating a complete deposition of the nanocrystals on the support surface. The nature of the solvent is crucial for a successful deposition. Reprinted with permission from ref 50. Copyright 2006 American Chemical Society.

In a previous study suggesting the important role of electrostatics in nanoparticle deposition, Grunwaldt and coauthors showed that the adsorption of small, negatively charged Au colloids could be performed on several supports only by regulating the solution pH such that hydroxyl groups were protonated and positively charged.<sup>51</sup> Therefore, multiple parameters such as solvent, temperature, concentration, and

presence of organic compounds (excess ligands) can play a role in the deposition process. This aspect further highlights the similarity between nanocrystal and atomic precursors in the preparation of catalysts, where specific intermolecular forces need to be taken into account to achieve satisfactory deposition and dispersion. As a consequence, specific processes for the deposition need to be implemented if the interactions are unfavorable: for example, by modifying the surface chemistry of the support<sup>52</sup> or by modifying the deposition conditions to manipulate the nanocrystal–support interactions.<sup>47</sup> An example of the latter is performing the deposition process in solution at high temperature, which leads to the facilitated diffusion of the nanocrystals into the inner pores of the support and their more homogeneous deposition.<sup>47</sup> Diffusion can be indeed one of the main issues in achieving optimal dispersions, as industrial carriers are usually pellets of macroscopic size (rather than powders) that pose further complications to the homogeneous dispersion of the active phase across the whole available surface area of the support. An inhomogeneous deposition of the active phase may in fact lead to sintering, loss of active surface area, and reduced catalytic performance.<sup>53</sup> Furthermore, successful deposition depends on the pore size and pore size distribution of the support since nanocrystals with hydrodynamic diameter (i.e., including organic ligands on their surface) larger than the average support pore size are excluded from most of the support available surface area. When this is the case, either a different support must be chosen or other strategies need to be implemented, such as, for example, the synthesis of the support material around the colloidal nanocrystals in core–shell-type structures.<sup>54–60</sup> Despite the recent increased amount of work on studying the deposition processes of colloidal nanocrystals to prepare well-defined catalysts, the science behind them remains still mostly empirical and a better understanding of the forces in play is needed in order to guarantee a better dispersion without mass transfer limitations. This area therefore represents a fruitful topic of investigation for both the colloids and the catalysis communities.

Following deposition of NCs on a support, ligand removal is an often necessary step for the activation of the materials for catalysis. Noteworthy are recent reports on the improvements in selectivity for certain processes when organic ligands are present on the surface of supported metal particles,<sup>61–63</sup> an exciting area of investigation. Nevertheless, in most cases ligands hinder the active surface accessibility, leading to much decreased, and most often completely blocked, catalytic activity. Several processes have been developed in order to remove ligands from supported colloidal nanocrystals depending on the nature of the ligands and materials. Treatments under an atmosphere of ozone and while exposing a catalyst powder to UV light (UV–ozone treatments) have been shown to promote ligand removal and catalyst activation.<sup>64,65</sup> These treatments could be very effective but tend to be limited by the availability of ozone and by the exposure of the materials' surface to the light and cannot therefore be scaled up very easily. Other treatments rely on washing steps to remove organics based on equilibrium reactions between adsorbed and free ligands<sup>66</sup> or on specific ligand chemistry such as acid–base interactions,<sup>67</sup> but their efficacy is not complete, this requires the use of large amounts of solvents, and this could cause changes in the supported catalysts during the treatment conditions. Electrochemical steps for removal of ligands from supported particles to prepare electrocatalysts have also been

shown to be promising in activating these materials,<sup>67</sup> although they can only be performed on conductive substrates (such as carbon). Finally, recently we also showed how rapid thermal treatments under oxidizing atmospheres can be used to activate colloidal catalysts by removing organic ligands without affecting particle size distribution and shape,<sup>68</sup> but the specific conditions and length of the thermal treatment need to be tailored based on the material system. Overall, for any method, there still is the question whether the carbon is completely removed from the particle surface, especially since recent studies showed that small amounts of residual carbon can be left behind even under conditions that are thought would lead to complete removal of organic species.<sup>69</sup> In addition to carbon, other elements contained in common surfactants (S, P, Cl, Br, etc.) must be carefully considered, as ligand removal strategies may remove carbon but leave other species behind that can result in the poisoning of the catalyst surfaces. Bottom line, there is no “one size fits all” type of treatment, and depending on the system of interest, a choice needs to be made over which process could be most effective.

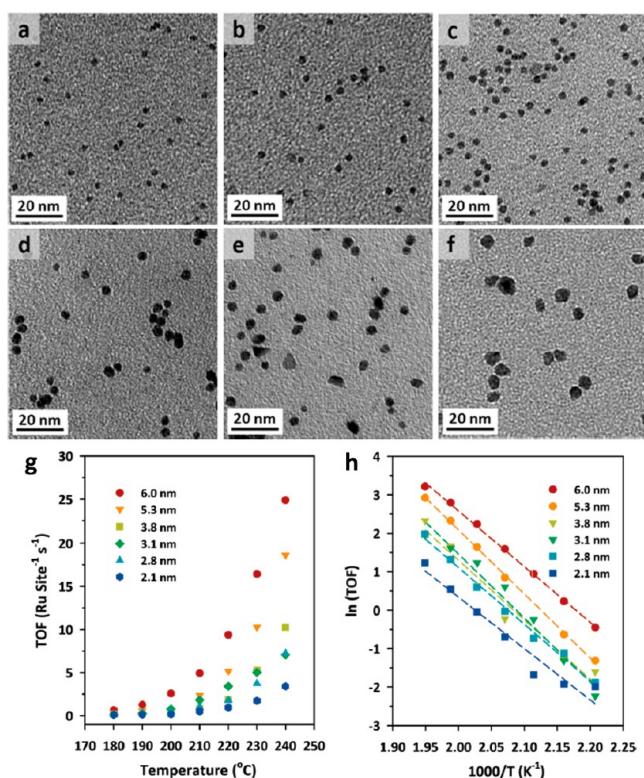
#### 4. WHAT CAN WE LEARN WITH CATALYSTS PREPARED USING COLLOIDAL NANOCRYSTALS?

Research interest in catalysts prepared using colloidal nanocrystals has been increasing in the past decade for a variety of catalytic applications. Among the work done in this area, common elements can be discerned in the way these materials have been used to increase the specific activity or selectivity of a certain catalytic process, but more importantly to gain fundamental understanding of several parameters that play a role in tuning and improving performance. Some of the most relevant topics that have been thoroughly investigated are reported here to highlight how colloidal materials can help elucidate different aspects of heterogeneous catalyzed reactions.

**4.1. Systematic Structure/Property Relationship Studies To Investigate the Effect of Individual Parameters in Catalytic Reactions.** The opportunity to investigate individual parameters and identify their role and importance on the final performance of a catalyst is one of the most appealing aspects of using colloidal building blocks. Obviously, not every parameter can be tuned via this approach, and not all catalysts can be studied, but certainly a large number of systems could be systematically investigated. Some of the most important parameters are discussed in the following sections.

**4.1.1. Size Effects.** In the large parameter space that researchers in catalysis and materials chemistry have to navigate when studying heterogeneous catalysts, the effect of particle size is prominent. Catalytic processes occur on surfaces, and atom coordination is crucial to break and form chemical bonds in reactants and products. At varying particle size, the fraction of particular sites being exposed to reactants can change drastically, and the coordination environment of surface atoms plays a significant role in their reactivity.<sup>70</sup> The different catalytic properties of sites or ensemble of sites as a function of particle size give rise to effects known to provide structure sensitivity.<sup>71</sup> Some reactions only depend on how many active sites are exposed, and these are structure-insensitive reactions, such as hydrocarbon hydrogenation reactions.<sup>72</sup> However, if a catalyst shows changes in rate (normalized by surface atoms) as the particle size is varied of at least a few times (more conservative views would suggest an order of magnitude), then the reaction is labeled structure-

sensitive. Understanding whether reactions are structure-sensitive is important to adequately tune the catalyst for maximum performance, but this aspect can be challenging because reactions can be sensitive to very small variations in active phase size even to few atoms.<sup>73,74</sup> Colloidal materials with precise control of size offer a unique opportunity to study the structure sensitivity of catalytic reactions. Even reactions that were previously thought to be structure-insensitive have then been found to be structure-sensitive using colloidal nanocrystal precursors, such as in the case of CO oxidation,<sup>75</sup> confirming observations from past work.<sup>76</sup> It was indeed more recently demonstrated that arrays of colloidal Ru (oxide) nanocrystals with uniform size showed up to 8 times difference in rates when the unsupported Ru phase was varied between 2 and 6 nm.<sup>77</sup> Interestingly, the largest particles showed the highest rate (Figure 4).



**Figure 4.** TEM images of Ru nanocrystals with different sizes: (a) 2.1, (b) 2.8, (c) 3.1, (d) 3.8, (e) 5.0, and (f) 6.0 nm. Arrays of these nanocrystals were tested for CO oxidation, resulting in turnover frequencies (g and h) that demonstrated structure sensitivity, with larger nanocrystals performing better than smaller ones. Adapted with permission from Reference<sup>77</sup>. Copyright 2010 American Chemical Society.

The same reaction may be structure-sensitive on some supports and structure-insensitive on others, depending on the conditions and materials used. For Pt-group metals supported onto inert oxides, like SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, the reaction rate is proportional to the exposed metal surface. However, we demonstrated that, by tuning the particle size between 1.6 and 12 nm for Ni, Pd, and Pt nanocrystals and depositing them onto a ceria support, the role played by the metal/ceria interface on the CO oxidation activity is to introduce structure sensitivity.<sup>78</sup> The same particles deposited onto alumina did not show structure sensitivity, thus further proving that the

ceria support participates in the reaction by providing activated oxygen species at the metal–support interface.<sup>79</sup> The knowledge can be used to design more active materials, such as single-atom catalysts with maximized efficiency in noble metal usage.<sup>80,81</sup> The structure sensitivity can be reversed when studying other reactions, such as is the case of methane steam reforming. We found that the production of CO and CO<sub>2</sub> (in addition to H<sub>2</sub>) was strongly correlated to the size of Pd nanocrystals on an alumina support but not on ceria; in this case, the oxygen-donating ability of ceria promotes the water–gas shift activity of supported Pd of any size, leading to the same catalytic output for different sizes. The Pd supported onto the inert alumina that does not participate in the catalytic cycle showed instead size-dependence in the reaction selectivity.<sup>68</sup>

The size-dependence may also result in complex behavior when relating performance with particle size. A well-known example of a structure-sensitive reaction is the Fischer–Tropsch synthesis on Co-based catalysts, where larger particles are known to be more productive than smaller ones, and several studies set an optimum nanoparticle size around 8–10 nm in terms of hydrocarbon productivity.<sup>82–84</sup> Colloidal cobalt nanocrystals have been used to shed further light on this topic, and well-defined Co<sub>3</sub>O<sub>4</sub> nanocrystals supported on alumina showed an optimum at 9.3 nm, with maximized CO conversion and hydrocarbon productivity, in line with previous studies. It is likely that this specific size shows an optimum content of Co atoms or ensembles with appropriate coordination geometry.<sup>85</sup> A similar conclusion is found with Fe-based catalysts that have also been prepared from colloidal nanocrystals.<sup>47,86</sup> The colloidal route certainly is a promising approach to exquisitely control the size of the active phase in reactions that are structure-sensitive.

Similar challenges and opportunities in explaining and exploiting size-dependent activity are found in electrocatalysis. In this field, complications arise not only because of the potential restructuring of the materials under applied potentials or due to leaching but also because of the adsorption of species during reaction conditions that can strongly modify the reactivity of specific facets/sites. In the case of Pt materials for oxygen reduction reaction it has been indeed observed that smaller Pt particles are poisoned by the adsorption of electrolyte compounds on some facets, thus leading to suppressed activity compared to larger particles.<sup>87</sup> This result is surprising given that, more commonly, smaller particles show higher rates because of the more favorable surface-to-volume ratio; however, this result was in line with previous studies on polycrystalline foils.<sup>88</sup> Size effect can play a role beyond adsorption and reactivity especially when multiple phases are involved, as it has been elegantly demonstrated in Au/Fe<sub>3</sub>O<sub>4</sub> heterodimer particles for electrocatalytic production of H<sub>2</sub>O<sub>2</sub>.<sup>89</sup>

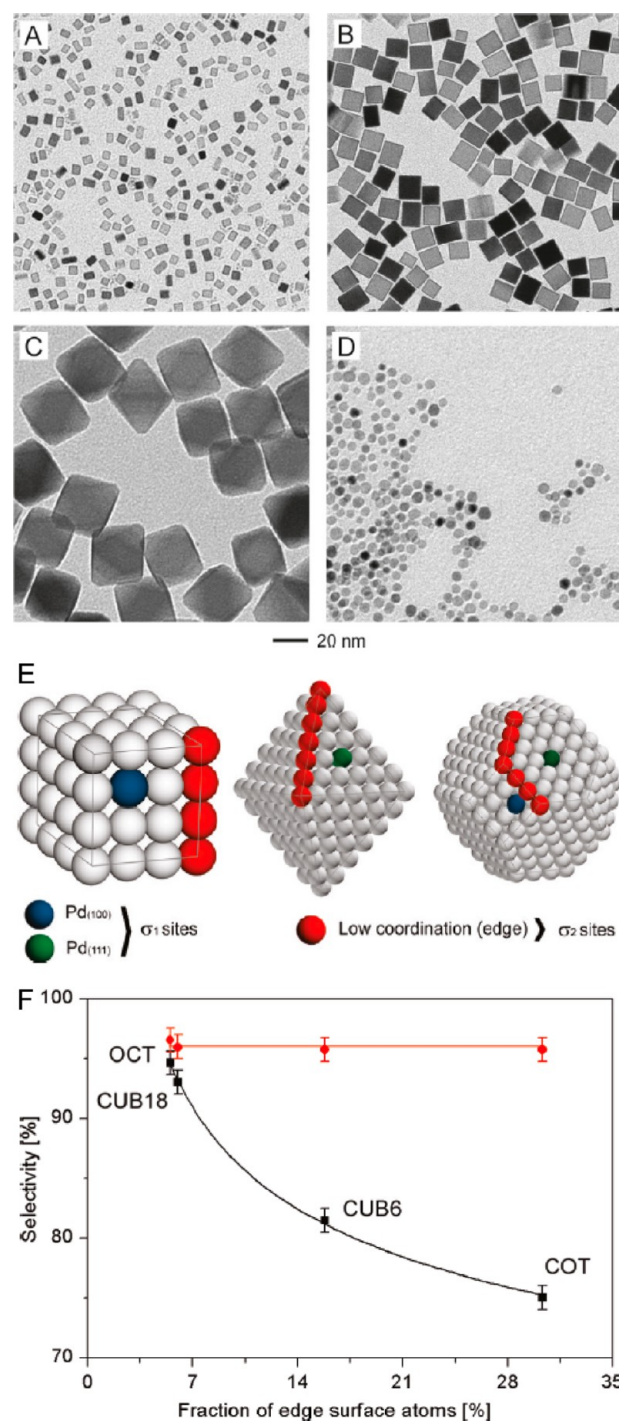
**4.1.2. Shape Effects.** Colloidal nanocrystals are particularly useful in correlating the catalytic performance with exposed crystallographic planes or facets in a way similar to the use of single crystal surfaces. Catalytic rates, for example, for nanocrystals that expose a specific facet are found to be very close to what is observed in single-crystal experiments,<sup>1,72</sup> but the catalysts can be operated under more realistic reaction conditions. Tuning the nanocrystal shape allows to control the type and fraction of exposed facets, thus providing the ability to study the influence of geometric arrangements of atoms on the catalytic performance.<sup>2</sup> Many excellent reviews showcase

the capabilities in synthesizing nanocrystals with controlled facets and morphology with impressive control.<sup>43,90,91</sup> Still, a deeper understanding of the mode of growth and morphology control in these materials is needed to discover mechanistic pathways to specific compounds.<sup>92,93</sup> In most cases, the presence of surface ligands helps stabilize facets that would otherwise not normally be formed according to Wulff construction rules.<sup>94</sup> However, because ligands need to be removed to allow catalytic reactions, reaction conditions unavoidably induce reconstructions that make shape control challenging to study. These effects must be taken into account when investigating this topic through accurate characterization of the materials before, after, and, if possible, during catalysis with in situ and operando techniques to evaluate eventual structural changes brought by the reaction conditions. Liquid-phase conditions may suffer less of these problems because of the possibility of using ligand-protected nanocrystals for reactivity studies. Especially when high-energy facets can be stabilized and exposed to reactants, it is possible to observe increased reaction rates when the most stable facets would instead show lower rates.<sup>95</sup>

In seminal work on shape-control of nanocrystals for liquid-phase catalysis, it has been shown how selectivity in hydrogenation reactions using Pd catalysts can be controlled and studied using shape-controlled nanocrystals (Figure 5).<sup>96,97</sup> With this level of control, turnover frequencies can be mathematically derived for atoms with different coordination and geometry, thus being able to extract kinetic parameters.

Shape control has been widely investigated in electrocatalytic applications, and Pt is one of the most studied systems and a prototypical example.<sup>98</sup> The field developed from the study of single-crystal materials with clean crystallographic orientations to the preparation of nanostructured materials with control over the exposed facets.<sup>99</sup> On this subject, there have been a countless number of examples where nanocrystal shapes expose mostly combinations of low-index facets but also more exotic shapes where high index planes are present.<sup>100,101</sup> Similar studies have been expanded to novel electrocatalytic materials such as transition metal phosphides as well, although with a more limited choice of shapes,<sup>102</sup> and to assemblies of nanocrystals.<sup>103</sup> However, some fraction of the work related to Pt-based electrocatalysts has been mostly focused on producing and testing materials, with sometimes poor fundamental understanding.

Shape effects are not only limited to metal phases: metal oxides have also been heavily investigated because of their wide applicability in catalysis.<sup>104,105</sup> The advantage in studying metal oxides is that they are usually more stable compared to their metal counterparts under reaction conditions, in particular at high temperature, such that methods to remove ligands and stabilize metal oxide nanocrystals can be successfully applied.<sup>106,107</sup> Shape-controlled metal oxide nanocrystals have been useful in clarifying trends on the reactivity of specific facets in debated areas, such as, for example, in the improved activity of TiO<sub>2</sub> facets with high surface energy such as the (001) facets.<sup>94,108</sup> Being able to produce titania nanocrystals with controlled fractions of exposed (101) and (001) planes was crucial to demonstrate that, under photoreforming conditions, the high-energy (001) facet delivers lower hydrogen production rates than nanocrystals with mostly (101) facets exposed.<sup>109</sup> Interestingly, samples with about 50% of each facet exposed delivered rates that were intermediate



**Figure 5.** TEM images of polyvinylpyrrolidone (PVP)-stabilized Pd nanocrystals: (A) 6 nm cubes (CUB6), (B) 18 nm cubes (CUB18), (C) 31 nm octahedral (OCT), and (D) 5.5 nm cuboctahedra (COT). (E) Studying the hydrogenation of 2-methyl-3-butyn-2-ol (MBY) on Pd nanocrystals, two types of active sites are involved: atoms on the planes, regardless of their crystallographic orientations, constitute one type of active site,  $\sigma_1$ ; low-coordination atoms, or atoms at the edges, represent another type of active site,  $\sigma_2$ . (F) Selectivity toward the target product, 2-methyl-3-buten-2-ol (MBE), at 50% (circles) and 95% (squares) conversion of MBY and as a function of  $\sigma_2$  sites. Adapted with permission from ref 96. Copyright 2011 American Chemical Society.

between the two extreme samples, validating the results regarding the activity of specific facets. These shape-controlled

titania nanocrystals could also be employed under conditions more commonly used in the surface science community, thus helping to bridge a gap with high-pressure reaction studies. Under these conditions, titania shape was shown to exhibit a strong influence on the reaction selectivity in the photocatalytic conversion of organic compounds.<sup>106,107,110,111</sup> Nanocrystal shape can also drastically affect the location of specific catalytic events,<sup>112</sup> such that shape engineering can result in improved activity thanks to better manipulation of reactivity patterns occurring on the surface as well as processes occurring in the bulk of the nanocrystals.<sup>113</sup> Despite it is certainly true that fluxionality and reconstructions can exist in solution during liquid-phase catalysis as well as in the gas phase,<sup>114,115</sup> this approach can nevertheless be useful in understanding how to tailor chemical selectivity in reactions where multiple product pathways are possible.

**4.1.3. Composition Effects.** The activity and selectivity of heterogeneous catalysts may very much benefit from the combination of multiple elements contributing to form the active site. There are countless examples of industrial processes that are performed using alloyed phases or mixed oxide solid solutions. One of the most useful properties of these materials is their tunability, which can be more widely manipulated compared to their single-element counterparts. Clearly, the same reason why these materials are more interesting also make them more challenging to study: more parameters and experimental conditions need to be controlled. Here again, the ability to control the concentration and location (in some cases) of several elements is crucial to understand the role of multiple phases on the overall final activity and stability of the catalysts. There are different reasons for tuning the composition in nanocrystal catalysts: (i) increase the intrinsic reactivity of a catalyst by introducing a bifunctional mechanism or promoter effects; (ii) increase its stability by limiting deactivation phenomena; and (iii) improve the efficiency in using precious elements.

Promoter effects are important but the understanding of if and how a second element promotes an active phase is not an easy task. Being able to precisely position the promoter atoms such that they can have an effect on the active phase is challenging, especially when relying on common impregnation techniques. In this case, the use of bimetallic nanocrystals as precursors to promote the localized segregation of a second metal<sup>116</sup> is a viable alternative to achieve geometric precision, such that multiple phases can be fairly compared under the same reaction conditions.<sup>117</sup>

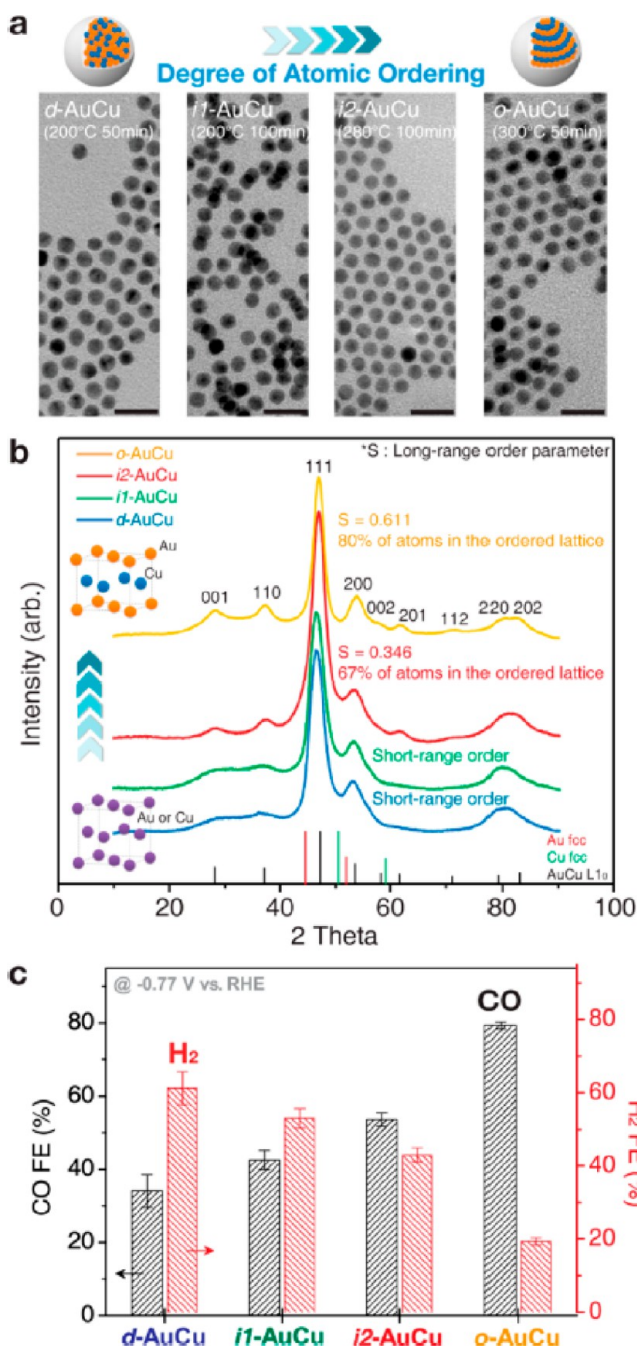
In thermal catalysis and especially in electrocatalysis, composition effects have been used to tune the adsorption energy of reactants on metal substrates by introducing strain, increasing the intrinsic reactivity of catalytic sites, and introducing novel adsorption binding motifs.<sup>118–120</sup> Compressive and tensile strain may lead to large changes in catalytic activity,<sup>121</sup> depending on the active phase and the reaction of interest. The possibility to tune strain by changing composition in surface alloys has led to a large number of investigations related to Pt-based nanocrystal systems for several electrocatalytic applications, and in particular for the oxygen reduction reaction.<sup>122–126</sup> In this case, tuning the strain leads to a change in the oxygen binding energy, which is slightly too strong in pure Pt resulting in nonoptimal performance. Therefore, the introduction of a second metal (or an alloy) in the core to support a thin shell of Pt has become one of the most studied nanocrystal systems.<sup>127–129</sup> Among these studies,

recent work on Pt supported on carbide and nitride materials using clever colloidal processing through silica templating is especially notable because of the high thermal stability of the obtained materials and their beneficial electrocatalytic properties.<sup>130,131</sup> It is interesting to note that similar concepts served as the hypothesis driving the development of materials using dealloying techniques, i.e., processes where a bimetallic or alloy nanocrystal is prepared, and then one of the components (usually a base metal) is removed through leaching or electrochemical processing.<sup>132,133</sup>

It is often the case that multiple effects may contribute to the overall performance of bimetallic phases, and being able to prepare nanocrystals with a range of compositions is especially useful. Libraries of nanocrystals can be prepared using seed-mediated approaches, where a nanocrystal seed is used to grow bimetallic or multimetallic materials with control over size provided by the initial seeds.<sup>117,134,135</sup> Libraries of Au/Cu nanocrystals prepared in this way, for example, have been used to demonstrate trends in the CO<sub>2</sub> electrocatalytic reduction to CO and other products, with Au-rich materials producing CO more selectively, whereas Cu-rich materials produce multiple products.<sup>136</sup> Interestingly, materials with intermediate composition provided a gradual transition in product formation between the two extreme pure phases. In similar work, it was also shown that the crystallographic order (or disorder) of alloyed phases could very much impact the catalytic properties to the point that disordered (alloyed) Au/Cu nanocrystals were shown to be more active for electrocatalytic hydrogen evolution, whereas ordered (intermetallic) counterparts were much more selective toward CO<sub>2</sub> reduction to CO (Figure 6).<sup>137</sup>

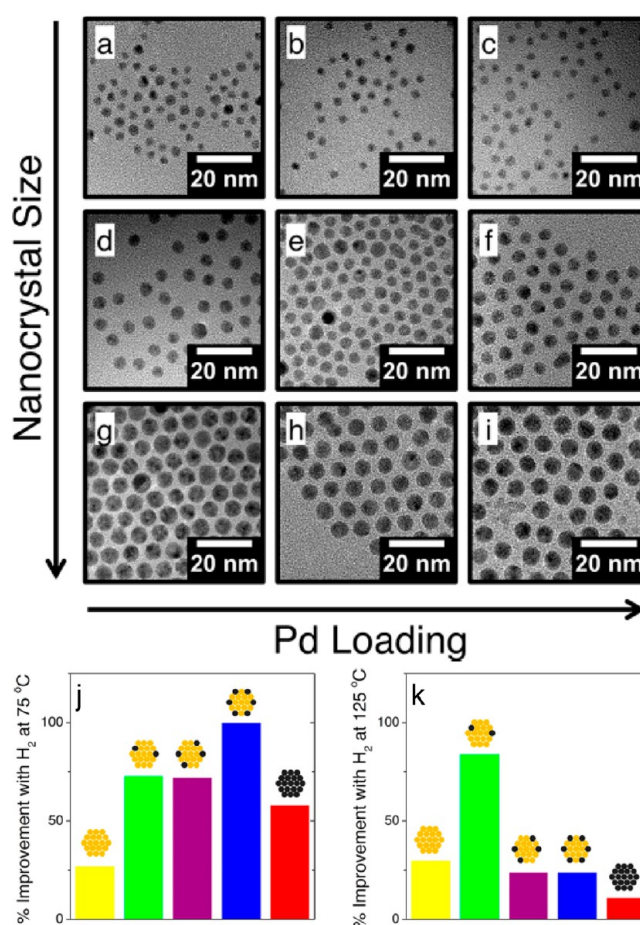
Compositional control provides an ideal way to study the effect of adding a second element to the stability of a given one. For reactions that require high temperatures, lowering the vapor pressure of certain elements (or compounds) and reducing the particle mobility are useful ways to limit deactivation mechanisms related to sintering.<sup>138</sup> In the case of volatile oxides, such as those formed by Pt, it is known that the addition of Pd helps their stabilization.<sup>139,140</sup> In a detailed study using composition-controlled Pd/Pt nanocrystals of similar small size (~3 nm) supported on alumina, we found that the addition of even small amounts of Pt to Pd decreases its activity for methane combustion in the absence of water but also improves its stability when water is present and at high temperatures.<sup>141</sup> Because conventional impregnation leads to supported particles with highly variable Pd/Pt ratios, it would be hard to elucidate these properties and trends that instead so clearly emerged through the use of colloidal nanocrystal catalysts.

Composition control may also be used to more efficiently utilize rare and expensive noble metals, such as when a small concentration of Pt-group metals is added to a base metal host, such as Cu<sup>142,143</sup> (alloys of this type with Au have been known for much longer time to be high-performing catalysts<sup>144,145</sup>). These systems, named diluted or single-atom alloys, were initially approached as single crystals and later developed in colloidal form and have been shown to be selective hydrogenation catalysts while also being resistant to poisoning,<sup>146</sup> to possess a different catalytic behavior than their corresponding pure metal counterparts,<sup>147</sup> and to be promising for selective catalytic oxidations as well.<sup>148</sup> Our recent results in this area show in particular that we can control the introduction of small amounts of Pd in Au nanocrystals, while



**Figure 6.** Demonstration of how atomic ordering in Au/Cu bimetallic nanocrystals impacts their electrocatalytic activity toward CO<sub>2</sub> reduction. (a) TEM images of Au/Cu bimetallic particles prepared with controlled degree of ordering from disordered (alloyed) to ordered (intermetallic) nanocrystals. (b) X-ray diffraction patterns of the nanocrystals demonstrating the variable degree of ordering. (c) Electrochemical CO<sub>2</sub> reduction activity of the samples where CO and H<sub>2</sub> faradaic efficiency are compared. Reproduced with permission from ref 137. Copyright 2017 American Chemical Society.

also simultaneously controlling the size of the nanocrystal phases and the support on which they are deposited (Figure 7).<sup>148</sup> These materials were supported on P25 titania and studied for the oxidation of isopropanol to acetone, a model reaction that is thought to proceed through a hydroperoxide (or hydrogen peroxide) intermediate.<sup>149</sup> By using a library of compositionally controlled Pd/Au nanocrystals, we were able



**Figure 7.** Simultaneous control over size and composition in Pd/Au nanocrystals containing isolated Pd sites (diluted or single-atom alloys). (a–i) TEM images of nanocrystals with different sizes and Pd concentrations. (j, k) These materials show that isolated Pd sites in Au supported on titania are more effective in catalyzing the hydro-oxidation of isopropanol to acetone than the corresponding Pd and Au counterparts. Adapted with permission from ref 148. Copyright 2018 American Chemical Society.

to unambiguously show the synergistic effects between these two metals in the hydro-oxidation pathway, with increase in activity as we increased the concentration of single Pd sites on the Au nanocrystals, thus opening up opportunities to use these materials for selective oxidation reactions.

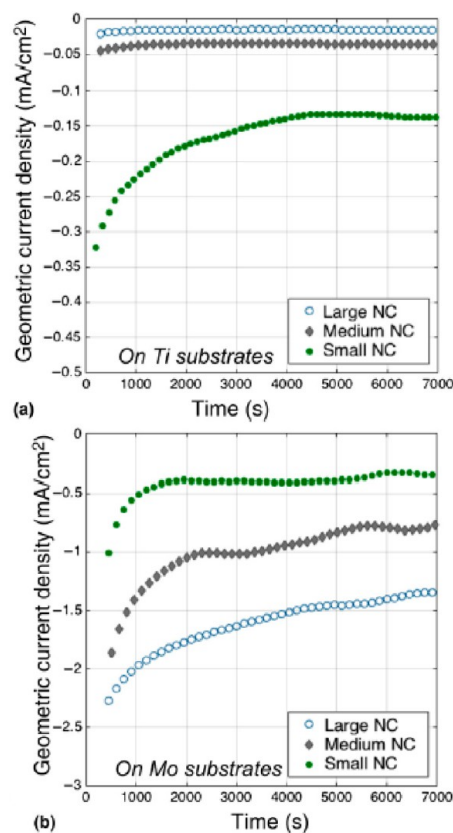
Intermetallic compounds are also interesting systems to investigate using colloidal nanocrystals,<sup>150</sup> and the ability to be able to precisely tune, at the individual nanocrystal level, the particle composition and stoichiometry is very crucial. In organic reactions, where different functional groups may react, it is important to find appropriate conditions to selectively affect a desired functionality,<sup>151</sup> and differences in performance and selectivity can be detected even between samples with small differences in metal ratios.<sup>152</sup> All these features provide a further justification for tuning the bimetallic composition to a very fine extent given the sensitivity of the catalytic output.

**4.1.4. Support Effects.** Another important parameter that may affect the performance of supported phases is the support. In conventional impregnation techniques, it is very likely that particle size and geometry is not the same when the impregnation is performed on several supports because of distinctly different interactions with the metal precursor. The

support surface area, morphology, chemistry, and hydroxylation density are all elements that play a role in determining the final characteristics of the supported particles. On the contrary, starting from the same preformed nanocrystals guarantees that supported phases on different materials are very similar in size, shape, and composition. This approach can be used to verify controversial hypotheses in the literature about the role of supports in catalysis, such as with gold catalysts for CO oxidation.<sup>153</sup> In a detailed study, researchers found that alumina-supported Au nanocrystals provided rates for the CO oxidation reaction as high as using titania as support, the typical choice.<sup>154</sup> The authors attributed this result to the change in supported Au shape induced by the support, in contrast to the oxygen donation ability that is most often invoked to explain these effects. However, these results are in contrast with what had been reported a few years earlier by other groups using small colloidal Au particles (2 nm) to prepare catalysts on TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. Interestingly, in this latter case, even catalysts that were only dried before catalysis (i.e., plausibly still with organic ligands on the Au surface) showed to be highly active for CO oxidation. This observation suggests that specific metal–support interactions may not be needed, although it cannot be excluded that, during the drying process or immediately under catalytic reactions, ligands were removed providing the interface sites for the reaction. Certainly, the use of preformed Au colloidal nanocrystals to investigate the role of the support is important because, in this example, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports did not provide catalysts as active as the Au/TiO<sub>2</sub> counterpart while having exactly the same Au phase. These examples demonstrate that there is still need to further investigate the high sensitivity of Au catalysts on many factors impacting their catalytic performance.

The study of support effects is not limited to thermocatalytic reactions. Electrode support materials can also play a major role in electrocatalytic reactions and determine activity and stability of the supported phases. In an attempt to understand the synergistic role played by Ni and Mo phases that leads to one of the best nonprecious metal systems for electrocatalytic hydrogen production in alkaline solutions, we prepared Ni nanocrystals of different sizes and drop-casted them onto Ti and Mo foils used as electrodes.<sup>155</sup> The samples supported on Mo foil showed much higher currents for hydrogen production; additionally, a surprising result was found when larger particles delivered much higher currents than smaller particles (Figure 8). The reverse trend was found true for the Ti substrate. The hypothesis we put forward is that the wetting of the Mo substrate by the Ni particles under electrocatalytic conditions promotes an electronic interaction between the two phases that provides Ni with multiple oxidation states when the particles are large and only metallic Ni if the particles are small. This multitude of oxidation states for larger nanocrystals promotes the reaction,<sup>156,157</sup> thus explaining how large particles that are affected by both the substrate and the reaction conditions could achieve higher rates. This example highlights how multiple control over particle size and support provides a systematic way to understand structure–property relationships.

**4.2. Systematic Understanding of Catalyst Deactivation Phenomena.** The performance of a catalyst is only partially described by activity and selectivity. Catalyst stability is of utmost importance in realistic applications because replacing a catalyst in a commercial process could be very



**Figure 8.** Electrochemical performance of submonolayer films of small, medium, and large Ni nanocrystals on (a) Ti and (b) Mo substrates at  $-0.27$  V versus the reversible hydrogen electrode (RHE). Normalizing the rates by Ni surface area exaggerates both trends. Reprinted with permission from ref 155. Copyright 2016 Cambridge University Press.

expensive and represents a loss of productivity if the process needs to be temporarily shut down. In automotive catalysis, precious metals are added in high amounts because of the drastic loss of activity experienced by the catalytic converter in the first short period of operation. Studying and improving catalyst stability can therefore truly result in great environmental improvements and financial savings.

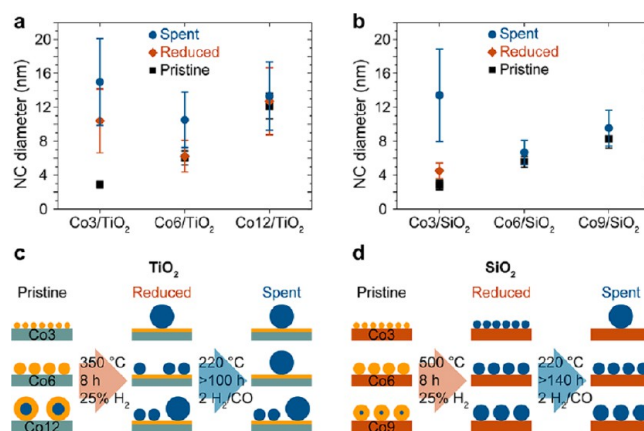
Multiple phenomena are responsible for catalyst deactivation.<sup>158,159</sup> Despite there being several different chemical, mechanical, and thermal causes, they all involve some process by which active surface area is lost, with consequences for catalyst activity and selectivity. Because these processes involve changes to the chemical and structural nature of the catalyst, control over these properties represents a very useful starting point to be able to identify these changes to the materials occurring under/after operation. The knowledge gained during these studies informs researchers about the potential strategies that could be used to reduce catalyst deactivation and find ways to limit the root causes of it.

Among deactivation phenomena that occur under high-temperature operating conditions, sintering is one of the main causes of performance loss.<sup>138,160</sup> This process is related to the movement of atomic species or entire particles on the surface of a support or through the gas phase, leading to agglomeration of the active phase and decrease in the surface area-to-volume ratio driven by the minimization of surface energy. The exact mechanisms leading to sintering are still under debate for many

systems. Two processes, particle migration and coalescence, and Ostwald ripening, are responsible for sintering. Strategies to mitigate them could involve very different approaches; hence, the knowledge of which process is active under specific reaction conditions is crucial. Using size-controlled particles it is possible to study this aspect, especially in conjunction with in situ and operando techniques that allow following the structural changes of the materials in real time and while they are performing catalytic reactions.

Both particle migration and Ostwald ripening depend on particle size (small particles have higher surface energy and systems tend to spontaneously minimize energy); however, ripening is particularly sensitive to particle size distributions because the driving force for this process is the difference in energy between particles of different sizes. Unfortunately, in conventional materials prepared by impregnation, particle size distributions are too wide to be able to extract useful information from them.<sup>161</sup> It has been demonstrated that catalysts with very narrow size distributions, such as those prepared by using cluster sources,<sup>162</sup> show substantially reduced driving force for ripening-induced sintering.<sup>163,164</sup> It is unlikely that the movement of atomic species is suppressed, but instead it is possible that the final overall result is a dynamic exchange of atomic species between uniform particles, which reduces the energetic differences between them such that no overall sintering is observed. With this in mind, in collaborative work we used uniform colloidal nanocrystals to investigate whether particle migration and coalescence or Ostwald ripening processes were responsible for Pt-based catalyst deactivation under high-temperature conditions.<sup>36</sup> By using uniform, small ( $2.2 \pm 0.4$  nm), and large ( $4.4 \pm 0.2$  nm) Pt particles, three samples were prepared: two in which an individual particle size was used, and one in which the two sizes were mixed and deposited onto the support to artificially simulate a difference in particle size distribution (see also Figure 2). In situ TEM studies at atmospheric pressure with a special cell under diluted hydrogen showed that whereas little changes occurred to the two materials with single particle distributions, much more noticeable effects were found for the sample with a bimodal particle size distribution, demonstrating that Ostwald ripening is indeed the main cause of particle sintering in this system. Much more recently, similar conclusions were reached in studies of Co-based catalysts for Fischer–Tropsch synthesis.<sup>165</sup> Preformed, size-controlled Co nanocrystals were used to investigate the effect of ligand removal on the performance and the sintering of the metal phase under reaction conditions. It was found that larger particles were stable under ligand removal and activation conditions but that small particles with higher mobility would sinter already during pretreatment conditions (Figure 9). The support played a further role, with titania leading to structural changes even for the large Co particles, whereas silica maintained particle size distributions more stable even after long exposure of the materials to reaction conditions. This behavior could be fully understood thanks to the very narrow size distribution of the initial Co nanocrystals used.

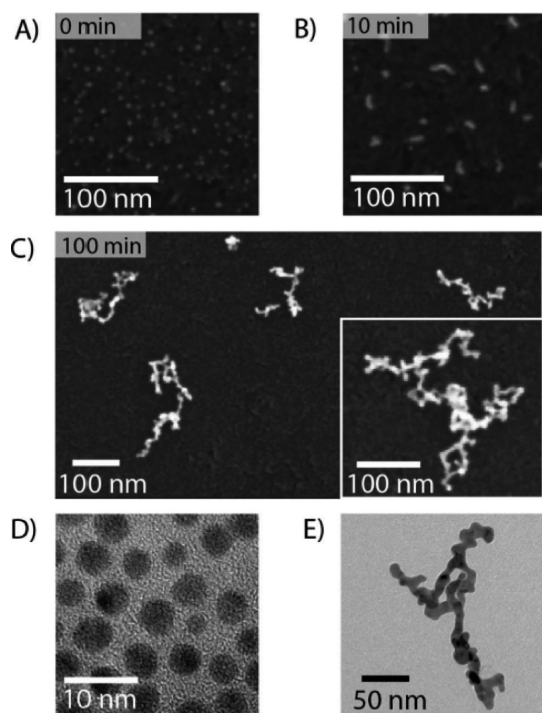
The strategies to understand and mitigate deactivation under photo- and electrocatalytic conditions need to be different compared to thermal heterogeneous catalysis. The solvent plays a big role in promoting not only the movement of species within the catalyst/electrode surface but also in accelerating processes of dissolution, leaching, and redeposition. Furthermore, mechanical and chemical stresses caused by changes in



**Figure 9.** Behavior of cobalt nanocrystals supported on either titania or silica for Fischer–Tropsch synthesis after different treatments. (a, b) Average Co nanocrystal sizes from TEM analysis of the TiO<sub>2</sub>- and SiO<sub>2</sub>-supported samples, respectively. Error bars report standard deviation of the average particle size. (c, d) Schematic illustration of the sintering behavior of the nanocrystals on TiO<sub>2</sub> and SiO<sub>2</sub>, respectively, after different treatments. Co(II) or Co(III) is depicted in yellow whereas Co(0) in blue. Reproduced with permission from ref 165. Copyright 2018 American Chemical Society.

oxidation state of catalyst species under start-up/shut-down operation or during cycling of reaction conditions between oxidizing and reducing potentials may also cause loss of activity over time, and appropriate choice of operating conditions is therefore crucial.<sup>166</sup> Clearly, there is a trade-off between catalyst activity and long-term stability that needs to be tailored based on appropriate requirements. Studying mechanisms of electrocatalyst deactivation is therefore important in order to understand how to tune catalyst structure, but also reaction conditions, to obtain high productivity. Colloidal nanocrystals have proven to be a great resource to understand these mechanisms. Gold nanocrystals protected by alkanethiol ligands and dispersed on a carbon substrate were recently used to demonstrate that particle mobility can be rather high even under the room temperature conditions of CO<sub>2</sub> electrocatalytic reduction.<sup>167</sup> Interestingly, the removal of capping agents under the applied potential and their solubility in the electrolyte was found to govern the formation rate of dendritic species by random walk and agglomeration of the “naked” gold nanocrystals (Figure 10).

Particle clustering was similarly found to be the main cause of degradation in Cu electrocatalysts prepared by deposition of Cu nanocrystals onto glassy carbon electrodes.<sup>168</sup> In this case, however, it was further discovered that restructuring of the particles occurred with time, with a change in shape and formation of small clusters of few Cu atoms probably responsible for the transport of Cu species across the electrode surface. These structural changes, which could be tracked very precisely because of the uniformity of the initial Cu nanocrystals, were found to drastically affect the CO<sub>2</sub> reduction reaction, with a decrease in Faradaic efficiency favoring instead hydrogen evolution. Other studies performed using Cu nanocubes as active phase for CO<sub>2</sub> reduction demonstrated that even deeper changes to these structures can occur, with complete restructuring of specific facets, formation of pores, and surface roughening.<sup>169</sup> This reconstruction led to a dramatic change in the electrocatalytic performance, decreasing the rate of formation of carbon-coupling products.



**Figure 10.** Scanning electron microscopy images of gold nanocrystals supported on glassy carbon after (A) 0, (B) 10, and (C) 100 min of polarization at  $-1.2$  V in  $0.1$  M  $\text{NaHCO}_3$  buffer. TEM of (D) as-synthesized gold nanoparticles and (E) a dendrite formed after 100 min of polarization. Reproduced with permission from ref 167. Copyright 2014 American Chemical Society.

Interestingly, the deposition of the same Cu nanocubes on a Cu substrate, rather than on carbon, showed improved stability, thus highlighting not only the importance of the substrate in determining activity and stability of supported phases but also that colloidal nanocrystals allow to truly isolate specific parameters that can guide the design of stable materials.

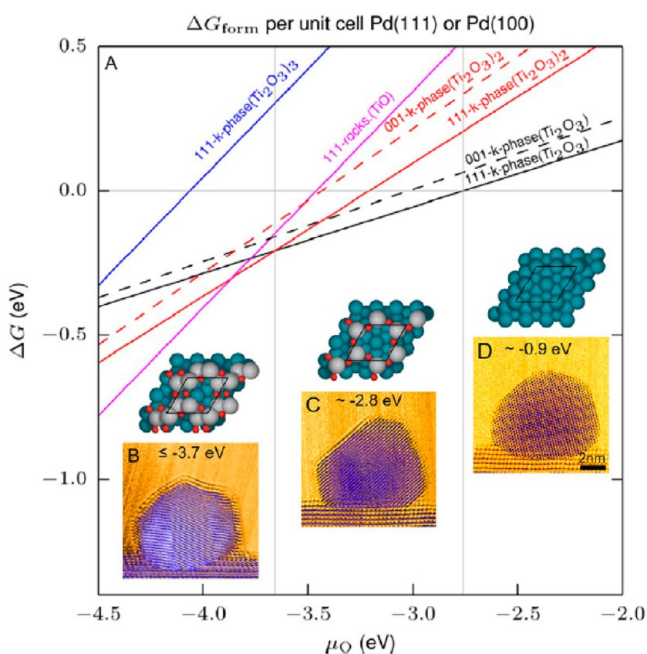
**4.3. Use of Colloidal Catalysts as Premier Materials for Spectroscopy/Microscopy Studies.** The use of colloidal nanocrystals for fundamental understanding of catalytic performance is not limited to their activity. An appealing aspect of these materials is that the structural features of an individual nanocrystal are very close to those of the average of many nanocrystals in a given sample. The same cannot be said for materials prepared by conventional impregnation approaches, where the wide size distributions mean that an individual particle can be located far away from the average (i.e., being much smaller or much larger, have a different shape, or be very different in composition). This important feature allows using averaged spectroscopic techniques to characterize atomic/local changes in the structure of the materials, and at the same time, using microscopic techniques to gain an understanding of the overall catalyst structure. This advantage is particularly useful in spectroscopic techniques where averaged features require extensive modeling and fitting to be able to extract meaningful information from experimental data.

Structural changes occurring at the atomic level are followed using microscopy techniques. Current strategies involve the use of in situ tools to investigate catalysts close to reaction conditions either with environmental TEM techniques or with

specialized cells that are transparent enough to electrons and where the sample is kept under liquid- or gas-phase conditions at atmospheric pressure and elevated temperatures. This second option is growing in popularity because of the high resolution achievable and with the opportunity to observe the sample while under conditions of interest in catalysis.<sup>170</sup> In particular, cells with appropriate design have been developed to the point of using single graphene sheets as transparent cell windows to contain liquids.<sup>171</sup> This environment could potentially be used to understand changes in catalyst structure under liquid-phase catalysis conditions and could help elucidate mechanisms of deactivation such as leaching. In the case of gas-phase catalysis, these special cells have already demonstrated the benefit of being able to observe supported nanocrystals as they undergo changes in their structure. Using  $\text{TiO}_2$ -supported Pd nanocrystals and a gas cell operating at atmospheric pressure in an aberration-corrected TEM, our collaborative research has shown how reductive pretreatments in hydrogen atmosphere promote a process termed strong metal–support interaction (SMSI).<sup>172</sup> This process, which has been first described nearly four decades ago,<sup>173,174</sup> consists in the migration of a reducible oxide support onto the surface of metallic crystallites induced by surface energy minimization. Thanks to observations performed using the in situ cell and to detailed computational predictions on the surface energy of the materials, we were able to describe the formation of two different crystallographic structures of the  $\text{TiO}_x$  layers migrating on top of the metallic Pd nanocrystals (Figure 11). The Pd nanocrystals also showed structural changes under the reducing conditions, and changes in shape were associated with a redistribution of the exposed facets as they underwent reduction. Because of the uniformity of the sample, the structural changes were observed to be reproducible in all of the supported nanocrystals.

Shape changes, i.e., reconstructions occurring to facets that lead to an overall rearrangement of lattice planes and thus to the overall shape of a material, can be easily followed and tracked in materials where shape uniformity is high. Sometimes, drastic changes in shape may occur but go unnoticed. Microscopy techniques are then very useful to correlate these shape changes with structural transformations, and in bimetallic materials, also with compositional changes occurring during the restructuring process. When these two events are correlated, an in-depth analysis using combined high-resolution electron microscopy and spectroscopic information on the composition results in very useful correlations. It must be kept in mind, however, that when using microscopy techniques, it must be demonstrated that beam effects are not affecting the structural modifications observed in the materials. These notions have been recently beautifully shown in octahedral Pt/Ni nanocrystals for the oxygen reduction reaction, with a clear correlation between the rearrangement of the two components, structural transformations of the overall nanocrystals, and their electrocatalytic activity.<sup>133</sup>

Other spectroscopic techniques can be used to directly follow the catalytic processes as they occur. Astute constructs prepared using colloidal building blocks result in unique systems to study these processes. One recent example consists in the deposition of Pt nanocrystals on the surface of silica spheres and the deposition of mesoporous silica around the spheres and surrounding the nanocrystals.<sup>175</sup> In this way, controlled channels were prepared to investigate the reactivity of Pt surfaces through single-molecule fluorescence events.

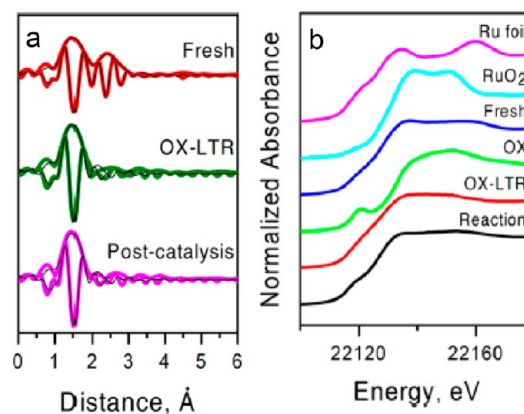


**Figure 11.** Computational predictions and experimental verification of SMSI effects in Pd/TiO<sub>2</sub> catalysts exposed to different atmospheres and oxygen chemical potential. (A) Theoretical calculations of free energy  $G$  for different TiO<sub>*x*</sub> phases on Pd(111) or Pd(100) surfaces as a function of oxygen chemical potential  $\mu_{\text{O}}$ . (B) TiO<sub>*x*</sub>/Pd double layer found under H<sub>2</sub> (5 vol %)/Ar at 1 atm total pressure and 500 °C. (C) TiO<sub>*x*</sub>/Pd single layer found under H<sub>2</sub> (4.9 vol %)/O<sub>2</sub> (2 vol %)/Ar at 1 atm total pressure and 500 °C. (D) No layer was observed under H<sub>2</sub> (4.7 vol %)/O<sub>2</sub> (5.7 vol %)/Ar at 1 atm total pressure and 500 °C. The top-down views of the corresponding simulated structures of the experimentally observed surface layers are shown above the TEM images. Pd is in dark green, Ti in gray, and oxygen in red. Reproduced with permission from ref 172. Copyright 2016 American Chemical Society.

The authors were able to demonstrate that Pt particles confined within the pores were more active and hypothesized that either an increased effective concentration of reactants within the pores or a specific adsorption of reactants or intermediates caused by the confinement of the particles could be the reason for the observed results. The ability to prepare well-defined structures using colloidal building blocks provided a real boost to the confidence of averaged results.

The ability to describe structural changes occurring to individual supported particles using averaged spectroscopic techniques has also been demonstrated using colloidal nanocrystals. Techniques such as X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) provide averaged signals due to the coexistence of multiple phases that need to be deconvoluted using appropriate models. In the case of uniform nanocrystals, it may occur that the averaged signal represents a spectroscopic signature relatable to the individual supported components. Therefore, structural changes that may go unseen in conventional materials can instead become easier to distinguish when using uniform phases. Related to this topic, we recently described the changes occurring to supported Ru nanocrystals under oxidizing conditions and mild temperatures.<sup>176</sup> Using X-ray absorption near-edge spectroscopy (XANES), we could identify the formation of oxidized, single-site Ru species on the surface of ceria upon mild oxidative treatment of supported Ru

nanocrystals at temperatures between 150 and 250 °C. This restructuring process could be followed using a spectroscopic pre-edge feature present in the XANES spectrum of the Ru K-edge, a feature that is dampened if multiple Ru species coexist in the sample (Figure 12). Because of the uniformity of the



**Figure 12.** (a) Ex situ EXAFS results in the R space for 2.6 nm Ru/CeO<sub>2</sub> after deposition (fresh), after a low-temperature (250 °C) oxidizing pretreatment (OX-LTR), and after catalytic reaction for CO<sub>2</sub> hydrogenation (postcatalysis). (b) In situ XANES spectra 4.4 nm Ru/CeO<sub>2</sub> catalyst under different environments. Here the OX temperature was 280 °C as the redispersion of the 4.4 nm Ru/CeO<sub>2</sub> catalyst occurred after oxidation at 280 °C with a CO selectivity >90%. Reproduced with permission from ref 176. Copyright 2018 American Chemical Society.

supported Ru particles and their similar restructuring history during the experiment, a strong pre-edge feature was observed that allowed us to follow the process. The structural transformation of the supported Ru nanocrystals resulted in a dramatic shift in CO<sub>2</sub> reduction selectivity from CH<sub>4</sub> to CO as main product. The use of uniform nanocrystals is therefore crucial in some cases to clearly observe structural transformations that could have a strong effect on the overall catalytic performance.

## 5. HOW CAN WE USE COLLOIDAL NANOCRYSTALS TO PREPARE ACTIVE AND STABLE CATALYSTS?

New knowledge provided by the fundamental understanding of structure–property relationships can be translated into better performing catalysts. This knowledge informs us on the next steps to take to create structures with the highest predicted performance either by increasing the specific intrinsic activity of certain sites or by increasing their density.<sup>177</sup> While preparing these structures may still be the limiting step, the field of colloidal nanocrystals synthesis has grown to the point that many different architectures can be made with impressive control over several parameters through the understanding of the thermodynamic and kinetic handles to achieve it.<sup>23,178</sup> This high level of control, coupled to the large number of structures that can be prepared, make this approach uniquely capable of preparing catalysts to achieve desired high activity, stability, and selectivity. These types of structures could be hardly fabricated with other conventional methods.

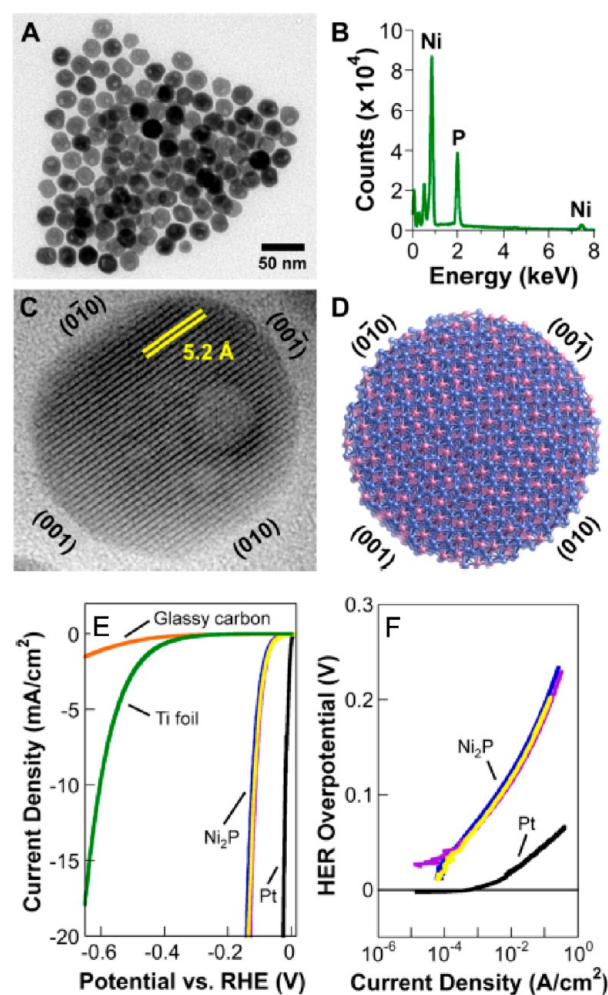
Among emerging architectures that are particularly interesting for catalysis are colloidal particles with programmed void structures, such as in nanoframe materials and in dealloyed particles. In these structures, an efficient utilization of active sites is achieved through the void spaces created within a larger

structure, thus increasing the available specific surface area. Additionally, sites with unusual coordination environments can be obtained within the concave surfaces of the materials.<sup>179,180</sup>

An exciting recent example of this approach is represented by the colloidal synthesis of Pt/Ni nanoframes realized by etching Ni away in acid from octahedral alloyed nanocrystals.<sup>181</sup> Preferential leaching of Ni compared to Pt leads to structures with hollow cores and Pt-rich surfaces.<sup>93</sup> These nanoframe nanocrystals are colloidally stable in solution, such that they can be deposited onto arbitrary substrates for catalysis. The authors explored the activity and stability of these materials for electrocatalysis after deposition onto carbon supports, demonstrating much higher specific activity for the oxygen reduction reaction when compared to commercial Pt/C materials, and very good, even surprising, stability after 10,000 cycles.<sup>181</sup> The same strategy to prepare Pt/Ni frame catalysts has been taken a step forward by coating these nanostructures with MOF layers.<sup>182</sup> The MOF layers serve to increase the H<sub>2</sub> uptake by the composites and also as sieving layers for organic molecules. With the combination of these two factors, the authors demonstrated that alkenes with molecular size small enough to enter the pore channels could be effectively hydrogenated, whereas others with larger size could not, thus providing evidence for shape selectivity in these systems. The leaching process utilized to create these frame structures is strongly related to dealloying methods that also rely on the preferential removal of one metal from an alloy, either using chemical etching<sup>183</sup> or in some cases using electrochemical methods.<sup>184</sup> Active oxygen reduction reaction electrocatalysts have been obtained in this way from Pt alloys, for example.<sup>132</sup> These materials show similar performance to Pt-based catalysts with shape and composition control,<sup>185</sup> demonstrating that active site motifs in both dealloyed and nanostructured Pt-based catalysts could be similar.

Colloidal nanocrystals have become very popular for the preparation of active electrocatalysts for multiple reactions. One of the reasons why this is the case is the fact that some carbon-based supports, which are commonly used in preparing electrocatalytic materials, are thermally sensitive and need to be handled differently than the commonly employed oxide supports for thermal catalysis. The advantage of colloidal nanocrystals is that active phases are already formed in solution and do not require high-temperature thermal activation steps.<sup>67</sup> Even phases that would require particularly harsh thermal treatments can be first prepared in solution and then dispersed on the electrode material. Sulfide and phosphide compounds, which would normally require treatments in sulfur- and phosphorus-containing atmospheres at several hundred degrees Celsius, can be prepared in solution in the form of well-defined clusters and nanoparticles (Figure 13).<sup>186</sup> These materials have shown a remarkable activity for the hydrogen evolution reaction that put them in close distance to the most active and precious Pt catalysts.<sup>187</sup> Another advantage of colloidal nanocrystals is that their density on support materials can be controlled, leading to ensemble effects that can be studied in detail. In one example, it was found that a density-dependent structural transformation occurring to Cu particles during CO<sub>2</sub> electroreduction led to improved performance after conversion of dense Cu arrays into larger cube structures.<sup>188</sup>

In looking for improved activity in thermal catalytic reactions, one element of interest is the coupling between multiple active sites at the metal–oxide interface, which has



**Figure 13.** Representative TEM image (A) and corresponding energy-dispersive X-ray spectrum (B) Ni<sub>2</sub>P nanocrystals synthesis through colloidal methods. High-resolution TEM reveals lattice fringes and exposed facets (C) leading to a proposed crystal model (D). These materials perform very well for the hydrogen evolution reaction (polarization data, E, and Tafel plots, F), almost reaching the activity of noble metals such as Pt. Reproduced with permission from ref 187. Copyright 2013 American Chemical Society.

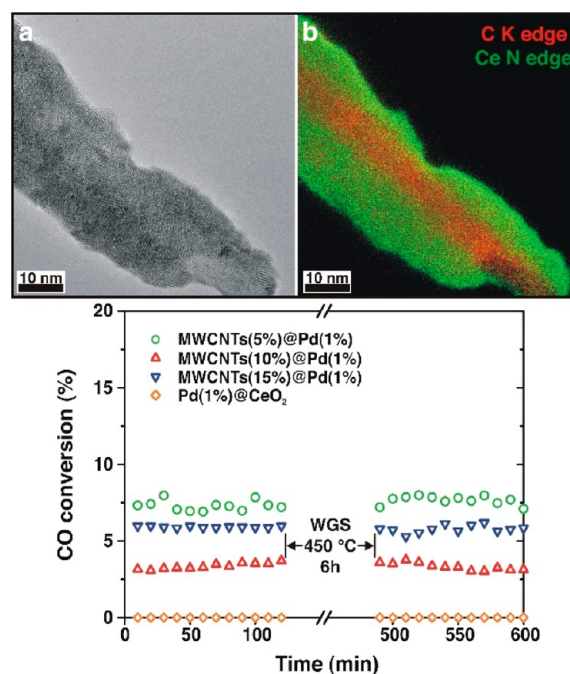
been recognized as a crucial reactive location in multiple systems.<sup>78,189,190</sup> Controlling these interface sites at the atomic scale is important to modulate reactivity and stability or to demonstrate that this contact area is required for catalysis.<sup>191</sup> It has been demonstrated that it is possible to engineer metal–metal oxide interfaces directly in the colloidal building blocks using a single structure that contains these interface sites in platinum/iron (and nickel) hydroxide nanocrystals.<sup>192</sup> These hybrid nanocrystals were first prepared in solution and then dispersed onto a high surface area support. Because of the low amount of Ni or Fe hydroxide added, only part of the Pt surface is covered, leaving much of the Pt surface available for reactivity with the high density of interface sites at the boundary with the deposited Ni or Fe hydroxide phase. These catalysts, supported onto thermally stable alumina, showed high and stable reactivity for CO oxidation. An alternative way to prepare metal–support interfaces with controllable length and composition was proposed few years ago by Somorjai, Yang, and co-workers using Langmuir–Blodgett deposition of alternate layers of nanocrystals.<sup>193</sup> These tandem bilayer

catalysts showed that only when certain interfaces were formed (e.g., A–B and B–C interfaces by stacking A–B–C nanocrystal phases), hydroformylation reactions were possible, which was not the case when the specific interfaces were absent (e.g., when using the A–C–B configuration). This work highlighted how interfaces are critical for activity and selectivity but also how to artificially create extended interfaces with multiple layers of control. Creating these interfaces at the atomic scale represents an exciting direction toward exploiting the potentially different reactivity that emerges from these systems compared with bare metallic surfaces. Another procedure to form metal–oxide interface sites is by segregation of alloyed nanocrystals, demonstrated in the preparation of Au/MnO nanoparticles by controlled oxidation of AuMn alloyed phases for sensitive H<sub>2</sub>O<sub>2</sub> detection<sup>116</sup> or for the systematic screening of promoters in the methane combustion reaction using bimetallic Pd nanocrystals.<sup>117</sup> In this latter example from our group, several Pd/M nanocrystals (M = V, Mn, Fe, Co, Ni, Zn, and Sn and potentially extendable to other metal combinations) were prepared and supported onto high-surface area alumina, and the catalysts calcined in air at high temperature to segregate the second metal in the form of an oxide phase closely localized near the Pd particles. With this strategy, we were able to demonstrate that some metals could improve the intrinsic activity of Pd for methane combustion, whereas some other metals improved its thermal stability. Overall, this method could be useful for the systematic screening of promoters for a variety of catalytic applications.

Control of nanocrystal shape can be taken to the extreme by forming sheet-like structures just a few atomic layers thick.<sup>194,195</sup> This strategy may prove useful in the efficient use of precious metals because the sheets may in principle expose 100% of their atoms to the gas phase, and these atoms are highly undercoordinated, thus making them attractive for catalysis. These materials are prepared using CO as reducing and capping agent; thanks to the strong binding of CO to specific facets, the growth is limited to two dimensions, thus leading to the particular sheet-like structure. For Rh, polyvinylpyrrolidone (PVP) is used to obtain shape control, but the decomposition of formaldehyde under the solvothermal conditions used might also lead to liberation of CO as a structure-directing agent. In both cases, supported Pd and Rh nanosheets showed catalytic performance on par with or better than commercial catalysts used for comparison.

When looking at potential structures for increasing the stability of supported catalysts under reaction conditions, strategies for mitigating sintering need to be tailored depending on the mechanism of deactivation.<sup>138,160,196</sup> Numerous works demonstrated that encapsulated particles are much more sinter-resistant compared to supported phases.<sup>197</sup> The cage effect offered by thermally stable inorganic shells represents a huge benefit to stop particle migration and coalescence, despite mass transport sometimes limiting the performance of these systems.<sup>198</sup> Supported phases in the form of small particles that would normally sinter at temperatures of 700–800 °C, such as Au and Pt, have been repeatedly shown to be stable when embedded within hollow spheres or silica shells.<sup>57,199</sup> Porous shells with appropriate pore diameters need to be built in order to be able to exploit the reactive surfaces of the metal cores. The thermal stability imposed by the oxide shells can also be used as a way to increase catalytic performance by specific interactions between the metal and the oxide. In the case of oxide shells that participate in the

reaction mechanisms, such as ceria, it is possible to observe the benefit of both improved thermal stability and increased activity.<sup>52,60,198,200</sup> We demonstrated that ceria-coated Pd nanocrystals, supported onto alumina, can be highly active for methane combustion and stable even after prolonged reactivity at high temperatures.<sup>52</sup> Taking this concept one step further, nanostructures made of carbon nanotubes embedded within porous shells of ceria, titania, or zirconia and containing dispersed Pd and Pt particles showed interesting catalytic performance for several reactions (Figure 14).<sup>201</sup> Interestingly,



**Figure 14.** TEM image of structures composed of carbon nanotubes embedded within layers of ceria containing Pd nanocrystals (a) and corresponding electron energy loss spectroscopy (EELS) mapping of the C and Ce content in the composites (b) showing that the carbon nanotubes are embedded inside the ceria layer. Palladium is not visible in this image due to its low loading. (c) CO conversion during the water–gas shift reaction at 250 °C over the materials containing different amounts of ceria. Reproduced with permission from ref 201. Copyright 2012 American Chemical Society.

carbon nanotubes were needed not only to guarantee the final overall morphology of the materials but also to act as the active component to steer electrons to and from the reducible oxide shell.

More widely considering core–shell (or yolk–shell) structures as those in which colloidal nanocrystals are embedded within a different second inorganic phase, nanocrystals encapsulated within layers of metal–organic frameworks (MOFs) have attracted much attention in the past few years.<sup>202</sup> More than for their thermal stability, which is limited by the organic component, the interest is due to the high structural ordering and controllable degree of porosity of the MOF materials that can act both as capture/storage units and as sieving layers to allow only certain molecules to interact with the encapsulated core materials (i.e., size/shape-selective catalysis).<sup>58</sup> It is also possible that the MOF layers play a more active role in determining the selectivity of catalytic processes when they interact directly with functional groups of reactant molecules to drive their catalysis.<sup>203,204</sup> Synthesis

techniques to incorporate metal particles within MOF channels had been existing for some time, but much more controlled ways to grow MOF layers from colloidal nanocrystal surfaces have been developed in more recent years.<sup>59,205</sup> Different strategies can be employed, by addition of ligand-capped particles during MOF growth,<sup>205</sup> by using sacrificial template layers that guarantee attachment of MOF monomers to the particles,<sup>59</sup> or with a two-step approach where preformed nanocrystals are added to the MOF surface, and additional MOF layers are grown around the particles.<sup>203</sup> These materials showed interesting shape- and size-selective catalysis for a variety of reactions. Remarkably, in some of these composites it was found that the MOF layers displayed interesting effects on activation energy barriers that could be attributed to either the diffusional pathways of the reacting molecules or to the geometry of the transition state that may be affected by MOF chains present around the active nanocrystal sites.<sup>59</sup> The ability to tune the chemistry of MOF channels in order to control the diffusion of species to active sites is a further exciting avenue that can be explored in these composites.<sup>206</sup>

The areas of interest and examples reported in this section should not be seen as limiting for the field. Colloidal nanocrystals offer many opportunities to design and realize systems of interest in catalysis, and it is expected that the number of examples showcasing the use of these materials will increase in the near future.

## 6. WHAT ARE THE CHALLENGES AND OPPORTUNITIES LYING AHEAD FOR THE FIELD?

As repeatedly highlighted in this perspective, there are two main goals of using colloidal nanocrystals in heterogeneous catalysis: to improve our fundamental understanding of structure–property relationships in catalysis and to prepare better performing materials by carefully engineering these nanostructures. Despite the fact that the former goal does not necessarily require planning for the use of scalable and cost-effective materials as much as the latter, it is important to keep in mind that in all cases heterogeneous catalysts are eventually used at a scale that is enormous. Every year, millions of tons of chemicals are produced using catalytic technologies. For a catalyst to be successfully employed on an industrial scale, many hurdles need to be overcome. A few of these hurdles have to deal with the scale of materials production, their cost, and their performance under realistic conditions. In all these three areas, there is a lot that needs to be done in order to be able to apply colloidal nanocrystals in industrial applications. For this reason, whether it is to gather fundamental understanding or to prepare better performing catalysts, it is important to consider the potential applicability of the knowledge and results that are obtained through fundamental research.

Regarding the scale of production, it is important for solvents and conditions used for the synthesis to be as scalable as possible. Synthesis techniques that are reproducible and relatively insensitive to small variations in the synthesis conditions are preferred. Moving synthesis processes from batch-type to flow-type would also be an important step.<sup>207</sup> There are current existing synthesis processes ran industrially to prepare colloidal quantum dots and colloidal Ag nanocrystals, but it must be stressed the fact that the quantities are rather low (<100 tons/year).<sup>208</sup> Therefore, market penetration of colloidal nanocrystals is still limited, and for catalytic materials to be prepared from these precursors, the synthesis processes

must be improved. The very high dilution requirements and the use of large volumes of solvents during purification are hurdles that need to be overcome, similarly to synthesis of other industrially relevant catalysts.<sup>209,210</sup> One particular issue is the necessary purification of the nanocrystals prior to deposition on the support. This step is rather energy- and materials-intensive but necessary to remove unreacted precursors and excess organic compounds from the mixture. Novel, convenient ways to purify nanocrystals need to be developed, and some studies emerged in the literature as particularly promising.<sup>211</sup> Another possibility is to directly deposit the as-synthesized particles onto support materials, which is currently used to prepare commercial catalysts for hydrogenations,<sup>33</sup> but these methods need to make sure that the nanocrystals are uniform and no undesired phases are codeposited (e.g., atomic precursors still present in the mixture).

A related issue or challenge to overcome is the cost of the materials. Clearly, for catalysts to be scalable, the cost of production should be as low as possible and at the very least compensated by the improved performance. For example, a catalyst made from nanocrystals could be more expensive to produce than a commercial one, but if it leads to a catalytic process with higher selectivity, such that savings are realized in limiting the separation steps downstream, then the overall financial savings could still counterbalance the production costs. However, finding ways to reduce production costs in colloidal nanocrystal synthesis are still important. As highlighted in the previous paragraph, flow-type synthesis and methods to ease the purification steps are promising avenues to explore in this case.

Finally, an important point is related to the performance of these materials under realistic conditions. Being able to test catalysts under conditions that at least simulate the presence of poisoning species or of species that induce leaching, during start-up/shut-down operations, or under conditions of high-temperature aging to simulate the stability of the materials are all important steps to take. Very often chosen conditions are too ideal, and the catalytic performance may not necessarily reflect the needs and demands of the particular application area. What conditions to choose is something that needs to be tailored for each specific application, but certainly the choice is important to guarantee depth and importance to these studies.

Overall, the use of colloidal nanocrystals as precursors for the preparation of heterogeneous catalysts offers a variety of potential approaches and structures for numerous applications. It is expected that this area will continue to grow with the number and type of structures and systems studied in the next years. Many opportunities to improve our fundamental knowledge of catalytic processes and prepare better catalysts are within reach.

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## Notes

The author declares no competing financial interest.

## Biography

Matteo Cargnello received his Ph.D. in Nanotechnology in 2012 at the University of Trieste (Italy) under the supervision of Prof. Paolo Fornasiero, and he was then a postdoctoral scholar in the Department of Chemistry at the University of Pennsylvania (Philadelphia) with Prof. Christopher B. Murray before joining the faculty at Stanford in January 2015. He is currently an Assistant Professor of Chemical Engineering and, by courtesy, of Materials Science and Engineering and Terman Faculty Fellow. General goals of the research in the Cargnello group are related to materials for catalysis, energy, and environmental applications. Uniform and tailored nanocrystals and nanostructures are synthesized, studied, and used, with emphasis on how to precisely control nanoarchitectures to understand and exploit interactions between well-defined building blocks.

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## REFERENCES

- (1) Somorjai, G. A.; Frei, H.; Park, J. Y. Advancing the Frontiers in Nanocatalysis, Biointerfaces, and Renewable Energy Conversion by Innovations of Surface Techniques. *J. Am. Chem. Soc.* **2009**, *131* (46), 16589–16605.
- (2) Somorjai, G. A.; Li, Y. Impact of surface chemistry. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (3), 917–924.
- (3) Ertl, G. Reactions at Surfaces: From Atoms to Complexity (Nobel Lecture). *Angew. Chem., Int. Ed.* **2008**, *47* (19), 3524–3535.
- (4) Nørskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. Towards the computational design of solid catalysts. *Nat. Chem.* **2009**, *1* (1), 37–46.
- (5) Heinemann, H. Technological Applications of Zeolites in Catalysis. *Catal. Rev.: Sci. Eng.* **1981**, *23* (1–2), 315–328.
- (6) Corma, A. State of the art and future challenges of zeolites as catalysts. *J. Catal.* **2003**, *216* (1), 298–312.
- (7) Weitkamp, J. Zeolites and catalysis. *Solid State Ionics* **2000**, *131* (1), 175–188.
- (8) Jiao, L.; Zha, Y.; Hao, X.; Regalbutto, J. R. Simple, Scientific Syntheses with Common Catalyst Precursors. In *Studies in Surface Science and Catalysis*; Gaigneaux, E. M., Devillers, M., De Vos, D. E., Hermans, S., Jacobs, P. A., Martens, J. A., Ruiz, P., Eds.; Elsevier: 2006; Vol. 162, pp 211–218.

(9) Wong, A.; Liu, Q.; Griffin, S.; Nicholls, A.; Regalbutto, J. R. Synthesis of ultrasmall, homogeneously alloyed, bimetallic nanoparticles on silica supports. *Science* **2017**, *358* (6369), 1427–1430.

(10) Zhu, X.; Cho, H.-r.; Pasupong, M.; Regalbutto, J. R. Charge-Enhanced Dry Impregnation: A Simple Way to Improve the Preparation of Supported Metal Catalysts. *ACS Catal.* **2013**, *3* (4), 625–630.

(11) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.

(12) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706–8715.

(13) Murray, C. B.; Sun, S.; Doyle, H.; Betley, T. Monodisperse 3d Transition-metal (Co, Ni, Fe) nanoparticles and their assembly into nanoparticle superlattices. *MRS Bull.* **2001**, *26* (12), 985–991.

(14) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices. *Science* **2000**, *287* (5460), 1989–1992.

(15) Sun, Y.; Xia, Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science* **2002**, *298* (5601), 2176–2179.

(16) Wiley, B.; Sun, Y.; Mayers, B.; Xia, Y. Shape-Controlled Synthesis of Metal Nanostructures: The Case of Silver. *Chem. - Eur. J.* **2005**, *11* (2), 454–463.

(17) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Adv. Mater.* **2003**, *15* (5), 353–389.

(18) Xiong, Y.; Xia, Y. Shape-Controlled Synthesis of Metal Nanostructures: The Case of Palladium. *Adv. Mater.* **2007**, *19* (20), 3385–3391.

(19) Park, J.; An, K.; Hwang, Y.; Park, J. E.-G.; Noh, H. J.; Kim, J. Y.; Park, J. H.; Hwang, N. M.; Hyeon, T. Ultra-large-scale syntheses of monodisperse nanocrystals. *Nat. Mater.* **2004**, *3* (12), 891–895.

(20) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of monodisperse spherical nanocrystals. *Angew. Chem., Int. Ed.* **2007**, *46* (25), 4630–4660.

(21) Yang, J.; Sargent, E.; Kelley, S.; Ying, J. Y. A general phase-transfer protocol for metal ions and its application in nanocrystal synthesis. *Nat. Mater.* **2009**, *8* (8), 683–689.

(22) Fenton, J. L.; Steimle, B. C.; Schaak, R. E. Tunable intraparticle frameworks for creating complex heterostructured nanoparticle libraries. *Science* **2018**, *360* (6388), 513–517.

(23) Buck, M. R.; Bondi, J. F.; Schaak, R. E. A total-synthesis framework for the construction of high-order colloidal hybrid nanoparticles. *Nat. Chem.* **2012**, *4* (1), 37–44.

(24) Kovalenko, M. V.; Manna, L.; Cabot, A.; Hens, Z.; Talapin, D. V.; Kagan, C. R.; Klimov, V. I.; Rogach, A. L.; Reiss, P.; Milliron, D. J.; Guyot-Sionnest, P.; Konstantatos, G.; Parak, W. J.; Hyeon, T.; Korgel, B. A.; Murray, C. B.; Heiss, W. Prospects of Nanoscience with Nanocrystals. *ACS Nano* **2015**, *9* (2), 1012–1057.

(25) Li, G.; Jin, R. Atomically Precise Gold Nanoclusters as New Model Catalysts. *Acc. Chem. Res.* **2013**, *46* (8), 1749–1758.

(26) Jin, R. Quantum sized, thiolate-protected gold nanoclusters. *Nanoscale* **2010**, *2* (3), 343–362.

(27) Qian, H.; Jin, R. Ambient Synthesis of Au<sub>144</sub>(SR)<sub>60</sub> Nanoclusters in Methanol. *Chem. Mater.* **2011**, *23* (8), 2209–2217.

(28) Zeng, C.; Chen, Y.; Li, G.; Jin, R. Magic Size Au<sub>64</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>32</sub> Nanocluster Protected by Cyclohexanethiolate. *Chem. Mater.* **2014**, *26* (8), 2635–2641.

(29) Yu, Y.; Chen, X.; Yao, Q.; Yu, Y.; Yan, N.; Xie, J. Scalable and Precise Synthesis of Thiolated Au<sub>10–12</sub>, Au<sub>15</sub>, Au<sub>18</sub>, and Au<sub>25</sub> Nanoclusters via pH Controlled CO Reduction. *Chem. Mater.* **2013**, *25* (6), 946–952.

(30) Cuenya, B. R. Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects. *Thin Solid Films* **2010**, *518* (12), 3127–3150.

- (31) Jia, C. J.; Schuth, F. Colloidal metal nanoparticles as a component of designed catalyst. *Phys. Chem. Chem. Phys.* **2011**, *13* (7), 2457–2487.
- (32) Kirby, F.; Moreno-Marrodan, C.; Baán, Z.; Bleeker, B. F.; Barbaro, P.; Berben, P. H.; Witte, P. T. NanoSelect Precious Metal Catalysts and their Use in Asymmetric Heterogeneous Catalysis. *ChemCatChem* **2014**, *6* (10), 2904–2909.
- (33) Witte, P. T.; Berben, P. H.; Boland, S.; Boymans, E. H.; Vogt, D.; Geus, J. W.; Donkervoort, J. G. BASF NanoSelect Technology: Innovative Supported Pd- and Pt-based Catalysts for Selective Hydrogenation Reactions. *Top. Catal.* **2012**, *55* (7), 505–511.
- (34) Soled, S. Silica-supported catalysts get a new breath of life. *Science* **2015**, *350* (6265), 1171–1172.
- (35) Agashe, K. B.; Regaluto, J. R. A Revised Physical Theory for Adsorption of Metal Complexes at Oxide Surfaces. *J. Colloid Interface Sci.* **1997**, *185* (1), 174–189.
- (36) Zhang, S.; Cargnello, M.; Cai, W.; Murray, C. B.; Graham, G. W.; Pan, X. Revealing particle growth mechanisms by combining high-surface-area catalysts made with monodisperse particles and electron microscopy conducted at atmospheric pressure. *J. Catal.* **2016**, *337*, 240–247.
- (37) Na, K.; Zhang, Q.; Somorjai, G. A. Colloidal Metal Nanocatalysts: Synthesis, Characterization, and Catalytic Applications. *J. Cluster Sci.* **2014**, *25* (1), 83–114.
- (38) Gadiyar, C.; Louidice, A.; Buonsanti, R. Colloidal nanocrystals for photoelectrochemical and photocatalytic water splitting. *J. Phys. D: Appl. Phys.* **2017**, *50* (7), 074006.
- (39) Huang, J.; Buonsanti, R. Colloidal nanocrystals as heterogeneous catalysts for electrochemical CO<sub>2</sub> conversion. *Chem. Mater.* **2019**, *31*, 13–25.
- (40) Yin, Y.; Alivisatos, A. P. Colloidal nanocrystal synthesis and the organic-inorganic interface. *Nature* **2005**, *437* (7059), 664–670.
- (41) van Embden, J.; Chesman, A. S. R.; Jasieniak, J. J. The Heat-Up Synthesis of Colloidal Nanocrystals. *Chem. Mater.* **2015**, *27* (7), 2246–2285.
- (42) Wiley, B.; Herricks, T.; Sun, Y.; Xia, Y. Polyol Synthesis of Silver Nanoparticles: Use of Chloride and Oxygen to Promote the Formation of Single-Crystal, Truncated Cubes and Tetrahedrons. *Nano Lett.* **2004**, *4* (9), 1733–1739.
- (43) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem., Int. Ed.* **2009**, *48* (1), 60–103.
- (44) Lim, B.; Jiang, M.; Tao, J.; Camargo, P. H. C.; Zhu, Y.; Xia, Y. Shape-Controlled Synthesis of Pd Nanocrystals in Aqueous Solutions. *Adv. Funct. Mater.* **2009**, *19* (2), 189–200.
- (45) Dong, A.; Ye, X.; Chen, J.; Kang, Y.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. A Generalized Ligand-Exchange Strategy Enabling Sequential Surface Functionalization of Colloidal Nanocrystals. *J. Am. Chem. Soc.* **2011**, *133* (4), 998–1006.
- (46) Rosen, E. L.; Buonsanti, R.; Llordes, A.; Sawvel, A. M.; Milliron, D. J.; Helms, B. A. Exceptionally Mild Reactive Stripping of Native Ligands from Nanocrystal Surfaces by Using Meerwein's Salt. *Angew. Chem., Int. Ed.* **2012**, *51* (3), 684–689.
- (47) Casavola, M.; Hermannsdörfer, J.; de Jonge, N.; Dugulan, A. I.; de Jong, K. P. Fabrication of Fischer–Tropsch Catalysts by Deposition of Iron Nanocrystals on Carbon Nanotubes. *Adv. Funct. Mater.* **2015**, *25* (33), 5309–5319.
- (48) Chou, J.; McFarland, E. W. Direct propylene epoxidation on chemically reduced Au nanoparticles supported on titania. *Chem. Commun.* **2004**, *14*, 1648–1649.
- (49) Hickey, N.; Larochette, P. A.; Gentilini, C.; Sordelli, L.; Olivi, L.; Polizzi, S.; Montini, T.; Fornasiero, P.; Pasquato, L.; Graziani, M. Monolayer protected gold nanoparticles on ceria for an efficient CO oxidation catalyst. *Chem. Mater.* **2007**, *19* (4), 650–651.
- (50) Zheng, N.; Stucky, G. D. A General Synthetic Strategy for Oxide-Supported Metal Nanoparticle Catalysts. *J. Am. Chem. Soc.* **2006**, *128* (44), 14278–14280.
- (51) Grunwaldt, J. D.; Kiener, C.; Wögerbauer, C.; Baiker, A. Preparation of supported gold catalysts for low-temperature CO oxidation via “size-controlled” gold colloids. *J. Catal.* **1999**, *181* (2), 223–232.
- (52) Cargnello, M.; Jaén, J. J. D.; Garrido, J. C. H.; Bakhmutsky, K.; Montini, T.; Gámez, J. J. C.; Gorte, R. J.; Fornasiero, P. Exceptional Activity for Methane Combustion over Modular Pd@CeO<sub>2</sub> Subunits on Functionalized Al<sub>2</sub>O<sub>3</sub>. *Science* **2012**, *337* (6095), 713–717.
- (53) Prieto, G.; Zečević, J.; Friedrich, H.; de Jong, K. P.; de Jongh, P. E. Towards stable catalysts by controlling collective properties of supported metal nanoparticles. *Nat. Mater.* **2013**, *12* (1), 34–39.
- (54) Hanaoka, T.; Kishida, M.; Nagata, H.; Wakabayashi, K. Control of Rh particle size of Rh/SiO<sub>2</sub> catalysts prepared from micro-emulsions - Effect of surfactant. *Sekiyu Gakkaishi* **1996**, *39* (4), 285–289.
- (55) Kishida, M.; Hanaoka, T.; Hayashi, H.; Tashiro, S.; Wakabayashi, K. Novel preparation method for supported metal catalysts using microemulsion - Control of catalyst surface area. *Stud. Surf. Sci. Catal.* **1998**, *118*, 265–268.
- (56) Kishida, M.; Ichiki, K. I.; Hanaoka, T.; Nagata, H.; Wakabayashi, K. Preparation method for supported metal catalysts using w/o microemulsion: Study on immobilization conditions of metal particles by hydrolysis of alkoxide. *Catal. Today* **1998**, *45* (1–4), 203–208.
- (57) Joo, S. H.; Park, J. Y.; Tsung, C. K.; Yamada, Y.; Yang, P.; Somorjai, G. A. Thermally stable Pt/mesoporous silica core-shell nanocatalysts for high-temperature reactions. *Nat. Mater.* **2009**, *8* (2), 126–131.
- (58) Hu, P.; Morabito, J. V.; Tsung, C. K. Core-shell catalysts of metal nanoparticle core and metal-organic framework shell. *ACS Catal.* **2014**, *4* (12), 4409–4419.
- (59) Kuo, C. H.; Tang, Y.; Chou, L. Y.; Sneed, B. T.; Brodsky, C. N.; Zhao, Z.; Tsung, C. K. Yolk-Shell Nanocrystal@ZIF-8 Nanostructures for Gas-Phase Heterogeneous Catalysis with Selectivity Control. *J. Am. Chem. Soc.* **2012**, *134* (35), 14345–14348.
- (60) Cargnello, M.; Wieder, N. L.; Montini, T.; Gorte, R. J.; Fornasiero, P. Synthesis of Dispersible Pd@CeO<sub>2</sub> Core-Shell Nanostructures by Self-Assembly. *J. Am. Chem. Soc.* **2010**, *132* (4), 1402–1409.
- (61) Kahsar, K. R.; Schwartz, D. K.; Medlin, J. W. Selective Hydrogenation of Polyunsaturated Fatty Acids Using Alkanethiol Self-Assembled Monolayer-Coated Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts. *ACS Catal.* **2013**, *3* (9), 2041–2044.
- (62) Marshall, S. T.; O'Brien, M.; Oetter, B.; Corpuz, A.; Richards, R. M.; Schwartz, D. K.; Medlin, J. W. Controlled selectivity for palladium catalysts using self-assembled monolayers. *Nat. Mater.* **2010**, *9* (10), 853–858.
- (63) Pang, S. H.; Schoenbaum, C. A.; Schwartz, D. K.; Medlin, J. W. Directing reaction pathways by catalyst active-site selection using self-assembled monolayers. *Nat. Commun.* **2013**, *4*, 2448.
- (64) Aliaga, C.; Park, J. Y.; Yamada, Y.; Lee, H. S.; Tsung, C. K.; Yang, P.; Somorjai, G. A. Sum Frequency Generation and Catalytic Reaction Studies of the Removal of Organic Capping Agents from Pt Nanoparticles by UV-Ozone Treatment. *J. Phys. Chem. C* **2009**, *113* (15), 6150–6155.
- (65) Borodko, Y.; Jones, L.; Lee, H.; Frei, H.; Somorjai, G. Spectroscopic Study of Tetradecyltrimethylammonium Bromide Pt-C<sub>14</sub>TAB Nanoparticles: Structure and Stability. *Langmuir* **2009**, *25* (12), 6665–6671.
- (66) Lopez-Sanchez, J. A.; Dimitratos, N.; Hammond, C.; Brett, G. L.; Kesavan, L.; White, S.; Miedzkiak, P.; Tiruvalam, R.; Jenkins, R. L.; Carley, A. F.; Knight, D.; Kiely, C. J.; Hutchings, G. J. Facile removal of stabilizer-ligands from supported gold nanoparticles. *Nat. Chem.* **2011**, *3* (7), 551–556.
- (67) Li, D.; Wang, C.; Tripkovic, D.; Sun, S.; Markovic, N. M.; Stamenkovic, V. R. Surfactant Removal for Colloidal Nanoparticles from Solution Synthesis: The Effect on Catalytic Performance. *ACS Catal.* **2012**, *2* (7), 1358–1362.
- (68) Cargnello, M.; Chen, C.; Diroll, B. T.; Doan-Nguyen, V. V. T.; Gorte, R. J.; Murray, C. B. Efficient Removal of Organic Ligands from Supported Nanocrystals by Fast Thermal Annealing Enables Catalytic

Studies on Well-Defined Active Phases. *J. Am. Chem. Soc.* **2015**, *137* (21), 6906–6911.

(69) Mohapatra, P.; Shaw, S.; Mendivelso-Perez, D.; Bobbitt, J. M.; Silva, T. F.; Naab, F.; Yuan, B.; Tian, X.; Smith, E. A.; Cademartiri, L. Calcination does not remove all carbon from colloidal nanocrystal assemblies. *Nat. Commun.* **2017**, *8* (1), 2038.

(70) Calle-Vallejo, F.; Tymoczko, J.; Colic, V.; Vu, Q. H.; Pohl, M. D.; Morgenstern, K.; Loffreda, D.; Sautet, P.; Schuhmann, W.; Bandarenka, A. S. Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors. *Science* **2015**, *350* (6257), 185–189.

(71) Boudart, M.; Djega-Mariadassou, G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University Press: 1984.

(72) Tsung, C. K.; Kuhn, J. N.; Huang, W.; Aliaga, C.; Hung, L. I.; Somorjai, G. A.; Yang, P. Sub-10 nm Platinum Nanocrystals with Size and Shape Control: Catalytic Study for Ethylene and Pyrrole Hydrogenation. *J. Am. Chem. Soc.* **2009**, *131* (16), 5816–5822.

(73) Xu, Z.; Xiao, F. S.; Purnell, S. K.; Alexeev, O.; Kawi, S.; Deutsch, S. E.; Gates, B. C. Size-dependent catalytic activity of supported metal clusters. *Nature* **1994**, *372* (6504), 346–348.

(74) Boudart, M. Fine-tuning metal clusters. *Nature* **1994**, *372*, 320.

(75) Freund, H. J.; Meijer, G.; Scheffler, M.; Schlögl, R.; Wolf, M. CO Oxidation as a Prototypical Reaction for Heterogeneous Processes. *Angew. Chem., Int. Ed.* **2011**, *50* (43), 10064–10094.

(76) Zafiris, G. S.; Gorte, R. J. CO Oxidation on Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001): Evidence for Structure Sensitivity. *J. Catal.* **1993**, *140* (2), 418–423.

(77) Joo, S. H.; Park, J. Y.; Renzas, J. R.; Butcher, D. R.; Huang, W.; Somorjai, G. A. Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation. *Nano Lett.* **2010**, *10* (7), 2709–2713.

(78) Cargnello, M.; Doan-Nguyen, V. V. T.; Gordon, T. R.; Diaz, R. E.; Stach, E. A.; Gorte, R. J.; Fornasiero, P.; Murray, C. B. Control of Metal Nanocrystal Size Reveals Metal-Support Interface Role for Ceria Catalysts. *Science* **2013**, *341* (6147), 771–773.

(79) Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P. Fundamentals and Catalytic Applications of CeO<sub>2</sub>-Based Materials. *Chem. Rev.* **2016**, *116* (10), 5987–6041.

(80) Qiao, B.; Wang, A.; Yang, X.; Allard, L. F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt<sub>1</sub>/FeO<sub>x</sub>. *Nat. Chem.* **2011**, *3* (8), 634–641.

(81) Jones, J.; Xiong, H.; DeLaRiva, A. T.; Peterson, E. J.; Pham, H.; Challa, S. R.; Qi, G.; Oh, S.; Wiebenga, M. H.; Pereira Hernández, X. I.; Wang, Y.; Datye, A. K. Thermally stable single-atom platinum-on-ceria catalysts via atom trapping. *Science* **2016**, *353* (6295), 150–154.

(82) Bezemer, G. L.; Bitter, J. H.; Kuipers, H. P. C. E.; Oosterbeek, H.; Holeywijn, J. E.; Xu, X.; Kapteijn, F.; van Dillen, A. J.; de Jong, K. P. Cobalt Particle Size Effects in the Fischer–Tropsch Reaction Studied with Carbon Nanofiber Supported Catalysts. *J. Am. Chem. Soc.* **2006**, *128* (12), 3956–3964.

(83) Prieto, G.; Martínez, A.; Concepción, P.; Moreno-Tost, R. Cobalt particle size effects in Fischer–Tropsch synthesis: structural and in situ spectroscopic characterisation on reverse micelle-synthesised Co/ITQ-2 model catalysts. *J. Catal.* **2009**, *266* (1), 129–144.

(84) Fischer, N.; van Steen, E.; Claeys, M. Structure sensitivity of the Fischer–Tropsch activity and selectivity on alumina supported cobalt catalysts. *J. Catal.* **2013**, *299*, 67–80.

(85) van Helden, P.; Ciobica, I. M.; Coetzer, R. L. J. The size-dependent site composition of FCC cobalt nanocrystals. *Catal. Today* **2016**, *261*, 48–59.

(86) Casavola, M.; Xie, J.; Meeldijk, J. D.; Krans, N. A.; Goryachev, A.; Hofmann, J. P.; Dugulan, A. I.; de Jong, K. P. Promoted Iron Nanocrystals Obtained via Ligand Exchange as Active and Selective Catalysts for Synthesis Gas Conversion. *ACS Catal.* **2017**, *7* (8), 5121–5128.

(87) Wang, C.; Daimon, H.; Onodera, T.; Koda, T.; Sun, S. A General Approach to the Size- and Shape-Controlled Synthesis of Platinum Nanoparticles and Their Catalytic Reduction of Oxygen. *Angew. Chem., Int. Ed.* **2008**, *47* (19), 3588–3591.

(88) Gamboa-Aldeco, M. E.; Herrero, E.; Zelenay, P. S.; Wieckowski, A. Adsorption of bisulfate anion on a Pt(100) electrode: A comparison with Pt(111) and Pt(poly). *J. Electroanal. Chem.* **1993**, *348* (1), 451–457.

(89) Lee, Y.; Garcia, M. A.; Frey Huls, N. A.; Sun, S. Synthetic Tuning of the Catalytic Properties of Au-Fe<sub>3</sub>O<sub>4</sub> Nanoparticles. *Angew. Chem., Int. Ed.* **2010**, *49* (7), 1271–1274.

(90) Ruditskiy, A.; Peng, H. C.; Xia, Y. Shape-Controlled Metal Nanocrystals for Heterogeneous Catalysis. *Annu. Rev. Chem. Biomol. Eng.* **2016**, *7*, 327–348.

(91) Tao, A. R.; Habas, S.; Yang, P. Shape Control of Colloidal Metal Nanocrystals. *Small* **2008**, *4* (3), 310–325.

(92) Gan, L.; Cui, C.; Heggen, M.; Dionigi, F.; Rudi, S.; Strasser, P. Element-specific anisotropic growth of shaped platinum alloy nanocrystals. *Science* **2014**, *346* (6216), 1502–1506.

(93) Niu, Z.; Becknell, N.; Yu, Y.; Kim, D.; Chen, C.; Kornienko, N.; Somorjai, G. A.; Yang, P. Anisotropic phase segregation and migration of Pt in nanocrystals en route to nanoframe catalysts. *Nat. Mater.* **2016**, *15*, 1188.

(94) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. Anatase TiO<sub>2</sub> single crystals with a large percentage of reactive facets. *Nature* **2008**, *453* (7195), 638–641.

(95) Hu, L.; Peng, Q.; Li, Y. Selective Synthesis of Co<sub>3</sub>O<sub>4</sub> Nanocrystal with Different Shape and Crystal Plane Effect on Catalytic Property for Methane Combustion. *J. Am. Chem. Soc.* **2008**, *130* (48), 16136–16137.

(96) Crespo-Quesada, M.; Yarulín, A.; Jin, M.; Xia, Y.; Kiwi-Minsker, L. Structure Sensitivity of Alkynol Hydrogenation on Shape- and Size-Controlled Palladium Nanocrystals: Which Sites Are Most Active and Selective? *J. Am. Chem. Soc.* **2011**, *133* (32), 12787–12794.

(97) Yarulín, A.; Yuranov, I.; Cárdenas-Lizana, F.; Alexander, D. T. L.; Kiwi-Minsker, L. How to increase the selectivity of Pd-based catalyst in alkynol hydrogenation: Effect of second metal. *Appl. Catal., A* **2014**, *478* (0), 186–193.

(98) Chen, J.; Lim, B.; Lee, E. P.; Xia, Y. Shape-controlled synthesis of platinum nanocrystals for catalytic and electrocatalytic applications. *Nano Today* **2009**, *4* (1), 81–95.

(99) Mistry, H.; Varela, A. S.; Kühn, S.; Strasser, P.; Cuenya, B. R. Nanostructured electrocatalysts with tunable activity and selectivity. *Nature Reviews Materials* **2016**, *1*, 16009.

(100) Chen, Q.; Jia, Y.; Xie, S.; Xie, Z. Well-faceted noble-metal nanocrystals with nonconvex polyhedral shapes. *Chem. Soc. Rev.* **2016**, *45* (11), 3207–3220.

(101) Xu, X.; Zhang, X.; Sun, H.; Yang, Y.; Dai, X.; Gao, J.; Li, X.; Zhang, P.; Wang, H.-H.; Yu, N.-F.; Sun, S.-G. Synthesis of Pt–Ni Alloy Nanocrystals with High-Index Facets and Enhanced Electrocatalytic Properties. *Angew. Chem., Int. Ed.* **2014**, *53* (46), 12522–12527.

(102) Seo, B.; Baek, D. S.; Sa, Y. J.; Joo, S. H. Shape effects of nickel phosphide nanocrystals on hydrogen evolution reaction. *CrystEngComm* **2016**, *18* (32), 6083–6089.

(103) Kang, Y.; Ye, X.; Chen, J.; Cai, Y.; Diaz, R. E.; Adzic, R. R.; Stach, E. A.; Murray, C. B. Design of Pt–Pd Binary Superlattices Exploiting Shape Effects and Synergistic Effects for Oxygen Reduction Reactions. *J. Am. Chem. Soc.* **2013**, *135* (1), 42–45.

(104) Qiao, Z.-A.; Wu, Z.; Dai, S. Shape-Controlled Ceria-based Nanostructures for Catalysis Applications. *ChemSusChem* **2013**, *6* (10), 1821–1833.

(105) Wu, Z.; Li, M.; Overbury, S. H. On the structure dependence of CO oxidation over CeO<sub>2</sub> nanocrystals with well-defined surface planes. *J. Catal.* **2012**, *285* (1), 61–73.

(106) Bennett, D. A.; Cargnello, M.; Diroll, B. T.; Murray, C. B.; Vohs, J. M. Shape-dependence of the thermal and photochemical reactions of methanol on nanocrystalline anatase TiO<sub>2</sub>. *Surf. Sci.* **2016**, *654*, 1–7.

(107) Bennett, D. A.; Cargnello, M.; Gordon, T. R.; Murray, C. B.; Vohs, J. M. Thermal and photochemical reactions of methanol on

nanocrystalline anatase TiO<sub>2</sub> thin films. *Phys. Chem. Chem. Phys.* **2015**, *17* (26), 17190–17201.

(108) Gong, X. Q.; Selloni, A. Reactivity of Anatase TiO<sub>2</sub> Nanoparticles: The Role of the Minority (001) Surface. *J. Phys. Chem. B* **2005**, *109* (42), 19560–19562.

(109) Gordon, T. R.; Cargnello, M.; Paik, T.; Mangolini, F.; Weber, R. T.; Fornasiero, P.; Murray, C. B. Nonaqueous Synthesis of TiO<sub>2</sub> Nanocrystals Using TiF<sub>4</sub> to Engineer Morphology, Oxygen Vacancy Concentration, and Photocatalytic Activity. *J. Am. Chem. Soc.* **2012**, *134* (15), 6751–6761.

(110) Pepin, P. A.; Diroll, B. T.; Murray, C. B.; Vohs, J. M. Morphological Dependence of the Thermal and Photochemical Reactions of Acetaldehyde on Anatase TiO<sub>2</sub> Nanocrystals. *Top. Catal.* **2018**, *61* (5), 365–378.

(111) Pepin, P. A.; Diroll, B. T.; Choi, H. J.; Murray, C. B.; Vohs, J. M. Thermal and Photochemical Reactions of Methanol, Acetaldehyde, and Acetic Acid on Brookite TiO<sub>2</sub> Nanorods. *J. Phys. Chem. C* **2017**, *121* (21), 11488–11498.

(112) Sambur, J. B.; Chen, T.-Y.; Choudhary, E.; Chen, G.; Nissen, E. J.; Thomas, E. M.; Zou, N.; Chen, P. Sub-particle reaction and photocurrent mapping to optimize catalyst-modified photoanodes. *Nature* **2016**, *530* (7588), 77–80.

(113) Cargnello, M.; Montini, T.; Smolin, S. Y.; Priebe, J. B.; Delgado Jaén, J. J.; Doan-Nguyen, V. V. T.; McKay, I. S.; Schwalbe, J. A.; Pohl, M.-M.; Gordon, T. R.; Lu, Y.; Baxter, J. B.; Brückner, A.; Fornasiero, P.; Murray, C. B. Engineering titania nanostructure to tune and improve its photocatalytic activity. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (15), 3966–3971.

(114) Tao, F.; Dag, S.; Wang, L. W.; Liu, Z.; Butcher, D. R.; Bluhm, H.; Salmeron, M.; Somorjai, G. A. Break-Up of Stepped Platinum Catalyst Surfaces by High CO Coverage. *Science* **2010**, *327* (5967), 850–853.

(115) Tao, F.; Grass, M. E.; Zhang, Y.; Butcher, D. R.; Renzas, J. R.; Liu, Z.; Chung, J. Y.; Mun, B. S.; Salmeron, M.; Somorjai, G. A. Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles. *Science* **2008**, *322* (5903), 932–934.

(116) Zhu, H.; Sigdel, A.; Zhang, S.; Su, D.; Xi, Z.; Li, Q.; Sun, S. Core/Shell Au/MnO Nanoparticles Prepared Through Controlled Oxidation of AuMn as an Electrocatalyst for Sensitive H<sub>2</sub>O<sub>2</sub> Detection. *Angew. Chem., Int. Ed.* **2014**, *53* (46), 12508–12512.

(117) Willis, J. J.; Goodman, E. D.; Wu, L.; Riscoe, A. R.; Martins, P.; Tassone, C. J.; Cargnello, M. Systematic Identification of Promoters for Methane Oxidation Catalysts Using Size- and Composition-Controlled Pd-Based Bimetallic Nanocrystals. *J. Am. Chem. Soc.* **2017**, *139* (34), 11989–11997.

(118) Mavrikakis, M.; Hammer, B.; Nørskov, J. K. Effect of Strain on the Reactivity of Metal Surfaces. *Phys. Rev. Lett.* **1998**, *81* (13), 2819–2822.

(119) Zhang, S.; Zhang, X.; Jiang, G.; Zhu, H.; Guo, S.; Su, D.; Lu, G.; Sun, S. Tuning Nanoparticle Structure and Surface Strain for Catalysis Optimization. *J. Am. Chem. Soc.* **2014**, *136* (21), 7734–7739.

(120) Peterson, A. A.; Nørskov, J. K. Activity Descriptors for CO<sub>2</sub> Electroreduction to Methane on Transition-Metal Catalysts. *J. Phys. Chem. Lett.* **2012**, *3* (2), 251–258.

(121) Wang, H.; Xu, S.; Tsai, C.; Li, Y.; Liu, C.; Zhao, J.; Liu, Y.; Yuan, H.; Abild-Pedersen, F.; Prinz, F. B.; Nørskov, J. K.; Cui, Y. Direct and continuous strain control of catalysts with tunable battery electrode materials. *Science* **2016**, *354* (6315), 1031–1036.

(122) Yilguma; Tang, Y.; Zheng, G. Colloidal nanocrystals for electrochemical reduction reactions. *J. Colloid Interface Sci.* **2017**, *485*, 308–327.

(123) Bu, L.; Zhang, N.; Guo, S.; Zhang, X.; Li, J.; Yao, J.; Wu, T.; Lu, G.; Ma, J.-Y.; Su, D.; Huang, X. Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. *Science* **2016**, *354* (6318), 1410–1414.

(124) Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y. M.; Duan, X.; Mueller, T.; Huang, Y.

High-performance transition metal-doped Pt<sub>3</sub>Ni octahedra for oxygen reduction reaction. *Science* **2015**, *348* (6240), 1230–1234.

(125) Wang, C.; Chi, M.; Li, D.; Strmcnik, D.; van der Vliet, D.; Wang, G.; Komanicky, V.; Chang, K.-C.; Paulikas, A. P.; Tripkovic, D.; Pearson, J.; More, K. L.; Markovic, N. M.; Stamenkovic, V. R. Design and Synthesis of Bimetallic Electrocatalyst with Multilayered Pt-Skin Surfaces. *J. Am. Chem. Soc.* **2011**, *133* (36), 14396–14403.

(126) Wang, C.; van der Vliet, D.; More, K. L.; Zaluzec, N. J.; Peng, S.; Sun, S.; Daimon, H.; Wang, G.; Greeley, J.; Pearson, J.; Paulikas, A. P.; Karapetrov, G.; Strmcnik, D.; Markovic, N. M.; Stamenkovic, V. R. Multimetallic Au/FePt<sub>3</sub> Nanoparticles as Highly Durable Electrocatalyst. *Nano Lett.* **2011**, *11* (3), 919–926.

(127) Wang, C.; Markovic, N. M.; Stamenkovic, V. R. Advanced Platinum Alloy Electrocatalysts for the Oxygen Reduction Reaction. *ACS Catal.* **2012**, *2* (5), 891–898.

(128) Park, J.; Zhang, L.; Choi, S.-I.; Roling, L. T.; Lu, N.; Herron, J. A.; Xie, S.; Wang, J.; Kim, M. J.; Mavrikakis, M.; Xia, Y. Atomic Layer-by-Layer Deposition of Platinum on Palladium Octahedra for Enhanced Catalysts toward the Oxygen Reduction Reaction. *ACS Nano* **2015**, *9* (3), 2635–2647.

(129) Rizo, R.; Arán-Ais, R. M.; Padgett, E.; Muller, D. A.; Lázaro, M. J.; Solla-Gullón, J.; Feliu, J. M.; Pastor, E.; Abruña, H. D. Pt-Rich<sub>core</sub>/Sn-Rich<sub>subsurface</sub>/Pt<sub>skin</sub> Nanocubes As Highly Active and Stable Electrocatalysts for the Ethanol Oxidation Reaction. *J. Am. Chem. Soc.* **2018**, *140* (10), 3791–3797.

(130) Hunt, S. T.; Milina, M.; Alba-Rubio, A. C.; Hendon, C. H.; Dumesic, J. A.; Román-Leshkov, Y. Self-assembly of noble metal monolayers on transition metal carbide nanoparticle catalysts. *Science* **2016**, *352* (6288), 974–978.

(131) Garg, A.; Milina, M.; Ball, M.; Zanchet, D.; Hunt, S. T.; Dumesic, J. A.; Román-Leshkov, Y. Transition-Metal Nitride Core@Noble-Metal Shell Nanoparticles as Highly CO Tolerant Catalysts. *Angew. Chem., Int. Ed.* **2017**, *56* (30), 8828–8833.

(132) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M. F.; Nilsson, A. Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts. *Nat. Chem.* **2010**, *2* (6), 454–460.

(133) Cui, C.; Gan, L.; Heggen, M.; Rudi, S.; Strasser, P. Compositional segregation in shaped Pt alloy nanoparticles and their structural behaviour during electrocatalysis. *Nat. Mater.* **2013**, *12*, 765.

(134) Cargnello, M.; Agarwal, R.; Klein, D. R.; Diroll, B. T.; Agarwal, R.; Murray, C. B. Uniform Bimetallic Nanocrystals by High-Temperature Seed-Mediated Colloidal Synthesis and Their Catalytic Properties for Semiconducting Nanowire Growth. *Chem. Mater.* **2015**, *27* (16), 5833–5838.

(135) DeSantis, C. J.; Sue, A. C.; Bower, M. M.; Skrabalak, S. E. Seed-Mediated Co-reduction: A Versatile Route to Architecturally Controlled Bimetallic Nanostructures. *ACS Nano* **2012**, *6* (3), 2617–2628.

(136) Kim, D.; Resasco, J.; Yu, Y.; Asiri, A. M.; Yang, P. Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold-copper bimetallic nanoparticles. *Nat. Commun.* **2014**, *5*, 4948.

(137) Kim, D.; Xie, C.; Becknell, N.; Yu, Y.; Karamad, M.; Chan, K.; Crumlin, E. J.; Nørskov, J. K.; Yang, P. Electrochemical Activation of CO<sub>2</sub> through Atomic Ordering Transformations of AuCu Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139* (24), 8329–8336.

(138) Goodman, E. D.; Schwalbe, J. A.; Cargnello, M. Mechanistic Understanding and the Rational Design of Sinter-Resistant Heterogeneous Catalysts. *ACS Catal.* **2017**, *7*, 7156–7173.

(139) Carrillo, C.; Johns, T. R.; Xiong, H.; DeLaRiva, A.; Challa, S. R.; Goeke, R. S.; Artyushkova, K.; Li, W.; Kim, C. H.; Datye, A. K. Trapping of Mobile Pt Species by PdO Nanoparticles under Oxidizing Conditions. *J. Phys. Chem. Lett.* **2014**, *5* (12), 2089–2093.

(140) Xiong, H.; Peterson, E.; Qi, G.; Datye, A. K. Trapping mobile Pt species by PdO in diesel oxidation catalysts: Smaller is better. *Catal. Today* **2016**, *272*, 80–86.

- (141) Goodman, E. D.; Dai, S.; Yang, A.-C.; Wrasman, C. J.; Gallo, A.; Bare, S. R.; Hoffman, A. S.; Jaramillo, T. F.; Graham, G. W.; Pan, X.; Cargnello, M. Uniform Pt/Pd Bimetallic Nanocrystals Demonstrate Platinum Effect on Palladium Methane Combustion Activity and Stability. *ACS Catal.* **2017**, *7* (7), 4372–4380.
- (142) Kyriakou, G.; Boucher, M. B.; Jewell, A. D.; Lewis, E. A.; Lawton, T. J.; Baber, A. E.; Tierney, H. L.; Flytzani-Stephanopoulos, M.; Sykes, E. C. Isolated Metal Atom Geometries as a Strategy for Selective Heterogeneous Hydrogenations. *Science* **2012**, *335* (6073), 1209–1212.
- (143) Marcinkowski, M. D.; Darby, M. T.; Liu, J.; Wimble, J. M.; Lucci, F. R.; Lee, S.; Michaelides, A.; Flytzani-Stephanopoulos, M.; Stamatakis, M.; Sykes, E. C. H. Pt/Cu single-atom alloys as coke-resistant catalysts for efficient C–H activation. *Nat. Chem.* **2018**, *10*, 325.
- (144) Chen, M.; Kumar, D.; Yi, C. W.; Goodman, D. W. Chemistry: The promotional effect of gold in catalysis by palladium-gold. *Science* **2005**, *310* (5746), 291–293.
- (145) Han, Y. F.; Wang, J. H.; Kumar, D.; Yan, Z.; Goodman, D. W. A kinetic study of vinyl acetate synthesis over Pd-based catalysts: Kinetics of vinyl acetate synthesis over Pd-Au/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> catalysts. *J. Catal.* **2005**, *232* (2), 467–475.
- (146) Liu, J.; Lucci, F. R.; Yang, M.; Lee, S.; Marcinkowski, M. D.; Therrien, A. J.; Williams, C. T.; Sykes, E. C. H.; Flytzani-Stephanopoulos, M. Tackling CO Poisoning with Single-Atom Alloy Catalysts. *J. Am. Chem. Soc.* **2016**, *138* (20), 6396–6399.
- (147) Yang, J.-W.; Zheng, W.-T.; Hu, Z.; Zhang, M.; Xu, B.-Q. Do Olefin Hydrogenation Reactions Remain Structure Insensitive over Pt in Nanostructured Pt-on-Au Catalyst? *ACS Catal.* **2018**, *8*, 10254–10260.
- (148) Wrasman, C. J.; Boubnov, A.; Riscoe, A. R.; Hoffman, A. S.; Bare, S. R.; Cargnello, M. Synthesis of Colloidal Pd/Au Dilute Alloy Nanocrystals and Their Potential for Selective Catalytic Oxidations. *J. Am. Chem. Soc.* **2018**, *140* (40), 12930–12939.
- (149) Akram, A.; Freakley, S. J.; Reece, C.; Piccinini, M.; Shaw, G.; Edwards, J. K.; Desmedt, F.; Miquel, P.; Seuna, E.; Willock, D. J.; Moulijn, J. A.; Hutchings, G. J. Gas phase stabiliser-free production of hydrogen peroxide using supported gold–palladium catalysts. *Chemical Science* **2016**, *7* (9), 5833–5837.
- (150) Wu, L.; Fournier, A. P.; Willis, J. J.; Cargnello, M.; Tassone, C. J. In Situ X-ray Scattering Guides the Synthesis of Uniform PtSn Nanocrystals. *Nano Lett.* **2018**, *18* (6), 4053–4057.
- (151) Pei, Y.; Qi, Z.; Goh, T. W.; Wang, L.-L.; Maligal-Ganesh, R. V.; MacMurdo, H. L.; Zhang, S.; Xiao, C.; Li, X.; Tao, F.; Johnson, D. D.; Huang, W. Intermetallic structures with atomic precision for selective hydrogenation of nitroarenes. *J. Catal.* **2017**, *356*, 307–314.
- (152) Luo, J.; Lee, J. D.; Yun, H.; Wang, C.; Monai, M.; Murray, C. B.; Fornasiero, P.; Gorte, R. J. Base metal-Pt alloys: A general route to high selectivity and stability in the production of biofuels from HMF. *Appl. Catal., B* **2016**, *199*, 439–446.
- (153) Haruta, M. Size- and support-dependency in the catalysis of gold. *Catal. Today* **1997**, *36* (1), 153–166.
- (154) Comotti, M.; Li, W. C.; Spliethoff, B.; Schuth, F. Support effect in high activity gold catalysts for CO oxidation. *J. Am. Chem. Soc.* **2006**, *128* (3), 917–924.
- (155) McKay, I. S.; Schwalbe, J. A.; Goodman, E. D.; Willis, J. J.; Majumdar, A.; Cargnello, M. Elucidating the synergistic mechanism of nickel–molybdenum electrocatalysts for the hydrogen evolution reaction. *MRS Commun.* **2016**, *6*, 241–246.
- (156) Danilovic, N.; Subbaraman, R.; Strmcnik, D.; Chang, K.-C.; Paulikas, A. P.; Stamenkovic, V. R.; Markovic, N. M. Enhancing the Alkaline Hydrogen Evolution Reaction Activity through the Bifunctionality of Ni(OH)<sub>2</sub>/Metal Catalysts. *Angew. Chem., Int. Ed.* **2012**, *51* (50), 12495–12498.
- (157) Gong, M.; Zhou, W.; Tsai, M.-C.; Zhou, J.; Guan, M.; Lin, M.-C.; Zhang, B.; Hu, Y.; Wang, D.-Y.; Yang, J.; Pennycook, S. J.; Hwang, B.-J.; Dai, H. Nanoscale nickel oxide/nickel heterostructures for active hydrogen evolution electrocatalysis. *Nat. Commun.* **2014**, *5*, 4695.
- (158) Argyle, M.; Bartholomew, C. Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts* **2015**, *5* (1), 145.
- (159) Bartholomew, C. H. Mechanisms of catalyst deactivation. *Appl. Catal., A* **2001**, *212* (1–2), 17–60.
- (160) Hansen, T. W.; DeLaRiva, A. T.; Challa, S. R.; Datye, A. K. Sintering of Catalytic Nanoparticles: Particle Migration or Ostwald Ripening? *Acc. Chem. Res.* **2013**, *46* (8), 1720–1730.
- (161) Datye, A. K.; Xu, Q.; Kharas, K. C.; McCarty, J. M. Particle size distributions in heterogeneous catalysts: What do they tell us about the sintering mechanism? *Catal. Today* **2006**, *111* (1–2), 59–67.
- (162) Kaden, W. E.; Wu, T.; Kunkel, W. A.; Anderson, S. L. Electronic Structure Controls Reactivity of Size-Selected Pd Clusters Adsorbed on TiO<sub>2</sub> Surfaces. *Science* **2009**, *326* (5954), 826–829.
- (163) Hu, K.-J.; Plant, S. R.; Ellis, P. R.; Brown, C. M.; Bishop, P. T.; Palmer, R. E. Atomic Resolution Observation of a Size-Dependent Change in the Ripening Modes of Mass-Selected Au Nanoclusters Involved in CO Oxidation. *J. Am. Chem. Soc.* **2015**, *137* (48), 15161–15168.
- (164) Wettergren, K.; Schweinberger, F. F.; Deiana, D.; Ridge, C. J.; Crampton, A. S.; Rötzer, M. D.; Hansen, T. W.; Zhdanov, V. P.; Heiz, U.; Langhammer, C. High Sintering Resistance of Size-Selected Platinum Cluster Catalysts by Suppressed Ostwald Ripening. *Nano Lett.* **2014**, *14* (10), 5803–5809.
- (165) van Deelen, T. W.; Nijhuis, J. J.; Krans, N. A.; Zečević, J.; de Jong, K. P. Preparation of Cobalt Nanocrystals Supported on Metal Oxides To Study Particle Growth in Fischer–Tropsch Catalysts. *ACS Catal.* **2018**, *8*, 10581–10589.
- (166) Wang, L.; Lavacchi, A.; Bellini, M.; D’Acapito, F.; Benedetto, F. D.; Innocenti, M.; Miller, H. A.; Montegrossi, G.; Zafferoni, C.; Vizza, F. Deactivation of Palladium Electrocatalysts for Alcohols Oxidation in Basic Electrolytes. *Electrochim. Acta* **2015**, *177*, 100–106.
- (167) Manthiram, K.; Surendranath, Y.; Alivisatos, A. P. Dendritic Assembly of Gold Nanoparticles during Fuel-Forming Electrocatalysis. *J. Am. Chem. Soc.* **2014**, *136* (20), 7237–7240.
- (168) Huang, J.; Hörmann, N.; Oveisi, E.; Louidice, A.; De Gregorio, G. L.; Andreussi, O.; Marzari, N.; Buonsanti, R. Potential-induced nanoclustering of metallic catalysts during electrochemical CO<sub>2</sub> reduction. *Nat. Commun.* **2018**, *9* (1), 3117.
- (169) Grosse, P.; Gao, D.; Scholten, F.; Sinev, I.; Mistry, H.; Roldan Cuenya, B. Dynamic Changes in the Structure, Chemical State and Catalytic Selectivity of Cu Nanocubes during CO<sub>2</sub> Electroreduction: Size and Support Effects. *Angew. Chem., Int. Ed.* **2018**, *57* (21), 6192–6197.
- (170) de Jonge, N.; Bigelow, W. C.; Veith, G. M. Atmospheric Pressure Scanning Transmission Electron Microscopy. *Nano Lett.* **2010**, *10* (3), 1028–1031.
- (171) Zheng, H.; Smith, R. K.; Jun, Y. w.; Kisielowski, C.; Dahmen, U.; Alivisatos, A. P. Observation of Single Colloidal Platinum Nanocrystal Growth Trajectories. *Science* **2009**, *324* (5932), 1309–1312.
- (172) Zhang, S.; Plessow, P. N.; Willis, J. J.; Dai, S.; Xu, M.; Graham, G. W.; Cargnello, M.; Abild-Pedersen, F.; Pan, X. Dynamical Observation and Detailed Description of Catalysts under Strong Metal–Support Interaction. *Nano Lett.* **2016**, *16* (7), 4528–4534.
- (173) Tauster, S. J.; Fung, S. C.; Baker, R. T. K.; Horsley, J. A. Strong Interactions in Supported-Metal Catalysts. *Science* **1981**, *211* (4487), 1121–1125.
- (174) Tauster, S. J.; Fung, S. C.; Garten, R. L. Strong metal-support interactions. Group 8 noble metals supported on TiO<sub>2</sub>. *J. Am. Chem. Soc.* **1978**, *100* (1), 170–175.
- (175) Dong, B.; Pei, Y.; Zhao, F.; Goh, T. W.; Qi, Z.; Xiao, C.; Chen, K.; Huang, W.; Fang, N. In situ quantitative single-molecule study of dynamic catalytic processes in nanoconfinement. *Nature Catalysis* **2018**, *1* (2), 135–140.
- (176) Aitbekova, A.; Wu, L.; Wrasman, C. J.; Boubnov, A.; Hoffman, A. S.; Goodman, E. D.; Bare, S. R.; Cargnello, M. Low-Temperature Restructuring of CeO<sub>2</sub>-Supported Ru Nanoparticles Determines

Selectivity in CO<sub>2</sub> Catalytic Reduction. *J. Am. Chem. Soc.* **2018**, *140* (42), 13736–13745.

(177) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355* (6321), eaad4998.

(178) Carbone, L.; Cozzoli, P. D. Colloidal heterostructured nanocrystals: Synthesis and growth mechanisms. *Nano Today* **2010**, *5* (5), 449–493.

(179) Wittstock, A.; Zielasek, V.; Biener, J.; Friend, C. M.; Baumer, M. Nanoporous Gold Catalysts for Selective Gas-Phase Oxidative Coupling of Methanol at Low Temperature. *Science* **2010**, *327* (5963), 319–322.

(180) Zugic, B.; Wang, L.; Heine, C.; Zakharov, D. N.; Lechner, B. A. J.; Stach, E. A.; Biener, J.; Salmeron, M.; Madix, R. J.; Friend, C. M. Dynamic restructuring drives catalytic activity on nanoporous gold-silver alloy catalysts. *Nat. Mater.* **2016**, *16* (5), 558–564.

(181) Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M.; Chi, M.; More, K. L.; Li, Y.; Markovic, N. M.; Somorjai, G. A.; Yang, P.; Stamenkovic, V. R. Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces. *Science* **2014**, *343* (6177), 1339–1343.

(182) Li, Z.; Yu, R.; Huang, J.; Shi, Y.; Zhang, D.; Zhong, X.; Wang, D.; Wu, Y.; Li, Y. Platinum–nickel frame within metal-organic framework fabricated in situ for hydrogen enrichment and molecular sieving. *Nat. Commun.* **2015**, *6*, 8248.

(183) Zhang, L.; Roling, L. T.; Wang, X.; Vara, M.; Chi, M.; Liu, J.; Choi, S.-I.; Park, J.; Herron, J. A.; Xie, Z.; Mavrikakis, M.; Xia, Y. Platinum-based nanocages with subnanometer-thick walls and well-defined, controllable facets. *Science* **2015**, *349* (6246), 412–416.

(184) Li, G. G.; Wang, H. Dealloyed Nanoporous Gold Catalysts: From Macroscopic Foams to Nanoparticulate Architectures. *Chem-NanoMat* **2018**, *4* (9), 897–908.

(185) Cui, C.; Gan, L.; Li, H.-H.; Yu, S.-H.; Heggen, M.; Strasser, P. Octahedral PtNi Nanoparticle Catalysts: Exceptional Oxygen Reduction Activity by Tuning the Alloy Particle Surface Composition. *Nano Lett.* **2012**, *12* (11), 5885–5889.

(186) Henkes, A. E.; Vasquez, Y.; Schaak, R. E. Converting Metals into Phosphides: A General Strategy for the Synthesis of Metal Phosphide Nanocrystals. *J. Am. Chem. Soc.* **2007**, *129* (7), 1896–1897.

(187) Popczun, E. J.; McKone, J. R.; Read, C. G.; Bicchieri, A. J.; Wiltrout, A. M.; Lewis, N. S.; Schaak, R. E. Nanostructured nickel phosphide as an electrocatalyst for the hydrogen evolution reaction. *J. Am. Chem. Soc.* **2013**, *135* (25), 9267–9270.

(188) Kim, D.; Kley, C. S.; Li, Y.; Yang, P. Copper nanoparticle ensembles for selective electroreduction of CO<sub>2</sub> to C<sub>2</sub>–C<sub>3</sub> products. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (40), 10560–10565.

(189) Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T. Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO<sub>2</sub> Catalyst. *Science* **2011**, *333* (6043), 736–739.

(190) Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T. Low-Temperature Catalytic H<sub>2</sub> Oxidation over Au Nanoparticle/TiO<sub>2</sub> Dual Perimeter Sites. *Angew. Chem., Int. Ed.* **2011**, *50* (43), 10186–10189.

(191) Kang, Y.; Ye, X.; Chen, J.; Qi, L.; Diaz, R. E.; Doan-Nguyen, V.; Xing, G.; Kagan, C. R.; Li, J.; Gorte, R. J.; Stach, E. A.; Murray, C. B. Engineering Catalytic Contacts and Thermal Stability: Gold/Iron Oxide Binary Nanocrystal Superlattices for CO Oxidation. *J. Am. Chem. Soc.* **2013**, *135* (4), 1499–1505.

(192) Chen, G.; Zhao, Y.; Fu, G.; Duchesne, P. N.; Gu, L.; Zheng, Y.; Weng, X.; Chen, M.; Zhang, P.; Pao, C. W.; Lee, J. F.; Zheng, N. Interfacial Effects in Iron-Nickel Hydroxide-Platinum Nanoparticles Enhance Catalytic Oxidation. *Science* **2014**, *344* (6183), 495–499.

(193) Yamada, Y.; Tsung, C. K.; Huang, W.; Huo, Z.; Habas, S. E.; Soejima, T.; Aliaga, C. E.; Somorjai, G. A.; Yang, P. Nanocrystal bilayer for tandem catalysis. *Nat. Chem.* **2011**, *3* (5), 372–376.

(194) Huang, X.; Tang, S.; Mu, X.; Dai, Y.; Chen, G.; Zhou, Z.; Ruan, F.; Yang, Z.; Zheng, N. Freestanding palladium nanosheets with plasmonic and catalytic properties. *Nat. Nanotechnol.* **2011**, *6* (1), 28–32.

(195) Duan, H.; Yan, N.; Yu, R.; Chang, C. R.; Zhou, G.; Hu, H. S.; Rong, H.; Niu, Z.; Mao, J.; Asakura, H.; Tanaka, T.; Dyson, P. J.; Li, J.; Li, Y. Ultrathin rhodium nanosheets. *Nat. Commun.* **2014**, *5*, 3093.

(196) Scott, S. L. A Matter of Life(time) and Death. *ACS Catal.* **2018**, *8* (9), 8597–8599.

(197) De Rogatis, L.; Cargnello, M.; Gombac, V.; Lorenzut, B.; Montini, T.; Fornasiero, P. Embedded Phases: A Way to Active and Stable Catalysts. *ChemSusChem* **2010**, *3* (1), 24–42.

(198) Zhou, H. P.; Wu, H. S.; Shen, J.; Yin, A. X.; Sun, L. D.; Yan, C. H. Thermally Stable Pt/CeO<sub>2</sub> Hetero-Nanocomposites with High Catalytic Activity. *J. Am. Chem. Soc.* **2010**, *132* (14), 4998–4999.

(199) Arnal, P. M.; Comotti, M.; Schuth, F. High-temperature-stable catalysts by hollow sphere encapsulation. *Angew. Chem., Int. Ed.* **2006**, *45* (48), 8224–8227.

(200) Cargnello, M.; Montini, T.; Polizzi, S.; Wieder, N. L.; Gorte, R. J.; Graziani, M.; Fornasiero, P. Novel embedded Pd@CeO<sub>2</sub> catalysts: a way to active and stable catalysts. *Dalton Transactions* **2010**, *39* (8), 2122–2127.

(201) Cargnello, M.; Grzelczak, M.; Rodríguez-González, B.; Syrgiannis, Z.; Bakhmutsky, K.; La Parola, V.; Liz-Marzán, L.; Gorte, R. J.; Prato, M.; Fornasiero, P. Multiwalled Carbon Nanotubes Drive the Activity of Metal@oxide Core-Shell Catalysts in Modular Nanocomposites. *J. Am. Chem. Soc.* **2012**, *134* (28), 11760–11766.

(202) Li, G.; Zhao, S.; Zhang, Y.; Tang, Z. Metal–Organic Frameworks Encapsulating Active Nanoparticles as Emerging Composites for Catalysis: Recent Progress and Perspectives. *Adv. Mater.* **2018**, *30* (51), 1800702.

(203) Zhao, M.; Yuan, K.; Wang, Y.; Li, G.; Guo, J.; Gu, L.; Hu, W.; Zhao, H.; Tang, Z. Metal–organic frameworks as selectivity regulators for hydrogenation reactions. *Nature* **2016**, *539*, 76.

(204) Na, K.; Choi, K. M.; Yaghi, O. M.; Somorjai, G. A. Metal nanocrystals embedded in single nanocrystals of MOFs give unusual selectivity as heterogeneous catalysts. *Nano Lett.* **2014**, *14* (10), 5979–5983.

(205) Lu, G.; Li, S.; Guo, Z.; Farha, O. K.; Hauser, B. G.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; DuChene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S. C. J.; Wei, W. D.; Yang, Y.; Hupp, J. T.; Huo, F. Imparting functionality to a metal–organic framework material by controlled nanoparticle encapsulation. *Nat. Chem.* **2012**, *4*, 310.

(206) Lee, H. K.; Koh, C. S. L.; Lee, Y. H.; Liu, C.; Phang, I. Y.; Han, X.; Tsung, C.-K.; Ling, X. Y. Favoring the unfavored: Selective electrochemical nitrogen fixation using a reticular chemistry approach. *Science Advances* **2018**, *4* (3), eaar3208.

(207) Zhang, L.; Niu, G.; Lu, N.; Wang, J.; Tong, L.; Wang, L.; Kim, M. J.; Xia, Y. Continuous and Scalable Production of Well-Controlled Noble-Metal Nanocrystals in Milliliter-Sized Droplet Reactors. *Nano Lett.* **2014**, *14* (11), 6626–6631.

(208) Piccinno, F.; Gottschalk, F.; Seeger, S.; Nowack, B. Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world. *J. Nanopart. Res.* **2012**, *14* (9), 1109.

(209) Behrens, M.; Kißner, S.; Girsgdies, F.; Kasatkin, I.; Hermerschmidt, F.; Mette, K.; Ruland, H.; Muhler, M.; Schlögl, R. Knowledge-based development of a nitrate-free synthesis route for Cu/ZnO methanol synthesis catalysts via formate precursors. *Chem. Commun.* **2011**, *47* (6), 1701–1703.

(210) Prieto, G.; de Jong, K. P.; de Jongh, P. E. Towards ‘greener’ catalyst manufacture: Reduction of wastewater from the preparation of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalysts. *Catal. Today* **2013**, *215*, 142–151.

(211) Shen, Y.; Gee, M. Y.; Greytak, A. B. Purification technologies for colloidal nanocrystals. *Chem. Commun.* **2017**, *53* (5), 827–841.