Synthesis, crystallinity control, and photocatalysis of nanostructured titanium dioxide shells

Ji Bong Joo, Qiao Zhang, Michael Dahl, Francisco Zaera, and Yadong Yin[a)]
Department of Chemistry, University of California, Riverside, California 92521

(Received 12 May 2012; accepted 20 July 2012)

In this article, we review our recent research efforts on the synthesis, crystallinity control, and photocatalysis of nanostructured titanium dioxide (TiO_2) shells. First, we introduce several synthetic methods for preparing TiO_2 shell structures using either template-free or template-assisted approaches. Several methods to change the structures from amorphous to crystalline and subsequently ways to enhance the crystallinity are then discussed, including those involving the "silica-protected calcination" and "partial etching and recalcination" strategies. We also discuss the photocatalytic applications of the TiO_2 nanoshells and the methods for improving their catalytic activities. Finally, we conclude with a summary and our perspective on the further development of the nanostructured TiO_2 shells. It is believed that more rational design and modification strategies such as well-controlled nonmetal doping, plasmonic metal decoration and the hybridization with other semiconducting materials will significantly enhance the photocatalytic efficiency of TiO_2-based catalyst materials.

I. INTRODUCTION

Titanium dioxide (Titania, TiO_2) has been considered to be one of the most important semiconductor materials due to its wide practical uses in several applications including energy storage, solar cells, catalysis and photocatalysis. It has a wide-band-gap energy (3.0–3.2 eV) that allows absorption of photon energy to excite electron- (e^-) hole (h^+) pairs that can induce redox reactions.[1] Since Honda and Fujishima first discovered its ability to decompose water and produce hydrogen under ultraviolet (UV) irradiation,[2] TiO_2-based materials have been intensively studied and used as photocatalysts.[1,3–5] Over the past decades, tremendous efforts have been devoted to improving the physical, chemical and catalytic properties of TiO_2 for enhanced photocatalytic efficiency.[6–10]

With continued development in nanomaterials synthesis, a variety of tailored TiO_2 nanostructures have been suggested and investigated for practical application in photocatalysis.[11–13] Among various TiO_2 nanostructures, there has been increasing interest in colloidal TiO_2 nanostructured shells due to their advantageous characteristics including facile functionalization, relatively large surface area-to-volume ratio, and improved accessibility for reactant molecules.[14–19] Various forms of hollow TiO_2 shells and metal (or metal oxide)-TiO_2 core–shell nanostructures with spherical or nonspherical morphologies have been studied from both the synthetic and application viewpoints.[6,19] In this article, we intend to summarize our recent research activities on the synthesis and photocatalytic applications of TiO_2 nanostructured shells. We organize this article as follows: we first introduce synthetic strategies for preparing TiO_2 shell structures using both template-free and typical template-assisted methods. Then we discuss how the crystallinity of the nanoshells can be manipulated by citing a few methods developed in our laboratory. We also discuss their photocatalytic applications as well as promising strategies for further enhancing the catalytic activity. Finally, we conclude with a summary and our perspective on the continued development of this field.

II. STRATEGIES FOR SYNTHESIS OF TiO_2 NANOSHELLS

Since the reporting of several pioneering works in the early 2000s, there have been many further reports on the formation of a TiO_2 layer on the surface of nanomaterials to produce core–shell nanostructures.[20–22] Most of these efforts have been devoted to depositing the nanoscale TiO_2 layer, formed by limited hydrolysis–condensation kinetics using small amounts of sol-gel precursors, on the modified surface of solid (metal, metal oxide, polymer, and/or carbon) cores.[18,19,23–25] Liz-Marzan et al. achieved a coating of a thin TiO_2 layer on simultaneously reduced silver (Ag) nanoparticles.[20] Xia et al. synthesized hollow TiO_2 nanoshells by hydrolyzing a TiO_2 precursor and then depositing the product onto the surface

[a)]Address all correspondence to this author.
e-mail: yadong.yin@ucr.edu
DOI: 10.1557/jmr.2012.280

 © Materials Research Society 2012

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press

of close-packed polystyrene (PS) spheres, followed by rapid evaporation of solvent and chemical etching of the sacrificial PS cores.[26]

TiO_2 shells can also be produced without the use of special templates.[27,28] Similar to the SiO_2 case which we reported recently, the core portion of TiO_2 spheres can be preferentially removed to form hollow capsules through a "surface-protected etching" process.[28,29] The Ostwald ripening mechanism has also been considered as a method for transforming solid TiO_2 particles into hollow ones without using specific templates.[27,30,31]

A. Template-free synthesis

We have developed a template-free method for preparing TiO_2 hollow shells by heating sol-gel-derived TiO_2 microspheres with poly(acrylic acid) (PAA) in diethylene glycol (DEG).[28] Initially, sol-gel-derived TiO_2 microspheres are solid particles containing micropores [Fig. 1(a)]. DEG is used as both a solvent and an etching agent because amorphous TiO_2 particles prepared through a sol-gel process can be dissolved in pure DEG at high temperatures. Interestingly, heating TiO_2 microspheres in the presence of PAA slows down the dissolution and eventually produces hollow shells [Fig. 1(b)]. Upon heating to high temperatures, PAA molecules can bind to the surface of TiO_2 spheres and act as protecting agents during the subsequent etching. With its multiple carboxylate groups on a polymer chain, PAA acts as a crosslinker to connect adjacent TiO_2 nanoparticles into a stable shell and protects them against rapid dissolution by DEG. Dissolution of TiO_2 preferentially occurs inside the microsphere after DEG penetrates through the protected outer layer and reacts with unprotected core material. Thus, preferential removal of core material through the formation of soluble titanate species leaves behind hollow shells. The shells become thinner after continuous heating at high temperature and are eventually completely dissolved by the solvent. As the PAA chains are stretchable, the separation between adjacent surface nanoparticles increases after the removal of the cores. This explains why the diameter of the shells is significantly larger in comparison to the primary microspheres [Fig 1(b), inset]. Also, because the PAA chains are flexible, the shells are unable to support themselves mechanically when they are dried on a solid substrate.

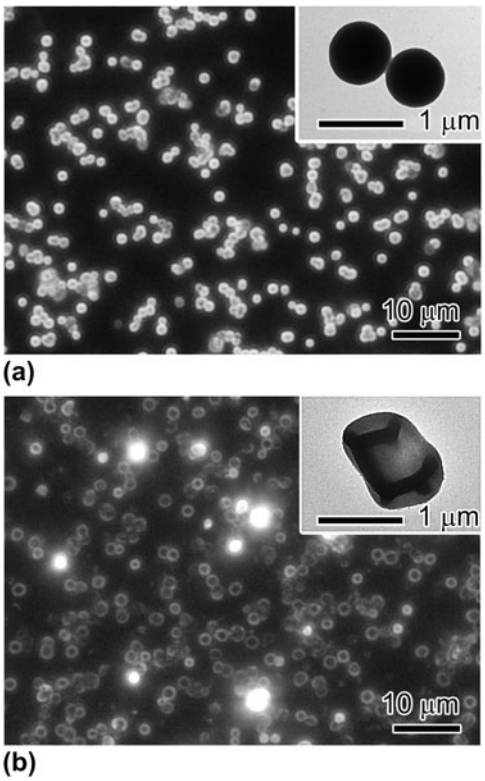


FIG. 1. Dark-field optical microscopy images of (a) the primary TiO_2 microspheres and (b) the corresponding hollow shells. The insets are TEM images of the primary particles and hollow shells. Adapted with permission from Ref. 28© 2007 American Chemical Society.

Ostwald ripening is a classical phenomenon in solid dispersions or liquid sols in which small crystals or sol particles dissolve and regrow on larger ones. For some time now, the Ostwald ripening mechanism has been widely used for explaining the formation of hollow nanostructures. Zeng et al. first proposed the mechanism in the formation of hollow TiO_2 shells through the hydrothermal treatment of titanium tetrafluoride (TiF_4) solution.[27] The TiF_4 precursor can first be hydrolyzed and condensed to produce solid TiO_2 microspheres. Core portions of the TiO_2 spheres can be continuously dissolved and then redeposited on the outer region to yield hollow TiO_2 shells. Li and Zeng have also extended the hollowing process via Ostwald ripening to the synthesis of hollow tin (Sn)-doped TiO_2 shell structures by using a similar hydrothermal treatment.[31] The ripening strategy has been extended to the preparation of other oxides including silicon dioxide (SiO_2),[32] tin dioxide (SnO_2),[33] cuprous oxide (Cu_2O),[34,35] cobalt (II,III) oxide (Co_3O_4),[36] and many others[37] through a similar formation mechanism.

B. Template-assisted method

Compared with the template-free synthesis, the template-assisted method represents a more universal process for synthesizing nanostructured shells.[38,39] In fact, template-assisted synthesis has been the most commonly used method during the past decades for the preparation of shell structures. The principle of this strategy is straightforward and involves several sequential steps: (i) preparing the original templates; (ii) depositing the shell materials on the surface of the templates; (iii) selective etching to remove the templates. Various types of colloidal particles have been reported as

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press

having been experimented as core templates including gold (Au) nanoparticles,[21] silver (Ag) nanoparticles,[20] PS,[16,17] glucose-derived carbon,[18,40,41] and silica.[6,19,38,39] Among them, uniform silica spheres prepared by the Stöber method have been the most popular template due to the ease of coating them with TiO_2 materials as well as their convenient removal by base etching.[6,19,42] Deposition of TiO_2 layers on the surface of silica spheres can be easily achieved through a sol-gel process which uses titanium tetrabutoxide (TBOT) as the TiO_2 precursor and hydroxypropyl cellulose (HPC) as surfactant.[6,19,42] The thickness of the TiO_2 shells can be conveniently increased by carrying out multiple coating steps. Hollow TiO_2 shells can then be obtained using an aqueous solution of NaOH to remove the silica cores [Fig. 2(a)]. In a typical synthesis, a single run of the TiO_2 coating procedure produces ~25 nm TiO_2 shells [Fig. 2(b)], while repeating the coating steps three and five times can increase the shell thickness to ~50 and ~70 nm, respectively [Figs. 2(c) and 2(d)].[38]

III. CRYSTALLINITY CONTROL

Typical sol-gel processes, which prepare TiO_2 shell nanostructures by direct hydrolysis and condensation of titanium alkoxides, cannot yield crystalline structures. However, good crystallinity is an important feature required for many practical applications including sensors, energy storage, and photocatalysis.[16,43,44] There is no doubt that anatase phase TiO_2 is considered to be the most active phase due to its higher reduction potential and lower recombination rate of electron-hole pairs in photocatalytic applications even though the rutile phase has the advantage of better absorption in the visible regime due to a lower band-gap energy. To achieve high activity in photocatalysis, it is important for the material to have a high surface area with well-developed porosity, which provides a large number of redox reaction sites on the catalyst surface as well as ensures easy diffusion of reactant molecules. It is therefore believed that well-crystallized anatase TiO_2 with large surface area and porosity is the preferred form for photocatalysis.

Calcination is considered to be a simple method to enhance the crystallinity of TiO_2 shells. Nevertheless, direct calcination of either hollow TiO_2 or SiO_2@TiO_2 core–shell structures cannot produce a stable shell morphology with the targeted anatase crystalline phase because the thin TiO_2 layer can be damaged during extensive structural reorganization at high calcination temperatures. Recently we have developed a "protected calcination method" to achieve crystalline TiO_2 shells with porous characteristics [Fig. 3(a)].[38] The "protected calcination" process not only improves the crystallinity of the samples

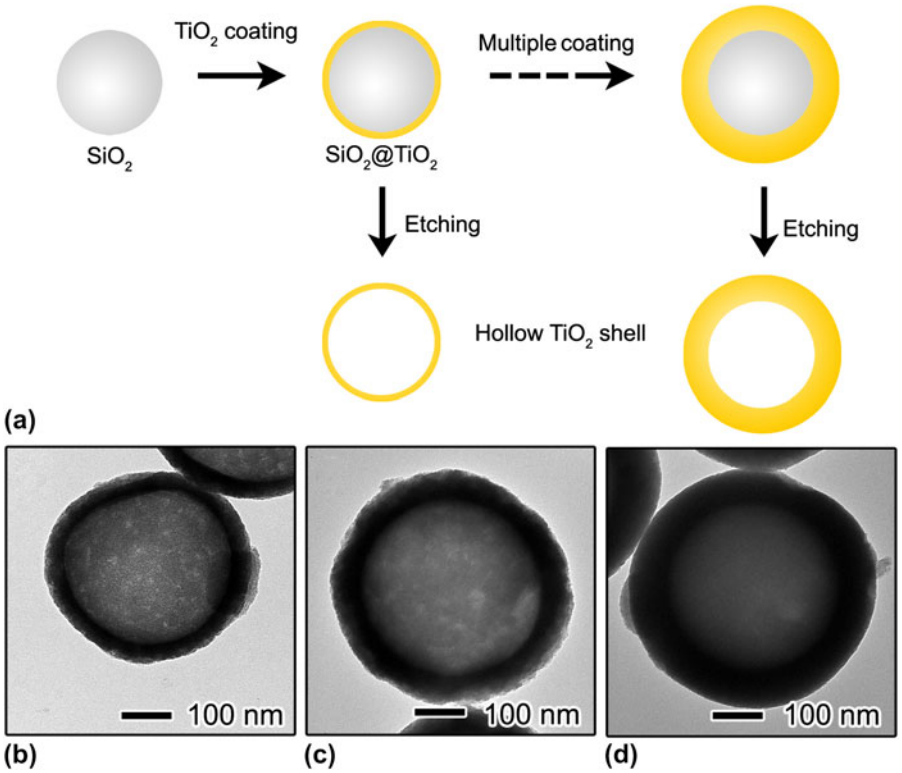


FIG. 2. (a) Schematic illustration showing the typical template-assisted synthesis for hollow TiO_2 shell nanostructure and corresponding TEM images of TiO_2 hollow spheres with different thicknesses prepared using multiple sol-gel coating processes: (b) once (c) three times, and (d) five times.

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press

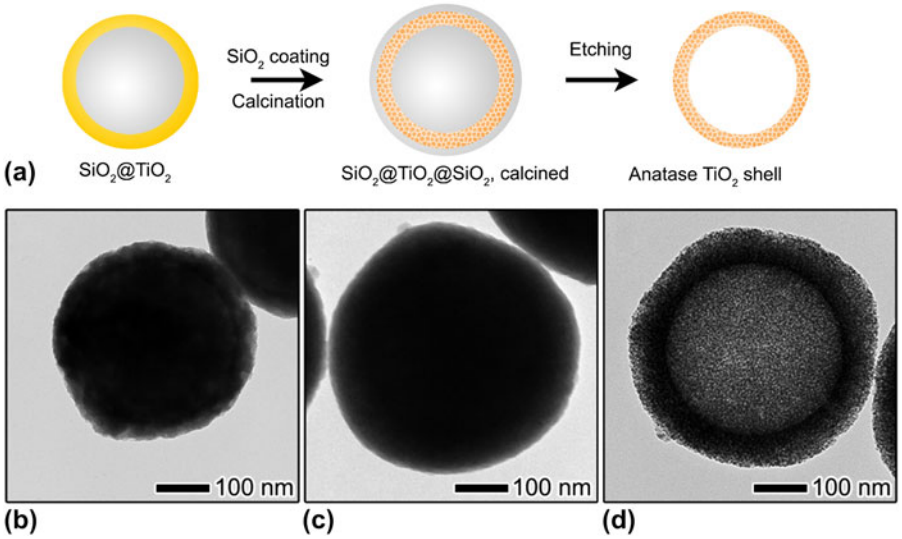


FIG. 3. (a) Schematic illustration of silica-protected calcination procedure and corresponding TEM images of the product at each step: (b) SiO_2@TiO_2 (c) SiO_2@TiO_2@SiO_2 after calcination, and (d) final hollow TiO_2 after the removal of the SiO_2.

but also brings additional benefits such as high surface area and well-developed mesoscale porosity. Compared with direct calcination, the major modification we introduced into this process is to protect the TiO_2 shells with an additional outer silica layer. Calcination of SiO_2@TiO_2@SiO_2 composites followed by chemical etching produced well-defined hollow TiO_2 shells containing mesopores which could be easily observed by transmission electron microscopy (TEM) imaging [Figs. 3(b)–3(d)]. Our results suggest that the outer silica layer not only suppresses the crystal growth of TiO_2 but also inhibits phase transformation. Similar to colloidal silica, the sol-gel-derived TiO_2 layer contains micropores with diameters typically below 2 nm. Silicate species may be able to penetrate into these pores and condense in the TiO_2 framework during the outer silica coating. The penetrated silica may then act as a barrier, preventing the extensive structural reorganization and growth of amorphous TiO_2 into large crystal grains during calcination. This behavior may result in smaller anatase grains than those produced at similar calcination temperatures without the protection of silica.

The presence of a silica layer significantly limits the growth of anatase grains to below ~5 nm even at a calcination temperature as high as 900 °C. Although the crystalline hollow TiO_2 structures have considerably large surface areas (above 300 m^2/g), the small grain size is not optimal for reactions such as the photocatalytic decomposition of organic molecules. For increasing the crystallinity of TiO_2 shells in a controllable manner, we have further developed a "partial etching and recalcination" process.[39] When the TiO_2 shell is coated with an additional layer of silica, the silica that penetrates into or near the TiO_2 layer has a more disrupted Si–O–Si network than silica in other regions, making it more vulnerable to etching in base solution. Indeed, preferential etching can be achieved, as evidenced by the appearance of a small gap between the TiO_2 layer and both the outer and inner SiO_2 layer in the TEM image [Fig. 4(a)]. The degree of preferential etching can be easily controlled by both the duration of etching and concentration of etchants. The preferential removal of surrounding silica in or near the TiO_2 layer allows further growth of anatase crystal domains during the recalcination process. Figures 4(b)–4(d) are TEM images showing the different sizes of TiO_2 crystal grains produced by recalcining a partially etched SiO_2@TiO_2@SiO_2 sample at different temperatures followed by the complete removal of SiO_2 using NaOH. Compared with the original TiO_2 shell samples produced simply by using the silica-protected calcination process [~4 nm grain size, Fig. 3(d)], the crystal grain size increased to 7 and 10 nm upon recalcination for 4 h at 700 and 800 °C, respectively [Figs. 4(b) and 4(c)]. Prolonged heating at 800 °C for a longer time period (16 h) gives crystal grains with an average size above 14 nm [Fig. 4(d)]. As discussed in Sec. IV, the TiO_2 nanostructured shells with controllable crystallinity are particularly interesting for photocatalytic applications due to their large active sites.

IV. PHOTOCATALYTIC APPLICATION AND ACTIVITY ENHANCEMENT

TiO_2 is the most studied and most promising photocatalytic material, which can absorb UV light to promote redox reactions. Its high photocatalytic activity can be improved by tuning several characteristics including surface area, surface properties, crystalline phase, and crystallinity.[39]

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press

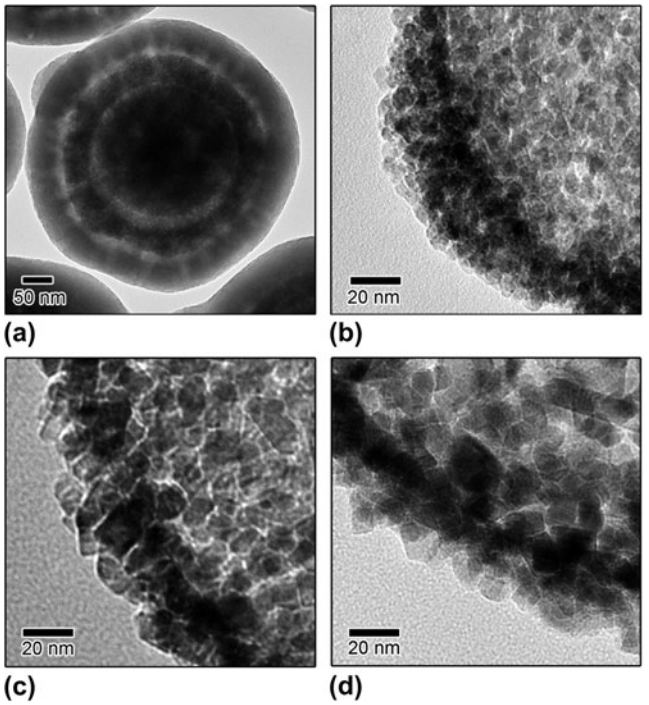


FIG. 4. TEM images of (a) partially etched SiO_2@TiO_2@SiO_2, and (b–d) final TiO_2 shell nanostructure after recalcining SiO_2@TiO_2@SiO_2 (partially etched) at different conditions and NaOH etching: (b) 700 °C for 4 h, (c) 800 °C for 4 h, and (d) 800 °C for 16 h.

Nanostructured TiO_2 shells are good candidates for photocatalysis due to their relatively large surface area, excellent water dispersity, and controllable anatase crystallinity. The hollow TiO_2 shells prepared through the "partial etching and recalcination" process show a well-developed anatase phase with the grain size tunable by adjusting the recalcination temperature and time [Figs. 5(a) and 5(b)]. When used for photocatalytic degradation of dye molecules such as Rhodamine B (RhB), the TiO_2 nanoshells significantly enhanced the decomposition rate while the control sample without catalyst showed the lowest apparent rate constant (k) values [Figs. 5(b) and 5(c)]. As expected, TiO_2 shells prepared without partial etching and recalcination [Sample A in Fig. 5(a)] showed the lowest k values among TiO_2 catalysts tested, while k continuously increased as recalcination temperature increased. Eventually, TiO_2 shells recalcined at 800 °C for 16 h (Sample E) showed the largest k value, indicating the highest catalytic efficiency. The improved catalytic activity should be attributed to the enhanced crystallinity of the anatase grains, resulting in better charge separation during photocatalysis. Although it is generally accepted in catalysis field that the activity of a catalyst benefits from a higher specific area, our studies however have clearly shown that photocatalytic activity can be promoted more by enhanced crystallinity due to better charge separation, even though the value of surface area decreases correspondingly.

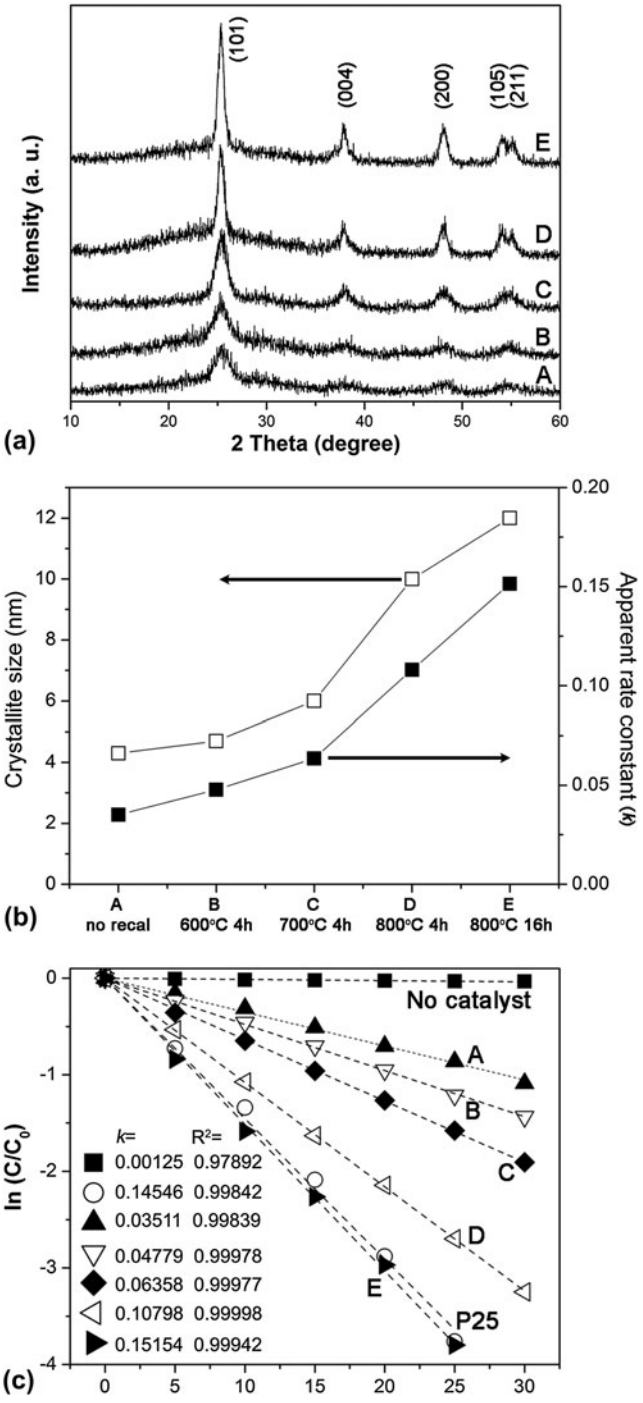


FIG. 5. (a) X-ray diffraction patterns, (b) calculated crystallite grain size and apparent rate constant value (k) during photocatalytic RhB decomposition, and (c) photocatalytic reaction results of TiO_2 samples: TiO_2 shells (A) without recalcination process, (B) recalcined at 600 °C for 4 h, (C) recalcined at 700 °C for 4 h, (D) recalcined at 800 °C for 4 h, (E) recalcined at 800 °C for 16 h. Adapted with permission from Ref. 39© 2011 Royal Society of Chemistry.

The synthesis of highly active visible-light-responsive photocatalysts has attracted intensive interest because they hold the promise of more efficient harvesting of

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press

solar energy. Modification of TiO_2 through nonmetal anion doping, metal cation doping or plasmonic metal decoration lowers its band-gap energy and allows for absorption of photon energy in the visible regime, thus utilizing a greater portion of the solar spectrum. Recently, we demonstrated the nitrogen doping of porous TiO_2 nanocrystal clusters by NH_3 treatment.[45] After gas phase treatment at high temperature, the white powder became yellowish, indicating the successful N doping which yielded particles capable of visible light absorption. It has been known that metal nanoparticles such as Au or Ag can enhance the activity of photocatalysts in visible light due to their plasmonic properties. By combining nonmetal doping with the plasmonic effect, we have designed SiO_2/Au/N-doped TiO_2 shell nanostructures for improving photocatalytic activity.[46] The catalyst has a sandwich structure that comprises a SiO_2 core, a layer of decorated gold nanoparticles (AuNPs), and a doped TiO_2 nanocrystalline shell. The TiO_2 shell was doped with both N and C using an unconventional method that involved introducing 3-aminopropyl-triethoxysilane (APTES), which originally acted as a ligand for immobilization of AuNPs on the surface of the SiO_2 support, but upon subsequent decomposition at high temperature served as a source of both the N and C dopants. Eventually, the sandwich-structured catalysts showed excellent catalytic activity for oxidation of organic compounds under UV, visible and direct sunlight. The enhanced photocatalytic efficiency can be attributed to the interfacial nonmetal doping which improves visible light absorption, and to the plasmonic metal decoration, which enhances light harvesting and charge separation.

V. CONCLUSIONS AND OUTLOOK

Extensive research efforts have been devoted to the synthesis of TiO_2-based hollow shells and core–shell nanostructures due to their promising applications in photocatalysis. In this article, we have reviewed our recent efforts in TiO_2 nanostructured shells, focusing on the synthesis, crystallinity control and photocatalytic performance. Two synthetic strategies for preparing TiO_2 shell nanostructures have been discussed, including template-free and template-assisted methods. We have also discussed the strategies for controlling the crystallinity of the TiO_2 shells, including "silica-protected calcination" and "partial etching and recalcination" methods. We finally discussed the performance of TiO_2 nanostructured shells in photocatalysis, and various approaches to enhance the catalytic activity.

The systems reviewed in this article represent our efforts in engineering TiO_2 materials at the nanometer scale with a high degree of control over the morphology, crystallinity, doping, and interface. We believe the fine manipulation of the nanostructures will eventually allow us to significantly enhance the photocatalytic efficiency of TiO_2-based catalyst materials. However, there are still challenging issues remaining in the synthesis of well-defined photocatalysts with high activity toward practical photocatalysis such as water-splitting and artificial photosynthesis. More rational design and modification strategies for TiO_2-based nanostructure photocatalysts such as well-controlled nonmetal doping, plasmonic metal decoration and the hybridization with other semiconducting materials will be examined as our next steps.

ACKNOWLEDGMENTS

Financial support of this work was provided by the Office of Basic Energy Sciences of the U.S. Department of Energy, SISGR-Catalysis for Energy Grant No. DE-SC0002247. Y.Y. also thanks the Research Corporation for Science Advancement for the Cottrell Scholar Award, 3M for the Nontenured Faculty Grant, and DuPont for the Young Professor Grant. J.B.J. was partially supported by a National Research Foundation of Korea Grant funded by the Korean Government (No. NRF-2009-352-D00056).

REFERENCES

1. M.A. Fox and M.T. Dulay: Heterogeneous photocatalysis. *Chem. Rev.* **93**, 341 (1993).
2. A. Fujishima and K. Honda: Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37 (1972).
3. A.L. Linsebigler, G. Lu and J.T. Yates: Photocatalysis on TiO_2 surfaces: Principles, mechanisms, and selected results. *Chem. Rev.* **95**, 735 (1995).
4. A. Kudo: Recent progress in the development of visible light-driven powdered photocatalysts for water splitting. *Int. J. Hydrogen Energy* **32**, 2673 (2007).
5. K. Maeda and K. Domen: Photocatalytic water splitting: Recent progress and future challenges. *J. Phys. Chem. Lett.* **1**, 2655 (2010).
6. M. Ye, Q. Zhang, Y. Hu, J. Ge, Z. Lu, L. He, Z. Chen, and Y. Yin: Magnetically recoverable core–shell nanocomposites with enhanced photocatalytic activity. *Chem. Eur. J.* **16**, 6243 (2010).
7. H.J. Yun, H. Lee, J.B. Joo, N.D. Kim, M.Y. Kang, and J. Yi: Facile preparation of high performance visible light sensitive photocatalysts. *Appl. Catal., B* **94**, 241 (2010).
8. H.J. Yun, H. Lee, J.B. Joo, N.D. Kim, and J. Yi: Tuning the band-gap energy of $TiO_{2-x}C_x$ nanoparticle for high performance photocatalyst. *Electrochem. Commun.* **12**, 769 (2010).
9. H.J. Yun, H. Lee, N.D. Kim, D.M. Lee, S. Yu, and J. Yi: A combination of two visible-light-responsive photocatalysts for achieving the Z-scheme in the solid state. *ACS Nano* **5**, 4084 (2011).
10. F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt, and P. Feng: Self-doped Ti^{3+} enhanced photocatalyst for hydrogen production under visible light. *J. Am. Chem. Soc.* **132**, 11856 (2010).
11. J. Zhang, J.H. Bang, C. Tang, and P.V. Kamat: Tailored TiO_2−$SrTiO_3$ heterostructure nanotube arrays for improved photoelectrochemical performance. *ACS Nano* **4**, 387 (2009).
12. X. Chen, L. Liu, P.Y. Yu, and S.S. Mao: Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* **331**, 746 (2011).

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press

13. T. Cao, Y. Li, C. Wang, C. Shao, and Y. Liu: A facile in situ hydrothermal method to $SrTiO_3/TiO_2$ nanofiber heterostructures with high photocatalytic activity. *Langmuir* **27**, 2946 (2011).
14. A.F. Demirörs, A. van Blaaderen, and A. Imhof: Synthesis of eccentric titania−silica core−shell and composite particles. *Chem. Mater.* **21**, 979 (2009).
15. T.H. Eun, S-H. Kim, W-J. Jeong, S-J. Jeon, S-H. Kim, and S-M. Yang: Single-step fabrication of monodisperse TiO_2 hollow spheres with embedded nanoparticles in microfluidic devices. *Chem. Mater.* **21**, 201 (2009).
16. P. Wang, D. Chen, and F-Q. Tang: Preparation of titania-coated polystyrene particles in mixed solvents by ammonia catalysis. *Langmuir* **22**, 4832 (2006).
17. A. Imhof: Preparation and characterization of titania-coated polystyrene spheres and hollow titania shells. *Langmuir* **17**, 3579 (2001).
18. R. Zheng, X. Meng, and F. Tang: A general protocol to coat titania shell on carbon-based composite cores using carbon as coupling agent. *J. Solid State Chem.* **182**, 1235 (2009).
19. J.W. Lee, M.R. Othman, Y. Eom, T.G. Lee, W.S. Kim, and J. Kim: The effects of sonification and TiO_2 deposition on the microcharacteristics of the thermally treated SiO_2/TiO_2 spherical core–shell particles for photocatalysis of methyl orange. *Microporous Mesoporous Mater.* **116**, 561 (2008).
20. I. Pastoriza-Santos, D.S. Koktysh, A.A. Mamedov, M. Giersig, N.A. Kotov, and L.M. Liz-Marzán: One-pot synthesis of $Ag@TiO_2$ core−shell nanoparticles and their layer-by-layer assembly. *Langmuir* **16**, 2731 (2000).
21. K.S. Mayya, D.I. Gittins, and F. Caruso: Gold−titania core−shell nanoparticles by polyelectrolyte complexation with a titania precursor. *Chem. Mater.* **13**, 3833 (2001).
22. H. Sakai, T. Kanda, H. Shibata, T. Ohkubo, and M. Abe: Preparation of highly dispersed core/shell-type titania nanocapsules containing a single Ag nanoparticle. *J. Am. Chem. Soc.* **128**, 4944 (2006).
23. K.S. Mayya, D.I. Gittins, A.M. Dibaj, and F. Caruso: Nanotubes prepared by templating sacrificial nickel nanorods. *Nano Lett.* **1**, 727 (2001).
24. Y. Yin, Y. Lu, B. Gates, and Y. Xia: Synthesis and characterization of mesoscopic hollow spheres of ceramic materials with functionalized interior surfaces. *Chem. Mater.* **13**, 1146 (2001).
25. Y. Lu, Y. Yin, and Y. Xia: Preparation and characterization of micrometer-sized "egg shells". *Adv. Mater.* **13**, 271 (2001).
26. Z. Zhong, Y. Yin, B. Gates, and Y. Xia: Preparation of mesoscale hollow spheres of TiO_2 and SnO_2 by templating against crystalline arrays of polystyrene beads. *Adv. Mater.* **12**, 206 (2000).
27. H.G. Yang and H.C. Zeng: Preparation of hollow anatase TiO_2 nanospheres via Ostwald ripening. *J. Phys. Chem. B* **108**, 3492 (2004).
28. Y. Hu, J. Ge, Y. Sun, T. Zhang, and Y. Yin: A self-templated approach to TiO_2 microcapsules. *Nano Lett.* **7**, 1832 (2007).
29. Q. Zhang, T. Zhang, J. Ge, and Y. Yin: Permeable silica shell through surface-protected etching. *Nano Lett.* **8**, 2867 (2008).
30. J. Li and H.C. Zeng: Size tuning, functionalization, and reactivation of Au in TiO_2 nanoreactors. *Angew. Chem. Int. Ed.* **44**, 4342 (2005).
31. J. Li and H.C. Zeng: Hollowing Sn-doped TiO_2 nanospheres via Ostwald ripening. *J. Am. Chem. Soc.* **129**, 15839 (2007).
32. T. Zhang, J. Ge, Y. Hu, Q. Zhang, S. Aloni, and Y. Yin: Formation of hollow silica colloids through a spontaneous dissolution–regrowth process. *Angew. Chem. Int. Ed.* **47**, 5806 (2008).
33. X.W. Lou, Y. Wang, C. Yuan, J.Y. Lee, and L.A. Archer: Template-free synthesis of SnO_2 hollow nanostructures with high lithium storage capacity. *Adv. Mater.* **18**, 2325 (2006).
34. Y. Chang, J.J. Teo, and H.C. Zeng: Formation of colloidal CuO nanocrystallites and their spherical aggregation and reductive transformation to hollow Cu_2O nanospheres. *Langmuir* **21**, 1074 (2004).
35. J.J. Teo, Y. Chang, and H.C. Zeng: Fabrications of hollow nanocubes of Cu_2O and Cu via reductive self-assembly of CuO nanocrystals. *Langmuir* **22**, 7369 (2006).
36. B. Liu and H.C. Zeng: Symmetric and asymmetric Ostwald ripening in the fabrication of homogeneous core–shell semiconductors. *Small* **1**, 566 (2005).
37. Q. Zhang, W. Wang, J. Goebl, and Y. Yin: Self-templated synthesis of hollow nanostructures. *Nano Today* **4**, 494 (2009).
38. J.B. Joo, Q. Zhang, I. Lee, M. Dahl, F. Zaera, and Y. Yin: Mesoporous anatase titania hollow nanostructures though silica-protected calcination. *Adv. Funct. Mater.* **22**, 166 (2012).
39. J.B. Joo, Q. Zhang, M. Dahl, I. Lee, J. Goebl, F. Zaera, and Y. Yin: Control of the nanoscale crystallinity in mesoporous TiO_2 shells for enhanced photocatalytic activity. *Energy Environ. Sci.* **5**, 6321 (2012).
40. Y. Ao, J. Xu, D. Fu, and C. Yuan: A simple method for the preparation of titania hollow sphere. *Catal. Commun.* **9**, 2574 (2008).
41. Y. Ao, J. Xu, D. Fu, and C. Yuan: A simple method to prepare N-doped titania hollow spheres with high photocatalytic activity under visible light. *J. Hazard. Mater.* **167**, 413 (2009).
42. I. Lee, J.B. Joo, Y. Yin, and F. Zaera: A Yolk@Shell nanoarchitecture for Au/TiO_2 catalysts. *Angew. Chem. Int. Ed.* **50**, 10208 (2011).
43. Z. Yang, Z. Niu, Y. Lu, Z. Hu, and C.C. Han: Templated synthesis of inorganic hollow spheres with a tunable cavity size onto core–shell gel particles. *Angew. Chem. Int. Ed.* **42**, 1943 (2003).
44. K. Kamata, Y. Lu, and Y. Xia: Synthesis and characterization of monodispersed core−shell spherical colloids with movable cores. *J. Am. Chem. Soc.* **125**, 2384 (2003).
45. Q. Zhang, J-B. Joo, Z. Lu, M. Dahl, D. Oliveira, M. Ye, and Y. Yin: Self-assembly and photocatalysis of mesoporous TiO_2 nanocrystal clusters. *Nano Res.* **4**, 103 (2011).
46. Q. Zhang, D.Q. Lima, I. Lee, F. Zaera, M. Chi, and Y. Yin: A highly active titanium dioxide based visible-light photocatalyst with nonmetal doping and plasmonic metal decoration. *Angew. Chem. Int. Ed.* **123**, 7226 (2011).

https://doi.org/10.1557/jmr.2012.280 Published online by Cambridge University Press