

## Core–Shell Nanostructured Catalysts

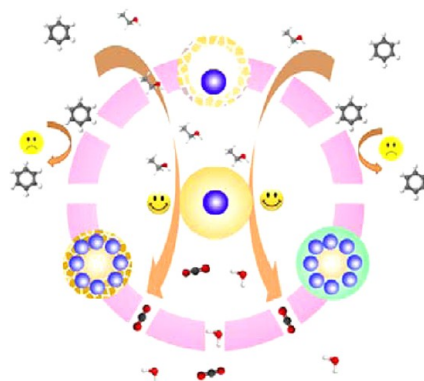
QIAO ZHANG, ILKEUN LEE, JI BONG JOO, FRANCISCO ZAERA,\*  
AND YADONG YIN\*

*Department of Chemistry, University of California, Riverside,  
California, 92521, United States*

RECEIVED ON JULY 31, 2012

### CONSPECTUS

**N**ovel nanotechnologies have allowed great improvements in the synthesis of catalysts with well-controlled size, shape, and surface properties. Transition metal nanostructures with specific sizes and shapes, for instance, have shown great promise as catalysts with high selectivities and relative ease of recycling. Researchers have already demonstrated new selective catalysis with solution-dispersed or supported-metal nanocatalysts, in some cases applied to new types of reactions. Several challenges remain, however, particularly in improving the structural stability of the catalytic active phase. Core–shell nanostructures are nanoparticles encapsulated and protected by an outer shell that isolates the nanoparticles and prevents their migration and coalescence during the catalytic reactions. The synthesis and characterization of effective core–shell catalysts has been at the center of our research efforts and is the focus of this Account.



Efficient core–shell catalysts require porous shells that allow free access of chemical species from the outside to the surface of nanocatalysts. For this purpose, we have developed a surface-protected etching process to prepare mesoporous silica and titania shells with controllable porosity. In certain cases, we can tune catalytic reaction rates by adjusting the porosity of the outer shell. We also designed and successfully applied a silica-protected calcination method to prepare crystalline shells with high surface area, using anatase titania as a model system. We achieved a high degree of control over the crystallinity and porosity of the anatase shells, allowing for the systematic optimization of their photocatalytic activity.

Core–shell nanostructures also provide a great opportunity for controlling the interaction among the different components in ways that might boost structural stability or catalytic activity. For example, we fabricated a  $\text{SiO}_2/\text{Au}/\text{N-doped TiO}_2$  core-shell photocatalyst with a sandwich structure that showed excellent catalytic activity for the oxidation of organic compounds under UV, visible, and direct sunlight. The enhanced photocatalytic efficiency of this nanostructure resulted from an added interfacial nonmetal doping, which improved visible light absorption, and from plasmonic metal decoration that enhanced light harvesting and charge separation.

In addition to our synthetic efforts, we have developed ways to evaluate the accessibility of reactants to the metal cores and to characterize the catalytic properties of the core–shell samples we have synthesized. We have adapted infrared absorption spectroscopy and titration experiments using carbon monoxide and other molecules as probes to study adsorption on the surface of metal cores in metal oxide–shell structures in situ in both gas and liquid phases. In particular, the experiments in solution have provided insights into the ease of diffusion of molecules of different sizes in and out of the shells in these catalysts.

### 1. Introduction

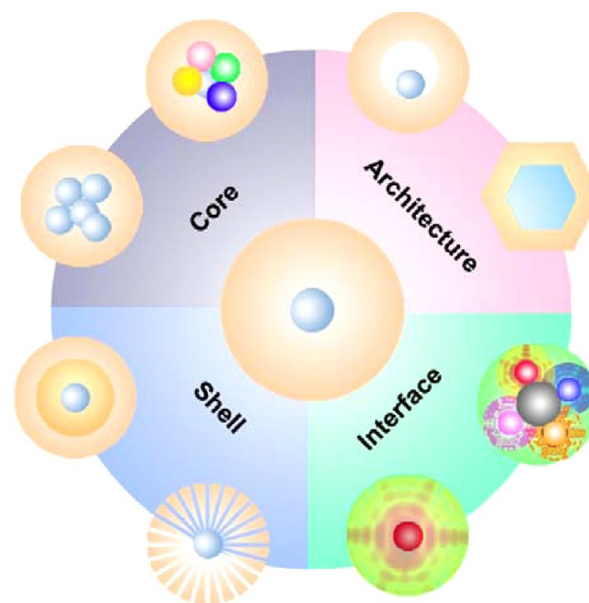
Catalysis now plays an essential role in many industrial applications such as oil refining, pharmaceutical production, and automotive emission control, which are of direct relevance to many aspects of our daily life. Since most catalysis is carried out by solids and the reaction occurs only when the reactants are adsorbed onto the catalyst

surface, the total surface area of the solid active phase has a substantial effect on the reaction rate. In fact, it has been established that the structure of the surfaces may affect catalytic activity and selectivity as well.<sup>1,2</sup> Long before the term “nanotechnology” was introduced, great effort had already been made in the field of catalysis to synthesize particles with sizes down to the nanometer scale in order to

enhance their specific surface area and, consequently, their catalytic activity. However, it has been with the rise of nanotechnology in the 1980s that the new tools have become available for the engineering of the structural details of catalysts, including their size, shape, and surface properties, needed to properly tune their catalytic performance.<sup>3–5</sup> It is now well accepted that fine structural manipulation with nanoscale precision may give rise to a new-generation of catalysts with high catalytic performance.<sup>6,7</sup> Designed nanostructures of transition metals with well-defined sizes and shapes, for instance, have already been recognized as promising catalysts with enhanced selectivity.<sup>8–11</sup>

The new synthetic advances available nowadays can also be used to address another common problem in catalysis, that of the stability of the dispersed active phases. Due to their high surface energy, nanoparticles tend to rapidly sinter into larger clusters, especially under the conditions typically used in catalysis. This sintering process leads to the reduction of the active surface area, and also to the loss of the unique properties of the nanostructured catalysts.<sup>12</sup> One dramatic example of the importance of this issue can be seen with gold catalysts: gold nanoparticles dispersed on high-surface-area supports have been shown to be quite active in many low-temperature reactions, including carbon monoxide and hydrocarbon oxidations,<sup>13</sup> but also to lose their activity over time as they sinter into larger particles. It would be desirable to use new approaches to prevent such sintering, by, for instance, partially encapsulating the dispersed metal nanoparticles with additional mesoporous materials.<sup>14,15</sup>

An alternative approach for the protection of catalytically active nanoparticles is to develop them into core–shell nanostructures.<sup>16</sup> There are many possibilities to tailor the structure of the core and shell components. Here, we point out the four major approaches that one can use when engineering the structures of the core–shell nanocatalysts, as indicated in Figure 1: (i) overall architectural engineering to yield core–shell nanomaterials with different shapes, including spherical and concentric core–shell nanoparticles, yolk–shell nanoparticles with a movable core, and anisotropic nanostructures;<sup>17,18</sup> (ii) structural engineering of the shell materials to produce single-shell, multishell, or porous-shell structures;<sup>14</sup> (iii) manipulation of the composition and structure of the core materials to prepare single-core or multicore structures, or even a multicomponent core structures;<sup>19</sup> and (iv) engineering of the interaction between multiple components in the core–shell composite structures to induce synergies that might boost catalytic activity, selectivity, and structural stability.<sup>20</sup>

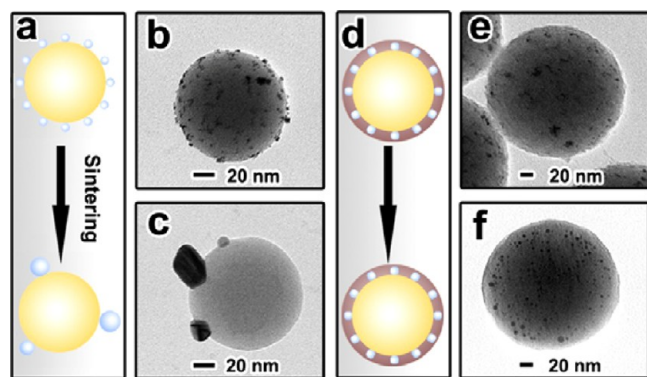


**FIGURE 1.** Schematic illustration of the four general components that can be engineered when preparing nanocatalysts with structures beyond simple core–shell configuration: the overall architecture, to obtain concentric yolk–shell structures or anisotropic structures; the core, to prepare multicore structures and multicomponent core structures; the shell, to get multishell structures and mesoporous shell structures; and the interface, to utilize the core–shell interaction to produce materials with enhanced catalytic activity, selectivity, and stability.

In this Account, we summarize our efforts toward the design and fabrication of various core–shell nanomaterials to produce catalysts with enhanced stability as well as improved activity and selectivity. First, we briefly discuss the growth of protective shells around the catalytically active nanoparticles to prevent them from sintering. To allow easy access of the reactants to the surface of the catalysts, a focus was placed on the creation of mesoscale porosity in the shell materials, a goal that was achieved by developing a “surface-protected etching” process. Second, we introduce a “silica-protected calcination” method for preparing crystalline shells with porous structures. This approach was used to prepare anatase titania shells, as required for photocatalytic applications. We then address the issue of the characterization of the accessibility of the shells and catalytic performance of these nanostructures. Finally, we discuss the unique features afforded by core–shell structures in the creation of synergetic interactions between the different components, which may lead to significantly enhanced catalytic efficiency.

## 2. Shell Stabilization of Nanostructured Catalysts

Metal nanoparticles dispersed on porous oxides, as seen in most heterogeneous catalysts, tend to sinter and lose their

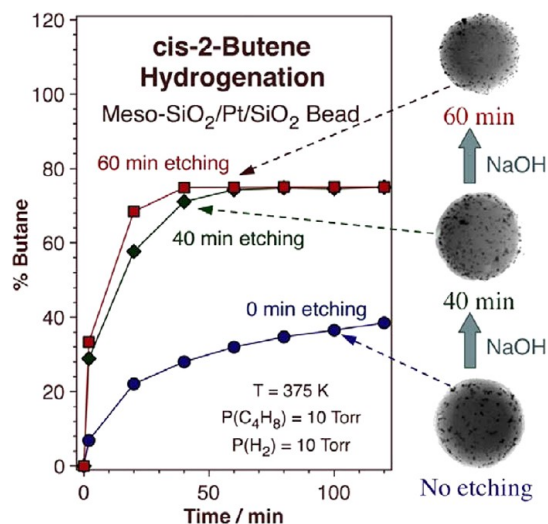


**FIGURE 2.** Illustration of the use of mesoporous silica layers for protection against sintering of dispersed metal nanoparticles.<sup>21</sup> As shown schematically in panel (a), the original small Pt nanoparticles supported on SiO<sub>2</sub> beads (panel (b)) coalesce into a few larger structures (panel (c)) upon calcination at 1075 K. The corresponding TEM images from a catalyst coated with a mesoporous SiO<sub>2</sub> shell, shown in panels (e) and (f), prove the enhanced stability afforded by such treatment (panel (d)). Adapted with permission from ref 21.

activity under reaction conditions. This is illustrated by the transmission electron microscopy (TEM) images provided in Figure 2b and c, which correspond to a model catalyst made out of platinum nanoparticles of 2–3 nm dispersed on the surface of ~100-nm-diameter silica beads.<sup>21,22</sup> When that sample was calcined at 1075 K, the Pt nanoparticles were seen to sinter into a few large crystalline particles ~10–20 nm in size (Figure 2c). In order to prevent this process, a thin layer of silica was deposited on the original silica-bead/Pt catalyst to form a core–shell structure (Figure 2d). As shown in the images in Figure 2e and f, this treatment completely suppresses sintering of the metal nanoparticles.

### 3. Addition of Porosity via Surface-Protected Etching

One problem with the use of additional materials to encapsulate the metal phase in catalysts is that it may reduce the accessibility of the reactants to the active phase. Therefore, assuring that the shells display adequate porosity is indispensable when designing active core–shell structured nanocatalysts. Several procedures, including layer-by-layer deposition techniques and sacrificial templating approaches, have been reported to make yolk–shell type nanostructures that can stabilize metal nanoparticles even under harsh reaction conditions.<sup>15,23</sup> It is however still a great challenge to systematically control the porosity of the shells in such multi-step procedures. We have recently introduced the new concept of “surface-protected etching” by which we have been able to explore the potential of producing core–shell nanostructured catalysts with porous shells and enhanced stability.<sup>14,24–26</sup>



**FIGURE 3.** Illustration of the use of our surface-protected etching procedure to regain the activity of encapsulated catalysts. The kinetics of hydrogenation of *cis*-2-butene, in the form of the accumulation of the butane product in the batch reactor as a function of reaction time, is reported for three catalysts, namely, for 10-nm-mesoporous-silica/1-wt %Pt/silica-bead catalysts as prepared (bottom TEM, blue) and after 40 (center TEM, green) and 60 (top TEM, red) min of etching.<sup>14</sup> Pt re-exposure and full catalytic activity are regained upon the 60 min etching treatment. Adapted with permission from ref 14.

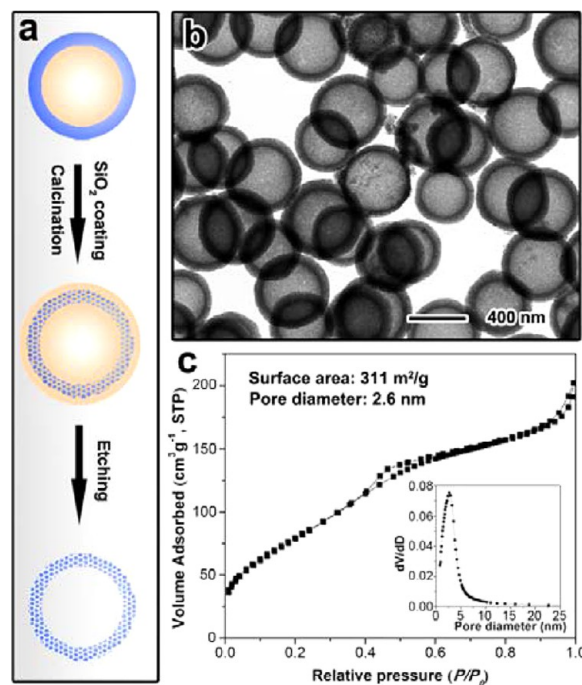
A typical surface-protected etching process involves pre-coating of the solid oxide shells with a protecting layer of polymeric ligands followed by preferential etching of the inner part of the shell material using an appropriate etching agent. The protection by the polymer allows the oxide shells to retain their original size, whereas the selective etching of the interior produces the porous structure. This procedure was in fact used to activate the mesoporous-silica/Pt/silica-bead catalyst discussed in the previous section, by using PVP as the protecting agent to take advantage of the fact that its carbonyl groups form strong hydrogen bonds with the hydroxyls on the silica surface.<sup>14,21,22</sup> The polymer chain, which contains multiple binding sites, can cross-link the SiO<sub>2</sub> subunits and dramatically increases their stability against the etching by NaOH. The unprotected silica is then gradually removed, leaving behind the porous SiO<sub>2</sub> framework. Our surface-protected etching process is quite general and can be applied to many systems, such as TiO<sub>2</sub>.<sup>27</sup> Figure 3 illustrates how the catalytic activity, in this case for the hydrogenation of *cis*-2-butene, was regained upon controlled surface-protected etching of the protective silica layer deposited on top of the dispersed platinum nanoparticles in our encapsulated samples: the initial rates of reaction, indicated by the slope of the traces at time zero, are significantly higher with the etched samples (by a factor of

almost an order of magnitude).<sup>14</sup> An important point illustrated in this example is the fact that the etching time needs to be fine-tuned to re-expose the catalytically active surfaces yet not remove too much of the support material, which would eliminate the metal nanoparticles themselves.

One limitation with the surface-protected etching strategy described here is that the overall metal content of these catalysts is typically quite low. To achieve higher catalyst loading, an alternative version of our synthetic strategy was developed to include multiple catalyst nanoparticles around each single inert core particle. In this case, a chemical linker needs to first be introduced in order to immobilize the metal nanoparticles to the surface of core particles. In one example, 3-aminopropyltriethoxysilane (APTES) was grafted to the surface of plain SiO<sub>2</sub> colloids, enabling controlled adsorption of a monolayer of metal nanoparticles such as Pt and Au thanks to the electrostatic interactions and coordinating bonds between the metal surface and the coupling agents.<sup>18</sup> The metal nanoparticle layer was subsequently coated with another layer of SiO<sub>2</sub> of desired thickness to fix them onto the surface of the initial support, and the surface-protected etching scheme was finally applied to transform the outer shell into a mesoporous structure, exposing the catalyst particles to the outside chemical species.

#### 4. Increased Shell Crystallinity by Surface-Protected Calcination

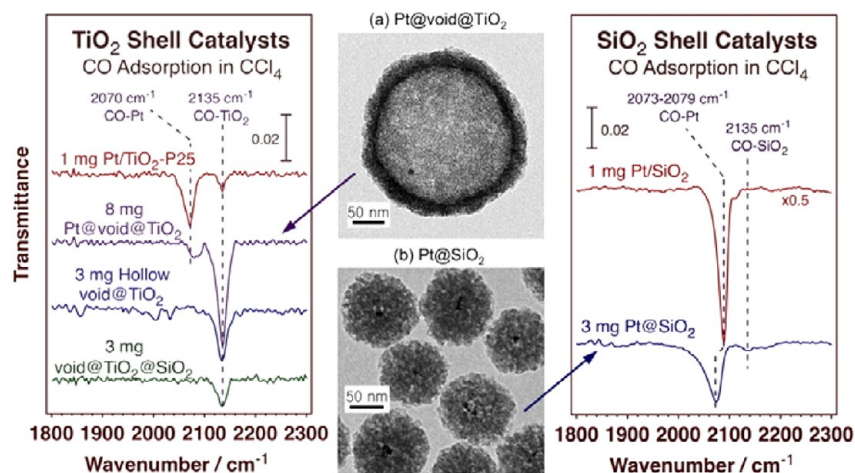
The sol–gel method, as used in the examples provided above, has proven to be an effective way to deposit inorganic oxide layers onto solid cores, to prepare various core–shell nanostructures. However, sol–gel deposition usually produces amorphous materials,<sup>28</sup> and for many catalytic applications, such as in photocatalyzed redox reactions by titania, the crystalline phases display significantly higher catalytic efficiency. Calcination at high temperatures is therefore sometimes required to convert the amorphous materials to their crystallized counterparts. Unfortunately, the porosity of the original amorphous shell is significantly diminished during calcination post-treatments, and the structural integrity of the shells may be compromised as well. We have recently developed a “surface-protected calcination” process to avoid these problems and produce mesoporous anatase titania shells with considerably large surface area and high crystallinity.<sup>29,30</sup> Our approach consists of the growth of another SiO<sub>2</sub> layer on top of the given titania nanostructure of interest using a sol–gel process, calcination of that structure at high temperature to induce a phase transformation from amorphous TiO<sub>2</sub> to anatase



**FIGURE 4.** (a) Schematic illustration of the surface-protected calcination procedure developed for the fabrication of mesoporous anatase TiO<sub>2</sub> hollow spheres; (b) corresponding TEM images of the final hollow products. (c) Nitrogen adsorption isotherm recorded for the final mesoporous anatase shells, showing a considerably higher surface area compared to that for anatase shells produced without silica protected calcination (several m<sup>2</sup> g<sup>-1</sup> in average). Adapted with permission from ref 29.

nanocrystals, and removal of both sacrificial silica layers by chemical etching to produce the final TiO<sub>2</sub> mesoporous anatase shells (Figure 4). If hollow titania shells are to be made, an amorphous titania shell is first grown on silica beads by a robust sol–gel method recently developed by our group.<sup>31,32</sup>

It was found that the coating of an additional silica layer onto the titania shells prevents the collapse of the shell porosity because of the impregnation of the amorphous network of the sol–gel derived titania with silicate species. Upon calcination, the silicate species limits grain growth within the titania, and leads to the formation of interconnected anatase nanocrystals.<sup>33</sup> Subsequent removal of the silica by selective chemical etching creates mesopores in the anatase shells. In a recent study, it was also determined that the amount of silica impregnation can be used to control the growth of the crystal grains.<sup>34</sup> Specifically, it was found that full impregnation with silicate species produces shells with small (<5 nm) anatase grains, small pores (average diameter ~2.6 nm), and high surface areas (up to 311 m<sup>2</sup> g<sup>-1</sup>) while still preserving the original hollow morphology (Figure 4b and c). Furthermore, the existence of a silica layer also



**FIGURE 5.** In situ transmission infrared absorption spectra in the CO stretching region for yolk–shell and core–shell catalysts in carbon tetrachloride solutions after exposure to CO.<sup>38</sup> Left (from top to bottom): (a) 1 mg of supported 1 wt % Pt/TiO<sub>2</sub>–P25 catalyst; (b) 8 mg of Pt@void@TiO<sub>2</sub> yolk@shell catalyst; (c) 3 mg of void@TiO<sub>2</sub> hollow shells; and (d) 3 mg of SiO<sub>2</sub>@TiO<sub>2</sub> core@shell nanostructures. Right: (e) 1 mg of supported 1 wt % Pt/SiO<sub>2</sub> catalyst (upper); and (f) 3 mg of Pt@SiO<sub>2</sub> core@shell catalyst (lower). TEM images of the key core–shell structures are provided in the center section of the figure. Adapted with permission from ref 38.

ensures a hydrophilic surface and, therefore, excellent water dispersibility. The mesoporous crystalline anatase shells made this way were shown to display significantly enhanced photocatalytic activity for the degradation of Rhodamine B (RhB) under UV irradiation.<sup>29</sup>

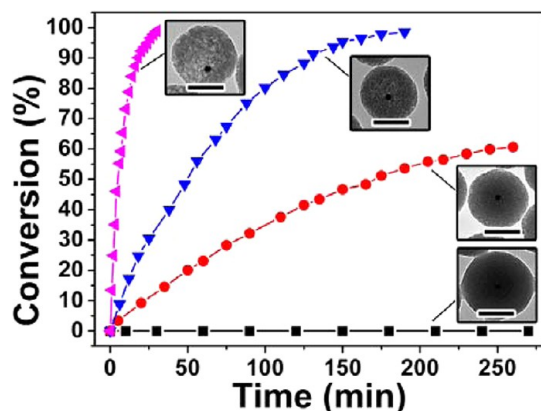
## 5. Evaluation of Diffusion through the Mesoporous Shells

Since adsorption of reactants on the surface of the active phase of the catalyst is necessary for reactions to take place, engineering the porosity of shell materials makes it possible to control the diffusion of reactant species and, consequently, the reaction kinetics. An understanding of the parameters that affect the diffusion of molecules through the shells of these structures may give rise to the design and synthesis of new catalysts with improved selectivities.<sup>35</sup> However, direct characterization of diffusion processes in these systems is difficult, and only a few examples have been reported of such studies to date, mostly in gas phase<sup>36,37</sup> but also in liquids.<sup>38</sup>

We have been exploring methods for the direct assessment of the diffusion of small molecules through the porous shells in core–shell nanostructures, mainly by in situ infrared (IR) absorption spectroscopy. The adsorption of carbon monoxide on the surface of metal nanoparticles in the core–shell samples is used here as the main way to probe surface accessibility, but adsorption of other more complex molecules, including NO and acetylene as well as cinchonidine and porphyrins, has been characterized as well.<sup>38,39</sup> In one case, the uptake of gas-phase CO onto the gold surface

in Au@Void@TiO<sub>2</sub> catalysts was identified, with specific adsorption on the surface of the metal surviving until temperatures of approximately 280 K.<sup>37</sup> In fact, the room-temperature rate of the oxidation of CO with O<sub>2</sub> promoted by the Au@Void@TiO<sub>2</sub> samples was determined to be comparable, normalized to the surface area of the gold phase, to that measured with a standard Au/TiO<sub>2</sub>–P25 catalyst, suggesting that mass transport does not play a limiting role in this case.<sup>37</sup> A similar CO IR titration approach was used to evaluate the accessibility of gas-phase species to the platinum surfaces in the encapsulated catalysts discussed in sections 2 and 3.<sup>21</sup> In all those examples, the rates of adsorption and reaction were deemed to be faster than the time resolution of the experiments, which amounts to approximately a couple of minutes.

Study of diffusion and adsorption in situ in liquid phase is more challenging.<sup>40</sup> We have recently developed an in situ IR absorption spectroscopy setup for this purpose, in transmission mode, where a cell previously designed for single reflection–absorption studies of flat surfaces<sup>41</sup> was modified so the back polished surface, made out of copper, acts as a mirror, and where the nanostructures to be studied are suspended in solution and trapped between that mirror and the front prism used as the optical element.<sup>5,38</sup> Figure 5 displays results from CO adsorption studies from a CCl<sub>4</sub> solution onto the surface of Pt nanoparticles in two core–shell structures, a Pt@Void@TiO<sub>2</sub> rattle-type nanoarchitecture (left), and a more conventional Pt@SiO<sub>2</sub> core–shell structure (right). In both cases, CO adsorption proved to be facile and extensive. Additionally, adsorption on the Pt cores was also



**FIGURE 6.** Conversion of 4-NP promoted by Au@SiO<sub>2</sub> catalysts which were prepared by etching for different period of time: 0 min (black square); 90 min (red circle); 150 min (blue down-pointing triangle); and 180 min (pink left-pointing triangle).<sup>24</sup> The corresponding TEM images show different porosities of the as-prepared product. All scale bars are 100 nm. Adapted with permission from ref 24. Copyright 2008 American Chemical Society.

shown to be feasible in other solvents such as ethanol. Because of additional mass transport limitations of the liquid in and out of the thin film area probed by the infrared absorption instrument, it has not been possible to measure diffusion rates for the adsorbates through the shells of the core–shell nanostructures in these studies, but full adsorption does occur within the ~10 min time required for the dissolved gases to reach the liquid surrounding the solid samples (as estimated by appropriate blank experiments). Since the core–shell structures have relatively big pores, large molecules such as cinchonidine can also penetrate those shells and adsorb on the metal surface. In fact, all of our studies so far have shown that the diffusion of small molecules through titania and silica shells in both gas and liquid phases is a general phenomenon.

## 6. Control of Reaction Rates by Varying Shell Porosity

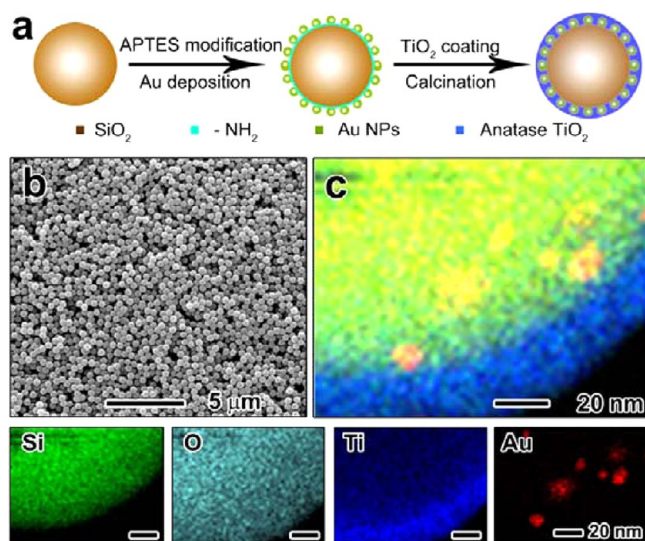
Future progress on our ongoing project to control shell porosity is required to prepare core–shell catalysts with high size-selectivity based on the blocking of the diffusion of either the reactants or the products for cases such as those discussed above. When larger molecules are involved, however, this is already possible. An example can be seen in our study using Au-encapsulated catalysts for the catalyzed reduction of 4-nitrophenol (4-NP) by NaBH<sub>4</sub>.<sup>24</sup> The non-etched SiO<sub>2</sub> shells were proven to be impenetrable by 4-NP, as no measurable catalytic activity was detected (Figure 6). However, by using our surface-protected etching process, the size of the pores in the silica shell could be

increased systematically (from ~1.5 nm after 10 min of etching to a wide distribution of pores with diameters well in excess of ~15 nm after 180 min of etching), to allow for the 4-NP molecules to access the center of the nanostructures and increase the catalytic performance. Indeed, as shown in Figure 6, the catalytic activity was observed to increase consistently in these nanocatalyst systems with increased etching time. Importantly, BET measurements indicated comparable surface areas for all samples etched more than 10 min (between approximately 220 and 270 m<sup>2</sup> g<sup>-1</sup>).

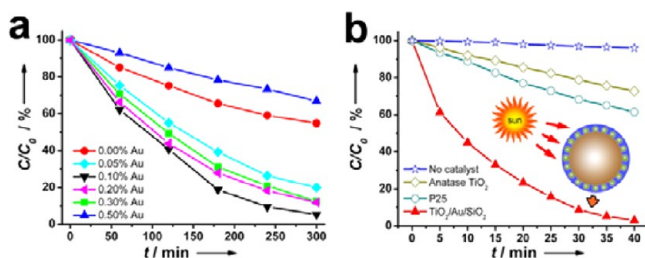
## 7. Core–Shell Interface Engineering

Besides enhanced stability, another major advantage that makes core–shell structured catalysts superior to single-component catalysts is the possible synergies derived from interactions between the core and shell materials. We have recently reported the preparation of a highly efficient, stable, and cost-effective TiO<sub>2</sub>-based photocatalyst by engineering the nature of the interfaces formed between the different components through a combination of simple sol–gel and calcination processes. The catalyst has a sandwich structure consisting of a SiO<sub>2</sub> core, a layer of gold nanoparticles (AuNPs), and a nitrogen-doped-TiO<sub>2</sub> nanocrystalline shell. The design of such a structure was based on a number of considerations. First, compared to traditional Au/TiO<sub>2</sub> composites in which AuNPs are loosely attached to the surface of the TiO<sub>2</sub> and unstable during calcination and subsequent photocatalysis, the sandwich structures with AuNPs embedded inside the TiO<sub>2</sub> matrix protects the former from moving together and coagulating.<sup>14,18,21</sup> Second, the encapsulation also increases the contact area between the AuNPs and the TiO<sub>2</sub> matrix and, therefore, allows for more efficient electron transfer. Third, nitrogen doping was incorporated to modify the electronic properties of the titania and to improve its photochemical behavior. By precontacting the Au with the TiO<sub>2</sub> surface, a significant increase in N loading could be achieved, by stabilizing the doped N inside the oxide, and the doped N could in turn enhance the adhesion of the AuNPs on the surface of the oxide through an electron transfer process.<sup>42</sup>

As illustrated in Figure 7a, these samples were prepared by following a procedure analogous to that described in section 3: the AuNPs were adsorbed onto the APTES-modified silica surface,<sup>18</sup> and the resulting Au/SiO<sub>2</sub> composite colloids were then coated with a layer of amorphous TiO<sub>2</sub> by hydrolyzing tetrabutyl orthotitanate (TBOT) in an ethanol solution in the presence of hydroxypropyl cellulose (HPC).<sup>31</sup> Calcination of the core–shell composites produced a blue



**FIGURE 7.** (a) Schematic illustration of the fabrication process of sandwich-structured  $\text{SiO}_2\text{@Au@TiO}_2$  photocatalyst. (b) Typical SEM image of the composite photocatalyst. (c) Elemental mapping of a single particle, with the distribution of individual elements shown in the bottom row. Adapted with permission from ref 20.



**FIGURE 8.** (a) Influence of AuNPs loading on the catalytic activity of  $\text{SiO}_2\text{@Au@TiO}_2$  sandwich structures, estimated by using the decomposition of RhB under visible light irradiation as the model reaction. (b) Photodegradation of RhB without catalyst and with anatase  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-P25}$ , and  $\text{SiO}_2\text{@Au@TiO}_2$  as the photocatalysts under direct sunlight illumination.<sup>20</sup> All conversions are referred to the same total weight of  $\text{TiO}_2$  catalyst. Adapted with permission from ref 20.

powder of uniform spheres, as shown in the scanning electron microscopy (SEM) image in Figure 7b. Energy dispersive X-ray (EDX) elemental mapping of a single sphere (Figure 7c) clearly confirms the expected sandwich structure, and observation under TEM at higher magnification reveals that the outer  $\text{TiO}_2$  shell is composed of small nanoparticle grains with  $\sim 8\text{--}15$  nm diameter, which are optimal for anatase photocatalysts.<sup>31,43</sup>

A systematic study was carried out to assess the effect of gold loading in these sandwich-structured samples on their photocatalytic performance, in this study the photodegradation of organic compounds under natural sunshine.<sup>20</sup> Interestingly, the visible-light activity of the samples was seen to peak at 0.1 wt % loading of AuNPs (Figure 8a). In fact, as seen

in Figure 8b, our samples outperform more standard catalysts: sunlight can completely decompose RhB molecules within 40 min of exposure with the aid of our sandwich-structured photocatalysts, whereas the conversion only reaches  $\sim 38\%$  with a commercial  $\text{TiO}_2\text{-P25}$  photocatalyst for the same reaction time, and  $\sim 27\%$  with a commercial anatase powder.

## 8. Conclusion and Outlook

In this Account, we have discussed the design and fabrication of core–shell nanostructured materials and their potential application in catalysis. Encapsulating nanoscale catalysts into oxide shells significantly enhances their thermal stability during reactions. We have mainly focused on the engineering of shell structures to create mesoscale porosity in the shells, to allow the diffusion of reactant species to the surface of the core, typically the catalytically active phase, where they can adsorb and react. To this end, we have developed a “surface-protected etching” process and successfully applied it to the fabrication of several nanostructured catalyst systems, including yolk-shell and core–satellite nanocatalysts, in which metal nanocatalysts are stabilized by porous shells. It was proven that the porosity of the resulting silica and titania shells, which can be used to control the reaction rates of catalytic processes using these nanocatalysts, can be well controlled during the etching process. In terms of the crystallinity of the mesoporous shells in these core–shell nanostructures, we have advanced a “surface-protected calcination” method to prepare anatase titania shells in which the added silica species can prevent the overgrowth of titania grain and help maintain its porous structure and structural integrity. We have also demonstrated the ability to exert a high degree of control over the porosity and crystallinity of titania shells, which, when optimized, can significantly enhance their photocatalytic activity. An additional important feature of the core–shell nanostructures discussed here is the opportunity of using synergies between the different components of core–shell structures to boost structural stability and catalytic activity/selectivity. This has been demonstrated by a highly active and stable photocatalyst featuring multi-layer core–shell structures.

One of the remaining challenges in this field is the control over the uniformity of the mesopores created in the shells. The etching-based method described above is simple to use, convenient in altering the pore size, and general for many oxide materials. However, the resulting pores can display wide distributions of sizes and shapes, making size-selective

catalysis difficult. It has been reported that highly uniform pores can be produced in oxide materials by using self-assembled surfactants as templates, but that approach lacks the flexibility to systematically tune the pore size. It would be interesting to see this process being adapted to create core–shell catalyst structures with uniform and size-tunable pores in the shells. The combination of surfactant templating and etching strategies might provide more opportunities for this endeavor.

Future research should also be extended to improve the stability of shape-controlled nanocatalysts. There are many reported examples of dramatically enhanced catalytic activity and selectivity by using shape-controlled nanoparticles whose surfaces contain higher ratios of active crystalline facets than spherical particles.<sup>3,9,10</sup> Although it is believed that coating such nanoparticles with a porous shell may help their shape stability,<sup>44</sup> this strategy needs to be tested further.

In terms of the characterization of the chemical behavior of these nanostructures in catalysis, new approaches are needed to directly evaluate the rate of diffusion and mass transport of chemicals in and out of the shells, and to separate those effects from the overall performance of the catalysts (or in other uses). This challenge is particularly critical when dealing with in situ studies in solutions, since it is in the liquid phase that most of the high-value selective catalysis that could benefit from the development of complex nanostructured catalysts takes place.<sup>40</sup>

The design and creation of composite core–shell structures with multiple components and well-controlled interactions is likely to bring new benefits to many catalytic reactions. Our primary interest currently is the design and characterization of efficient composite catalyst for photocatalysis, which requires multiple elements to fulfill various functions, including light absorption, electron and hole separation and transport, and redox reactions. More rational designs of composite structures with appropriate components, spatial arrangements, and interface engineering should help produce highly efficient photocatalysts for solar water splitting, which has been deemed the Holy Grail in the field of renewable energy. Other complex nanostructures with well-defined structured surfaces may also be developed to control selectivity in other catalytic syntheses. It should be mentioned that, at present, it may be thought that the preparation cost of these nanostructures may limit their ultimate applications in industrial applications. However, as with many other new technologies, production costs can be significantly reduced if the synthesis can be scaled up to fulfill increased demand. It should also be indicated

that, in many cases, in the making of fine and specialty chemicals in particular, where the added value of the product is quite large, catalyst manufacturing may represent only a minor fraction of the total cost of production. These are areas where our new nanostructured catalyst may have a particularly large impact.

---

*We are thankful for the financial support provided for this project by the U.S. Department of Energy (DE-FG02-09ER16096). Yin also thanks the Research Corporation for Science Advancement for the Cottrell Scholar Award and DuPont for the Young Professor Grant. F.Z. acknowledges additional funding from the U.S. National Science Foundation.*

---

#### BIOGRAPHICAL INFORMATION

**Qiao Zhang** received his Ph.D. in physical chemistry from the University of California, Riverside, in 2012 under the supervision of Prof. Yadong Yin. His research interests include synthesis and utilization of nanostructured materials for applications in fields such as catalysis, photonics, and biomedical research.

**Ilkeun Lee** received his Ph.D. in physical chemistry from Sungkyunkwan University. After working with Prof. John M. White at the University of Texas at Austin for a year, he joined Prof. Zaera's lab as a postdoctoral fellow in 2001 and then as an Assistant Chemist since 2007. His research interests are in nanocatalysis, heterogeneous enantioselective catalysis, and surface chemistry.

**Ji Bong Joo** received his Ph.D. degree in chemical and biological engineering from Seoul National University in 2009. He then moved to University of California Riverside, where he is a postdoctoral fellow under the supervision of Prof. Zaera and Prof. Yin. His research interests are in synthesis of nanostructured catalysts and their application in photocatalysis, heterogeneous catalysis, and electrochemical catalysis.

**Francisco Zaera** received his Ph.D. from the University of California, Berkeley in 1984, was then an Assistant Chemist at the National Synchrotron Light Source of Brookhaven National Laboratory, in a joint appointment with Exxon Research Laboratories, and became a faculty member at the University of California, Riverside in 1986, where he is presently a Distinguished Professor of Chemistry. His research interests are in the areas of surface and materials chemistry and of heterogeneous catalysis, with particular emphasis on surface reaction kinetics and in situ spectroscopic characterization of surface species.

**Yadong Yin** received his Ph.D. in Materials Science and Engineering from the University of Washington in 2002, then worked as a postdoctoral fellow at the University of California, Berkeley and the Lawrence Berkeley National Laboratory, and became a staff scientist at LBNL in 2005. In 2006 he joined the faculty at the Department of Chemistry at the University of California, Riverside. His research interests include the synthesis and application of nanostructured materials, self-assembly processes, and colloidal and interface chemistry.



## FOOTNOTES

\*To whom correspondence should be addressed.  
The authors declare no competing financial interest.

## REFERENCES

- Somorjai, G. A.; Park, J. Y. Molecular Factors of Catalytic Selectivity. *Angew. Chem., Int. Ed.* **2008**, *47*, 9212–9228.
- Zaera, F. New Challenges in Heterogeneous Catalysis for the 21st Century. *Catal. Lett.* **2012**, *142*, 501–516.
- Xiong, Y.; Wiley, B. J.; Xia, Y. Nanocrystals with Unconventional Shapes - a Class of Promising Catalysts. *Angew. Chem., Int. Ed.* **2007**, *46*, 7157–7159.
- Tao, A. R.; Habas, S.; Yang, P. Shape Control of Colloidal Metal Nanocrystals. *Small* **2008**, *4*, 310–325.
- Albiter, M.; Crooks, R.; Zaera, F. Adsorption of Carbon Monoxide on Dendrimer-Encapsulated Platinum Nanoparticles: Liquid Versus Gas Phase. *J. Phys. Chem. Lett.* **2010**, *1*, 38–40.
- Pernicone, N. Catalysis at the Nanoscale Level. *CATTECH* **2003**, *7*, 196–204.
- Somorjai, G. A.; Tao, F.; Park, J. Y. The Nanoscience Revolution: Merging of Colloid Science, Catalysis and Nanoelectronics. *Top. Catal.* **2008**, *47*, 1–14.
- Bell, A. T. The Impact of Nanoscience on Heterogeneous Catalysis. *Science* **2003**, *299*, 1688–1691.
- Lee, I.; Morales, R.; Albiter, M. A.; Zaera, F. Synthesis of Heterogeneous Catalysts with Well Shaped Platinum Particles to Control Reaction Selectivity. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 15241–15246.
- Lee, I.; Delbecq, F.; Morales, R.; Albiter, M. A.; Zaera, F. Tuning Selectivity in Catalysis by Controlling Particle Shape. *Nat. Mater.* **2009**, *8*, 132–138.
- Grunes, J.; Zhu, J.; Somorjai, G. A. Catalysis and Nanoscience. *Chem. Commun.* **2003**, 2257–2260.
- Bartholomew, C. H. Mechanisms of Catalyst Deactivation. *Appl. Catal., A* **2001**, *212*, 17–60.
- Hutchings, G. J.; Haruta, M. A Golden Age of Catalysis: A Perspective. *Appl. Catal., A* **2005**, *291*, 2–5.
- Zhang, Q.; Lee, I.; Ge, J.; Zaera, F.; Yin, Y. Surface-Protected Etching of Mesoporous Oxide Shells for the Stabilization of Metal Nanocatalysts. *Adv. Funct. Mater.* **2010**, *20*, 2201–2214.
- Lu, J.; Fu, B.; Kung, M. C.; Xiao, G.; Elam, J. W.; Kung, H. H.; Stair, P. C. Coking- and Sintering-Resistant Palladium Catalysts Achieved through Atomic Layer Deposition. *Science* **2012**, *335*, 1205–1208.
- Schärtl, W. Current Directions in Core-Shell Nanoparticle Design. *Nanoscale* **2010**, *2*, 829–843.
- Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. Formation of Hollow Nanocrystals through the Nanoscale Kirkendall Effect. *Science* **2004**, *304*, 711–714.
- Ge, J.; Zhang, Q.; Zhang, T.; Yin, Y. Core-Satellite Nanocomposite Catalysts Protected by a Porous Silica Shell: Controllable Reactivity, High Stability, and Magnetic Recyclability. *Angew. Chem., Int. Ed.* **2008**, *47*, 8924–8928.
- Chen, C.; Fang, X.; Wu, B.; Huang, L.; Zheng, N. A Multi-Yolk-Shell Structured Nanocatalyst Containing Sub-10 Nm Pd Nanoparticles in Porous CeO<sub>2</sub>. *ChemCatChem* **2012**, *4*, 1578–1586.
- Zhang, Q.; Lima, D. Q.; Lee, I.; Zaera, F.; Chi, M.; Yin, Y. A Highly Active Titanium Dioxide Based Visible-Light Photocatalyst with Nonmetal Doping and Plasmonic Metal Decoration. *Angew. Chem., Int. Ed.* **2011**, *50*, 7088–7092.
- Lee, I.; Zhang, Q.; Ge, J.; Yin, Y.; Zaera, F. Encapsulation of Supported Pt Nanoparticles with Mesoporous Silica for Increased Catalyst Stability. *Nano Res.* **2011**, *4*, 115–123.
- Lee, I.; Albiter, M. A.; Zhang, Q.; Ge, J.; Yin, Y.; Zaera, F. New Nanostructured Heterogeneous Catalysts with Increased Selectivity and Stability. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2449–2456.
- Ikeda, S.; Ishino, S.; Harada, T.; Okamoto, N.; Sakata, T.; Mori, H.; Kuwabata, S.; Torimoto, T.; Matsumura, M. Ligand-Free Platinum Nanoparticles Encapsulated in a Hollow Porous Carbon Shell as a Highly Active Heterogeneous Hydrogenation Catalyst. *Angew. Chem., Int. Ed.* **2006**, *45*, 7063–7066.
- Zhang, Q.; Zhang, T.; Ge, J.; Yin, Y. Permeable Silica Shell through Surface-Protected Etching. *Nano Lett.* **2008**, *8*, 2867–2871.
- Zhang, Q.; Wang, W.; Goebel, J.; Yin, Y. Self-Templated Synthesis of Hollow Nanostructures. *Nano Today* **2009**, *4*, 494–507.
- Zhang, Q.; Ge, J.; Goebel, J.; Hu, Y.; Lu, Z.; Yin, Y. Rattle-Type Silica Colloidal Particles Prepared by a Surface-Protected Etching Process. *Nano Res.* **2009**, *2*, 583–591.
- Hu, Y.; Ge, J.; Sun, Y.; Zhang, T.; Yin, Y.; Self-Templated, A. Approach to TiO<sub>2</sub> Microcapsules. *Nano Lett.* **2007**, *7*, 1832–1836.
- Hench, L. L.; West, J. K. The Sol-Gel Process. *Chem. Rev.* **1990**, *90*, 33–72.
- Joo, J. B.; Zhang, Q.; Lee, I.; Dahl, M.; Zaera, F.; Yin, Y. Mesoporous Anatase Titania Hollow Nanostructures Through Silica-Protected Calcination. *Adv. Funct. Mater.* **2012**, *22*, 166–174.
- Joo, J. B.; Zhang, Q.; Dahl, M.; Lee, I.; Goebel, J.; Zaera, F.; Yin, Y. Control of the Nanoscale Crystallinity in Mesoporous TiO<sub>2</sub> Shells for Enhanced Photocatalytic Activity. *Energy Environ. Sci.* **2012**, *5*, 6321–6327.
- Ye, M.; Zhang, Q.; Hu, Y.; Ge, J.; Lu, Z.; He, L.; Chen, Z.; Yin, Y. Magnetically Recoverable Core-Shell Nanocomposites with Enhanced Photocatalytic Activity. *Chem.—Eur. J.* **2010**, *16*, 6243–6250.
- Ye, M.; Zorba, S.; He, L.; Hu, Y.; Maxwell, R. T.; Farah, C.; Zhang, Q.; Yin, Y. Self-Assembly of Superparamagnetic Magnetite Particles into Peapod-Like Structures and Their Application in Optical Modulation. *J. Mater. Chem.* **2010**, *20*, 7965–7969.
- Okada, K.; Yamamoto, N.; Kameshima, Y.; Yasumori, A.; MacKenzie, K. J. D. Effect of Silica Additive on the Anatase-to-Rutile Phase Transition. *J. Am. Ceram. Soc.* **2001**, *84*, 1591.
- Dahl, M.; Joo, J. B.; Zhang, Q.; Dang, S.; Yin, Y. Control of the Crystallinity in TiO<sub>2</sub> Microspheres through Silica Impregnation. *CrystEngComm* **2012**, *14*, 7680–7685.
- Zaera, F. Outstanding Mechanistic Questions in Heterogeneous Catalysis. *J. Phys. Chem. B* **2002**, *106*, 4043–4052.
- Kim, S. H.; Yin, Y.; Alivisatos, A. P.; Somorjai, G. A.; Yates, J. T. IR Spectroscopic Observation of Molecular Transport through Pt@CoO Yolk-Shell Nanostructures. *J. Am. Chem. Soc.* **2007**, *129*, 9510–9513.
- Lee, I.; Joo, J. B.; Yin, Y.; Zaera, F. A New Yolk@Shell Nanoarchitecture for Au/TiO<sub>2</sub> Catalysts. *Angew. Chem., Int. Ed.* **2011**, *50*, 10208.
- Liang, X.; Li, J.; Joo, J. B.; Gutiérrez, A.; Tillekaratne, A.; Lee, I.; Yin, Y.; Zaera, F. Diffusion through the Shells of Yolk-Shell and Core-Shell Nanostructures in the Liquid Phase. *Angew. Chem., Int. Ed.* **2012**, *51*, 8034–8036.
- Zaera, F. Infrared Absorption Spectroscopy of Adsorbed CO: New Applications in Nanocatalysis for an Old Approach. *ChemCatChem* **2012**, *4*, 1525–1533.
- Zaera, F. Probing Liquid/Solid Interfaces at the Molecular Level. *Chem. Rev.* **2012**, *112*, 2920–2986.
- Kubota, J.; Ma, Z.; Zaera, F. In-Situ Characterization of Adsorbates in Solid-Liquid Interfaces by Reflection-Absorption Infrared Spectroscopy. *Langmuir* **2003**, *19*, 3371–3376.
- Graciani, J.; Nambu, A.; Evans, J.; Rodriguez, J. A.; Sanz, J. F. Au <-> N Synergy and N-Doping of Metal Oxide-Based Photocatalysts. *J. Am. Chem. Soc.* **2008**, *130*, 12056–12063.
- Anpo, M.; Shima, T.; Kodama, S.; Kubokawa, Y. Photocatalytic Hydrogenation of Propyne with Water on Small-Particle Titania: Size Quantization Effects and Reaction Intermediates. *J. Phys. Chem.* **2002**, *91*, 4305.
- 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*, 126–131.