Tailored Synthesis of C@TiO₂ Yolk-Shell Nanostructures for Highly Efficient Photocatalysis

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Abstract

Composite nanostructures with well-defined characteristics are often advantageous catalysts for highly efficient photocatalytic processes. Here, we report the tailored synthesis of C@TiO₂ yolk-shell nanostructures and their photocatalytic applications in the degradation of organic dyes. The conductive carbon core serves as an electron-sink to promote the separation of electron-hole pairs photo-excited in the TiO₂ shell, improve their lifetime, and enhance the photocatalytic performance of the system. The yolk-shell nanostructures were synthesized through a sol-gel coating of TiO₂ on resorcinol-formaldehyde (RF) resin spheres followed by silica-protected calcination and ultimately NaOH etching to remove the silica layer and produce C@TiO₂ yolk-shell nanostructures. In order to improve the crystallinity of the TiO₂ shell, post-processing including acid treatment and re-calcination was also carried out. The resulting yolk-shell structures have many desirable properties for photocatalytic applications including the existence of a conductive core, well-maintained structural integrity, uniform particle dimensions, favorable mesoscale porosity, tunable crystallinity, and controllable crystalline phase of TiO₂. As a result, we have been able to optimize the structure and property of the composite photocatalysts and achieve superior photocatalytic performance to commercial P25-TiO₂ catalysts.

Keywords: Carbon, Titania, Yolk-shell nanostructure, Crystallinity, Mesoporous, Photocatalyst

1. Introduction

Photocatalysis over a semiconducting metal oxide has been considered as one of the most sustainable methods to convert solar energy to chemical energy.¹⁻⁶ Titanium dioxide (Titania, TiO_2) is one of the most representative semiconductor photocatalysts, being used in not only fundamental studies but also practical setups for solar energy conversion.⁷⁻¹² Since Honda and Fujishima first achieved hydrogen production via electrochemical photolysis of water under UV irradiation¹³, TiO_2 has been intensively studied and used in these fields.¹⁴⁻¹⁸ Generally, photocatalysis on TiO_2 is considered to occur according to three sequential steps: 1) TiO_2 absorbs photon energy greater than its band-gap energy and generates photo-excited electron-hole pairs; 2) the photo-excited electrons in the conduction band (CB) and holes in the valence band (VB) are separated and then migrate to the surface if they do not recombine on their way out; and 3) the electrons and holes initiate redox reactions on the surface of TiO_2 .

Although TiO_2 itself has been intensively studied over the last couple of decades, the use of TiO_2 for practical photocatalytic processes has still been limited. In particular, the fast recombination of photo-excited charge carriers leads to their short lifetime which hampers achieving maximum activity of TiO_2 photocatalysts and therefore often results in lower efficiency in solar energy conversion systems such as water-splitting and artificial photosynthesis.^{6,19} In order to overcome this limitation, several approaches have been endeavored for elongating electron-hole lifetime by finding effective ways to separate them from recombination, including deposition of conducting metal particles,^{20,21} introduction of sacrificial reagents,²⁰⁻²² and combination with other semiconductors to form a p-n junction^{23,24} and solid state Z-scheme.^{25,26} Deposition of noble metal particles (especially Pt or Au) on the surface of TiO_2 has been widely investigated to enhance lifetime of charge carriers and achieve high photocatalytic performance by inhibiting the electron-hole recombination.²⁷ Under UV light irradiation, photo-generated electrons in the CB of TiO_2 can

be transferred to noble metal particles as the Fermi level of these metals are positioned below the CB of the n-type TiO₂ semiconductor. Although Pt is well known as one of the best electron sinks and an excellent co-catalyst in photocatalysis, it is too expensive to be used for practical environmental applications and also suffers from rapid reverse H₂/O₂ recombination reaction particularly in photocatalytic water-splitting.¹⁹ Other precious metals such as Au, Pd, Ag, and Rh are also prohibitively expensive for large scale applications, with additional problems for Pd and Ag being unstable in low pH conditions.

It is desirable to replace noble metals with other cheap, conductive and chemically inert materials as a co-catalyst to synthesize economically feasible photocatalysts with improved charge separation and low electron-hole recombination rates. Carbon-based materials including carbon black,^{28,29} carbon nanotube,³⁰⁻³² reduced graphene oxide,^{33,34} and commercial activated carbon³⁵⁻³⁸ have been utilized to synthesize carbon-TiO₂ composite-type photocatalysts. Usually, well-purified carbon materials are mixed with pre-synthesized TiO₂ particles and/or TiO₂ precursors and then post-treated by hydrothermal or calcination processes to produce carbon-TiO₂ composites.^{28,29,37,39} Though these methods are convenient for mass production and involve relatively less time and energy for producing catalysts, the distribution of carbon materials around TiO₂ particles is not always homogeneous due to severe aggregation of carbon materials resulting in limited contact area between carbon and TiO₂, which is one of the most important factors determining the charge separation efficiency. It has been reported that a carbonizable polymer shell can be synthesized on the surface of TiO₂ materials through hydrothermal treatment of a sugar such as sucrose and/or glucose. Subsequent heat-treatment under inert conditions may convert the polymer shell to carbon and form a TiO₂@C core-shell structure.³⁹ However, although carbon shells could be formed homogeneously and the contact area with TiO₂ might be high, the dense carbon layer often poses difficulty to molecular diffusion to/from the TiO₂ surface.

Further, complete coverage of the photocatalytically active sites on TiO_2 surface could eventually result in negative impact to the catalytic activity.

Positioning carbon materials inside the TiO_2 shell may lead to a more appropriate structure for photocatalysis:⁴⁰ the TiO_2 surface could be exposed to reactants and the conductive carbon is uniformly positioned on the TiO_2 surface without significantly covering the active surface. In the past few years, we have developed a series of synthetic methods to produce crystalline TiO_2 hollow shells,⁴¹⁻⁴³ with very good control over the crystallinity, crystal size and phase, porosity and surface properties. The incorporation of carbon into these TiO_2 hollow shells is expected to reduce electron-hole recombination and further improve the photocatalytic activity.

In this work, we report a new synthetic process for preparing C@TiO_2 yolk-shell nanostructures consisting of a conductive carbon core and a photocatalytically active TiO_2 shell with tunable crystallinity and phase. Specifically, the TiO_2 shells were produced by depositing a layer of amorphous TiO_2 onto the surface of resorcinol-formaldehyde (RF) resin spheres through a sol-gel process, followed by coating with an additional SiO_2 layer. Calcination under inert conditions (e.g. Ar) at a high temperature transformed the amorphous TiO_2 shells into anatase counterparts and the RF spheres into conductive carbon cores. Finally, the silica layer was removed by chemical dissolution with an aqueous NaOH solution to produce C@TiO_2 yolk-shell nanostructures. To further optimize photocatalytic activity, the crystallinity and crystalline phase of the TiO_2 shells could be further fine tuned by post-treatment using an acid treatment-re-calcination method recently developed by our group.^{8,43} The resulting C@TiO_2 yolk-shell particles showed advantageous characteristics such as the existence of a conducting carbon core in the void space, well-maintained structural integrity, uniform particle dimensions, favorable mesoporosity, tunable crystallinity, and controllable crystalline phase. Correspondingly, with such C@TiO_2 composite photocatalysts it was

possible to achieve outperformance in photocatalytic dye degradation compared to commercial P25-TiO₂ photocatalyst. To the best of our knowledge, this work represents the first report on the controllable synthesis of C@crystalline TiO₂ yolk@shell nanostructures for photocatalysis.

2. Experimental

Synthesis: RF resin spheres were prepared through a modified sol-gel method recently developed by Liu and co-workers.⁴⁴ Resorcinol (0.1 g, Sigma) was mixed with de-ionized water (20 mL), ethanol (8 mL), and formaldehyde (0.14 mL). After stirring for 10 min, an aqueous solution of ammonia (28%, 0.1 mL) was added into the above solution. The color of the solution continuously changed from colorless, to white, grayish-brown, and finally brown. After stirring 24 h at ambient conditions, the temperature was increased to 80 °C under vigorous stirring for 4h. The RF resin spheres were separated by centrifugation, washed with water and ethanol, and then re-dispersed in 10 mL of ethanol. Coating of RF with a TiO₂ shell was carried out by using a sol-gel coating method in mixed solvent in the presence of an aqueous ammonia solution. Into a mixture containing the above RF resin solution (5 mL), ethanol (16 mL), acetonitrile (ACN, 7 mL), and aqueous ammonia (0.2 mL), a solution of tetrabutyl titanate (TBOT, 0.1 ~ 1 mL) in ethanol (3 mL) and ACN (1 mL) was quickly injected using a syringe. The mixture was stirred for 4 hr under ambient conditions. The precipitate was isolated by centrifugation, washed with ethanol and re-dispersed into 20 mL of ethanol to give RF@TiO₂ core-shell particles.

The RF@TiO₂ particles were treated with polyvinylpyrrolidone (PVP, Mw ~ 40,000, 0.2 g) overnight to allow for the adsorption of PVP onto the TiO₂ surface. The PVP treated RF@TiO₂ was separated from the solution, washed with water and ethanol, and re-dispersed in 10 mL of ethanol. The RF@TiO₂ was mixed with tetraethyl orthosilicate (TEOS, 0.86 mL),

de-ionized water (4 mL), ethanol (23 mL) and an aqueous solution of ammonia (0.65 mL). After stirring for 4 h, the precipitated particles were centrifuged, washed 3 times with ethanol and dried under vacuum to give RF@TiO₂@SiO₂. Finally, the RF@TiO₂@SiO₂ was calcined in Ar at 800 °C for 4 h to carbonize the RF polymer and to crystallize the amorphous TiO₂ to the anatase phase. After calcination under Ar, the light brown color of the sample was changed to grayish-black. The sample was then re-dispersed in water (30 mL) under sonication and heated to 90 °C. After etching the particles with an aqueous NaOH solution (2 mL, 2.5 M) for 4 h, the C@TiO₂ yolk-shells were isolated by centrifugation and washed 5 times with de-ionized water and ethanol and finally dried under vacuum.

In order to control the crystallinity of the TiO₂ shells, we used acid treatment-re-calcination method which was recently developed by our group⁴³. The dried C@TiO₂ sample was dispersed in de-ionized water (150 mg/10 mL), mixed with an aqueous HCl solution (10 mL, 100 mM) and stirred for 30 min. the resulting precipitates were isolated by centrifugation, washed with de-ionized water and ethanol, dried under vacuum, and re-calcined at the desired temperature under Ar for 2 hrs to obtain C@TiO₂ shells with controllable crystallinity.

Characterization: The sample morphology was characterized using transmission electron microscopy (TEM, Tecnai12). Crystal phases were determined by X-ray diffraction (XRD) analysis using a Bruker D8 advance Diffractometer with Cu-K α radiation ($\lambda = 1.5406$ Å). Nitrogen adsorption isotherms were obtained at 77 K using a nitrogen sorption instrument (Quantachrome NOVA 4200e). Thermogravimetric analysis (TGA) was conducted by using a Seiko 220U TG-DTA instrument

Catalytic activity tests: The photocatalytic activity was evaluated by following the degradation of Rhodamine B (RhB) as a function of time. Before the photocatalytic test was initiated, the catalyst was first irradiated under UV light for 30 min to remove any residual organic contaminants. The catalyst (5 mg of TiO₂) was dispersed in an aqueous RhB solution

(25 mL, 2×10^{-5} M) in a 50 ml reactor cell and the solution was stirred in the dark for 30 min to ensure adsorption of the dye on the catalyst surface. A 300 W Hg lamp with a 365 nm filter was used as the light source (Xujiang XPA-7). The concentration of RhB was measured using a UV-Vis spectrophotometer (HR2000CG-UV-NIR, Ocean Optics). High-performance liquid chromatography (HPLC, Waters 2790) and liquid chromatography–mass spectrometry (LC-MS, Agilent 6210 TOF) were used for verifying reaction intermediates during photocatalytic RhB decomposition. The small molecular intermediates were identified by gas chromatography-mass spectrometry (GC-MS, Agilent 5973).

3. Results and Discussion

C@TiO₂ yolk-shell nanostructures can be synthesized by a templating method followed by silica protected-calcination and silica etching processes (Figure 1). More specifically, the synthesis consists of the following steps: (i) preparation of RF resin spheres; (ii) coating them with a TiO₂ layer via sol-gel reaction of TBOT to form the RF@TiO₂ core-shell structure; (iii) coating the composite with a SiO₂ protection layer; (iv) calcination under Ar at high temperatures (e.g. 800 °C). During calcination, RF cores can shrink and convert to carbon via pyrolysis and the amorphous TiO₂ shells can be crystallized to the anatase crystal phase. After chemical etching of the outer SiO₂ shell by aqueous NaOH solution, C@TiO₂ yolk-shell nanostructures can be produced. Due to the inhibition effect of the outer silica layer on the crystallization of the TiO₂ shells, the as-synthesized C@TiO₂ structures have relatively small (~ 5 nm) crystalline domains which limited the photocatalytic performance.⁴² In order to improve the crystallinity of the TiO₂ shells, post treatment including acid-treatment and re-calcination processes recently developed by our group were applied.⁴³ Ultimately, the final C@TiO₂ particles have well defined yolk-shell nanostructures with conducting carbon cores and tunable anatase TiO₂ shells. As expected, photo-generated

charge carriers (electron-hole pairs) are separated during photocatalysis under UV light irradiation: electrons prefer to migrate toward conductive carbon cores and holes should remain on the TiO₂ shells resulting in lowering recombination between electrons and holes and elongating the lifetime of each charge carrier. Holes on the TiO₂ shell surface can induce the oxidation of water to hydroxyl radicals resulting in oxidation of organic molecules.

Coating a TiO₂ shell on the RF core can be controlled by varying the concentration of the precursors during the synthesis. As shown in Figure 2a, when 0.1 mL of TBOT was used, the as-synthesized RF@TiO₂ sample showed a thin shell, about 15 nm in thickness. As the amount of TBOT increased, the shell thickness continuously increased (Figure 2b-d). As shown in the low magnification image in Figure 2e, it is apparent that all particles have uniform core-shell nanostructures, confirming the effectiveness of the TiO₂ coating process (Figure 2e). The average thicknesses of the TiO₂ shells are estimated to be approximately 15, 24, 44 and 68 nm for the samples prepared with 0.1, 0.3, 0.6 and 1.0 mL of TBOT, respectively (Figure 2f). To crystallize TiO₂ shells and improve the photocatalytic activity, we deposited a silica coating on the TiO₂ surface followed by calcination and etching processes. Considering its high uniformity in size and dispersibility in water, we use the sample in Figure 2c and its carbonized derivative as the standard samples for the following discussions.

Figure 3 displays the representative TEM images of the samples at each synthetic step with corresponding schematic illustrations of the structures shown in the insets. The RF resin spheres were synthesized by modifying a method developed by Liu and co-workers.⁴⁴ The synthesized RF spheres were monodisperse and well dispersible in both water and alcohol solvents (Figure 3a). In addition, the particle size of the RF spheres can be easily controlled by changing the synthetic parameters such as precursor concentration, water to ethanol ratio, ammonia concentration, addition of surfactants, and reaction temperature. We have also been able to synthesize RF spheres with varying sizes in the range of ca. 60 to 600

nm simply by changing synthetic conditions (Figure S1 in the Supporting information). As shown in Figure 3b, we coated a TiO₂ layer on the surface of RF spheres by sol-gel reaction of TBOT using mixed solvent (Ethanol-Acetonitrile) in the presence of base catalyst such as aqueous ammonia solution. It is well known that the hydrolysis of TBOT molecules results in the formation of hydrolysates,^{45,46} which coexist with TBOT molecules in the solution. According to Tang et al., TBOT molecules and their hydrolysates have a high solubility in ethanol but not in acetonitrile.^{45,46} As a result, when a certain amount of acetonitrile is added into the TBOT/ethanol solution, the TBOT hydrolysate molecules are forced to precipitate out of the solution in the form of deposition on the surface of template particles and then hydrolyze and condense, as catalyzed by NH₄⁺ ions, to form a titania layer on the surface of the template rather than self-nucleated titania particles dispersed in solution. The thickness and smoothness of coated TiO₂ layers can be easily tuned through controlled diffusion rates of TBOT and their hydrolysates by regulating the acetonitrile/ethanol ratio.⁴⁵ We then deposited SiO₂ as a protection layer on the TiO₂ surface to obtain RF@TiO₂@SiO₂ structures (Figure 3c). As reported previously, the outer silica plays an important role in maintaining the structural integrity of the TiO₂ shell during high temperature calcination (e.g. 800 °C).^{42,43} Practically, when direct heat treatment was applied to the RF@TiO₂ particles without the protection layer, the TiO₂ shell completely broke and the less active rutile phase was obtained (Figure S2), which displayed rather poor photocatalytic activity although it has considerably high crystallinity and high adsorption efficiency of RhB dye (Figure S3). Calcination of RF@TiO₂@SiO₂ led to crystallization of the amorphous TiO₂ shells into their anatase counterparts with small crystalline grains. When calcination was carried out under air followed by silica etching with NaOH solution, mesoporous hollow TiO₂ shells with anatase crystallinity were obtained due to TiO₂ crystallization and burning out the RF cores (Figure 3d). However, when we used an inert environment (Ar or N₂) instead, the final product

showed a different morphology. As shown in Figure 3e, the dark carbon spheres which resulted from carbonization of RF resin spheres could be easily observed in the void space with less contrast difference between cores and porous TiO₂ shells indicating C@TiO₂ yolk-shell nanostructures. As shown in both our previous reports and later discussion, since TiO₂ shells prepared through silica-protected calcination have limited crystal grain size which may hamper the photocatalytic performance, we treated the samples with acid and then re-calcined them under inert conditions to improve crystallinity. The acid treatment was intended to remove the possible sodium titanate species remaining on the titania surface due to NaOH etching. As shown in Figure 3f, the structural integrity of yolk-shell particles was well maintained and the grain size of the TiO₂ shells was increased after post treatment.

We also investigated pore properties of the samples at each synthetic step. Figure 4 shows the N₂ adsorption-desorption isotherms and the corresponding pore size distribution for each sample as calculated by Barrett-Joyner-Halenda (BJH) method. The as-synthesized RF@TiO₂ core-shell samples showed main uptake of N₂ adsorption at a low relative pressure range ($< 0.1 P/P_0$) (Figure 4a), indicating microporous characteristics. However, it lacks an obvious increase of adsorption at higher relative pressures, indicating the absence of mesopores and macropores. Further, the sample showed no obvious peaks in pore size distribution, except for a small increase below 1 nm (Figure 4b), which was consistent with the N₂ adsorption isotherm results. Although the sample does not have meso- and macropores, the surface area of as-synthesized RF@TiO₂ was 132 m²/g, which can be attributed to the micropores of the amorphous TiO₂ shells. The hollow TiO₂ sample prepared by silica-protected calcination at 800 °C under air followed by NaOH etching showed a type IV isotherm with well-defined hysteresis loop and steeply increased adsorption volume in the region of monolayer adsorption ($0.1 < P/P_0 < 0.2$), suggesting well developed mesoporous characteristics. The measured Brunauer–Emmett–Teller (BET) surface area for the hollow

TiO₂ sample is 341 m²/g, a considerably high value for crystalline TiO₂. Consistent with our previous study, silica-protected calcination employed in this work can cause minimal crystal grain growth in the shells leading to relatively high surface area.⁴² In addition, it has an obvious peak around ~ 3.4 nm in the BJH pore size distribution suggesting the existence of relatively uniform pores in the TiO₂ shells. The C@TiO₂ sample prepared by silica-protected calcination at 800 °C under Ar followed by NaOH etching also displayed a type IV isotherm with a hysteresis loop indicating mesoporous characteristics. It also showed gradually increased adsorption volume in the region of monolayer adsorption. The BET surface area of C@TiO₂ sample was found to be 234 m²/g. By considering that the weight percent of carbon in C@TiO₂ sample is about 75 % (as estimated from TGA analysis), this value is reasonable. The BJH pore size distribution shows some obvious peaks in the range of 1~10 nm indicating the presence of majorly mesopores with a small portion of micropores. When the samples were subjected to additional re-calcination at high temperatures, the small TiO₂ grains grew by fusion, resulting in decreased porosity and reduced surface area. The C@TiO₂-HCl-750 sample prepared by silica-protected calcination, silica etching, HCl treatment, and re-calcination at 750 °C, also showed a type IV isotherm with a decreased BET surface area of 188 m²/g and mesopores within the range of 2 to 5 nm.

The carbon content and thermal decomposition behavior of C@TiO₂ yolk-shell samples were investigated by thermogravimetric analysis (TGA). Figure 5 shows TGA data and representative TEM images of hollow TiO₂ and C@TiO₂ prepared by silica-protected calcination at 800 °C under air and Ar environments, respectively. Both samples displayed 7 ~ 8 % weight loss before heating to ca. 200 °C, which can be attributed to desorption of weakly adsorbed water molecules. In the case of hollow TiO₂, it showed minor weight loss from 200 to 700 °C, which could be attributed to the desorption of the strongly adsorbed water molecules and the dehydroxylation on the surface of oxides. Total weight loss of the

hollow TiO₂ sample was estimated to be ca. 11 %. The C@TiO₂ sample showed significantly different thermogravimetric behavior. The sample displayed a dramatic weight loss in the range of 300 to 550 °C which could be attributed mainly to the decomposition of the carbon core. Minor weight loss after 550 °C was also observed, indicating the dehydroxylation process on the surface of oxides. The total weight loss of the C@TiO₂ sample was measured to be ca. 32 %.

Figure 6 compares the development of the crystalline grains of the final C@TiO₂ samples before and after being re-calcined at different temperatures. The C@TiO₂ sample prepared by silica-protected calcination at 800 °C has a highly mesoporous structure with the smallest crystal grains (ca. 4 nm, Figure 6a). After HCl treatment and re-calcination at 600 °C, C@TiO₂-HCl-600 showed a similar size of TiO₂ crystalline grains because the re-calcination temperature was not high enough to re-crystallize the TiO₂ and increase the grain size. By increasing calcination temperature above 700 °C, the crystal grain size increased continuously (Figure 6c-e). A closer observation of the TEM images clearly indicated that the porosity of the TiO₂ shell was progressively reduced with the increasing re-calcination temperature. In addition, it should be noted that C@TiO₂ yolk-shell structures can be well maintained (Figure 6f), even after re-calcination at high temperatures (i.e. 800 °C).

Crystalline structures of the prepared C@TiO₂ samples were investigated by XRD (Figure 7). Because carbon cores converted from the RF resin have nearly amorphous characteristics under the calcination temperatures used in this work, the diffraction peaks are more related to the crystalline phase of the TiO₂. As shown in Figure 7a, the C@TiO₂ sample prepared by silica-protected calcination at 800 °C under Ar displayed relatively broad peaks of the anatase phase at $2\theta = 25.4, 37.9, 48.1, 54$ and 55° , which could be attributed to the (101), (004), (200), (105) and (211) planes, respectively. While re-calcination at 600 °C after acid treatment did not cause apparent change to the peak width, re-calcination above 700 °C

increased the relative intensity and sharpness of the peaks, indicating enhanced crystallinity. At 800 °C, new XRD peaks corresponding to the rutile phase were seen at $2\theta = 27.6, 36.6, 38.0, 41.4$ and 54.5° . The average anatase grain sizes of samples, calculated from the widths of the anatase (101) peak in the XRD data by using the Scherrer formula, were estimated at approximately 4.4, 4.6, 6.4, 9.1 and 10.4 nm for C@TiO₂, C@TiO₂-HCl-600, C@TiO₂-HCl-700, C@TiO₂-HCl-750, and C@TiO₂-HCl-800, respectively.

The photocatalytic activity of the C@TiO₂ samples was evaluated by monitoring the degradation of Rhodamine B (RhB) under UV light irradiation. Figure 8a shows typical absorption spectra for an aqueous RhB solution after UV irradiation for various time periods using C@TiO₂-HCl-750 as the catalyst. The strong absorption peak at 554 nm dramatically decreased and finally disappeared after 30 min, indicating the complete photo-degradation of RhB molecules. The performance of the photocatalysts toward RhB degradation, measured by monitoring the peak intensity at 554 nm versus time, is summarized in Figure 8b. Before UV irradiation, the mixture containing the catalyst and RhB was stirred in dark for 30 min to ensure saturation of RhB adsorption on the surface of the catalysts. C@TiO₂ samples employed in this work show much higher RhB adsorption capacity than P25-TiO₂, which has only 6 % C/C₀ adsorption capacity. The as-etched C@TiO₂ sample has the highest adsorption capacity in the range of 38 % of C/C₀ of RhB due to presence of the hydrophobic and microporous carbon core. The re-calcined C@TiO₂-HCl-x yolk-shell catalysts showed adsorption capacities in the range of 17-19 % of C/C₀, indicating that microporous characteristics of the carbon core may be reduced after the post-treatment processes. In the blank test without catalyst, RhB was degraded by only 4.5 % after UV irradiation for 30 min, while degradation was significantly enhanced in the presence of catalysts. The C@TiO₂ catalyst showed the lowest catalytic activity among all the catalysts tested in this work. After acid-treatment and re-calcination at different temperatures, the catalytic activity was

enhanced greatly. In particular, the RhB degradation over C@TiO₂-HCl-750 and C@TiO₂-HCl-800 catalysts was slightly faster than that over commercial P25-TiO₂. The relative photocatalytic activity of the catalysts for RhB degradation follows the order: C@TiO₂-HCl-750 > C@TiO₂-HCl-800 > P25-TiO₂ > C@TiO₂-HCl-700 > C@TiO₂.

In order to compare the reaction kinetics, we re-plotted the previous results to fit the first-order reaction rate equation. Figure 8c displays the data in semilogarithmic form which can facilitate calculation of reaction kinetic values. As expected, the blank test result (no catalyst) showed the lowest rate constant (0.0009 min⁻¹). As-etched C@TiO₂ catalyst without re-calcination showed the lowest k value among all the catalysts tested in this work, and the k value increased after the sample was re-calcined. The re-calcined C@TiO₂-HCl-750 catalysts showed the highest k value, indicating the highest photocatalytic efficiency. C@TiO₂-HCl-750 and C@TiO₂-HCl-800 showed comparable or slightly better catalytic performance than commercial P25-TiO₂ catalysts. In addition, the catalysts show excellent chemical and photostability in the RhB decomposition reaction. As shown in Figure 8d, the photocatalytic performance of C@TiO₂-HCl-750 on RhB degradation was well maintained during 5 cycles of repeated experiments.

In order to explore the reaction pathway and final products of RhB decomposition, we investigated the intermediates in the solution sample obtained during photocatalysis reactions. Figure S4 shows HPLC chromatograms of solution samples for three different time periods when photocatalytic decomposition of RhB was carried out by using C@TiO₂-HCl-750 as the catalyst. At the beginning of the reaction (0 min), a strong RhB peak was clearly observed and disappeared after 20 min. The peak of reaction intermediates appeared at 20 min and eventually disappeared after 120 min, indicating that the intermediates can also be fully decomposed after prolonged reaction.

It is well known that the photocatalytic decomposition of RhB is mainly attributed to

N-deethylation and cleavage of the chromophore.⁴⁷⁻⁴⁹ Yu et al. reported that adsorbed RhB on the surface of the catalyst can be N-deetylated to various kinds of intermediates by photocatalytic reaction, and mass difference between a series of product molecules is 28 mass units.⁴⁷ In order to identify the reaction intermediates, LC-MS analysis was conducted. Figure S5 shows the positive ion mass spectra of solution sample at 20 min during the photocatalytic degradation of RhB. As expected, various N-deethylated intermediates were observed, with peaks being assigned to N,N-diethylrhodamine (DR), N-ethyl-N'-ethyl-rhodamine (EER), N-ethylrhodamine (ER), and rhodamine (R). Although we didn't observe N,N-diethyl-N'-ethylrhodamine (DER) of 415.2 m/z in our experiment due to too fast photocatalysis reaction under UV irradiation, mass difference between a series of decomposition products was found to be 28 mass units, indicating that successive decomposition of RhB occurred to the N-deethylated intermediates. The results are well consistent with other reports in literature.^{47,48} We also used GC-MS to verify finally degraded molecules during photocatalytic decomposition of RhB and the results have been summarized in Table S1. On the basis of the previous studies⁴⁸⁻⁵¹, either RhB can be decomposed to small molecule intermediates directly or the N-deethyleated intermediates can be further degraded to small molecules containing benzene ring such as 2-(methoxycarbonyl)-benzoic acid, benzoic acid and terephthalic acid. Although we didn't observe the small organic acids such as benzoic acid and terephthalic acid, we detected 2-(methoxycarbonyl)-benzoic acid. In addition, glutaric acid and butan-2,3-diol were also observed, indicating a decomposition pathway similar to that proposed in previous works. It should be also noted that small molecular products such as methyl acetate and butane-2,3-diol were resulted from cleavage of the xanthene ring in RhB and N-deethyleated intermediates.⁵¹

4. Conclusions

We have developed a novel synthetic method for the production of C@TiO₂ yolk-shell nanostructures and demonstrated the ability to optimize their structures and properties for enhanced performance in photocatalysis. This process involves the synthesis of carbonizable RF resin spheres, coating TiO₂ on the RF templates to form RF@TiO₂ core-shell structures, additional SiO₂ coating on the surface of RF@TiO₂, calcination at high temperature under Ar, and finally NaOH etching to produce C@TiO₂ yolk-shell particles. During calcination at high temperatures, the RF resin core in the RF@TiO₂@SiO₂ spheres can be transformed into its carbon counterpart and at the same time the amorphous TiO₂ shell can be crystallized into anatase phase with nanoscale crystalline grains. In order to control the crystalline properties of the TiO₂ shell, post-treatment including acid treatment and re-calcination was applied. The synthesis process not only adds a conductive carbon core to the TiO₂ catalyst for elongating life-time of excitons, but also maintains the mesoporous characteristics and the crystallinity and structural integrity of the catalyst shells. As such, the C@TiO₂ yolk-shell samples showed significantly enhanced photocatalytic activity in the degradation of RhB with greater enhancement for C@TiO₂ samples re-calcined at high temperatures.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, & Biosciences (CSGB) Division, under Award No. DE-SC0002247. FZ and YY are members of the Center for Catalysis at the University of California, Riverside. More details can be found at catalysis.ucr.edu.

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Graphical Abstract

Figures

Figure 1. Schematic illustration of the procedure for the synthesis of C@TiO₂ yolk-shell nanostructure and the expected photocatalysis mechanism under UV light irradiation

Figure 2. TEM images of as-synthesized RF@TiO₂ core-shell particle when different amounts of TBOT were used during synthesis: (a) 0.1, (b) 0.3, (c) 0.6 and (d) 1.0 mL. (e) low magnification TEM image of RF@TiO₂ core-shell particle prepared by using 0.3 mL TBOT. (f) The relationship between the amount of TBOT and shell thickness of RF@TiO₂ core-shell samples. Other synthetic conditions are identical.

Figure 3. TEM images and corresponding schematic illustrations (inset) of the particle at each synthetic step: (a) RF resin sphere, (b) RF@TiO₂, (c) RF@TiO₂@SiO₂, (d) Hollow TiO₂ produced by calcination of RF@TiO₂@SiO₂ under air followed by etching of silica, (e) C@TiO₂ yolk-shell particle produced by calcining RF@TiO₂@SiO₂ under Ar followed by etching of silica, and (f) C@TiO₂ yolk-shell particle with improved crystallinity by post-

treatment including acid treatment and re-calcination.

Figure 4. (a) Nitrogen adsorption isotherms and (b) pore size distributions for the sample at each synthetic step: as-synthesized RF@TiO₂, hollow TiO₂ prepared by silica protected calcination at 800 °C under air followed by NaOH etching, C@TiO₂ prepared by silica protected calcination at 800 °C under Ar followed by NaOH etching and C@TiO₂-HCl-750 prepared by silica-protected calcination, silica etching and HCl treatment followed by re-calcination at 750 °C.

Figure 5. TGA results and corresponding TEM images of hollow TiO₂ and C@TiO₂ prepared by silica-protected calcination at 800 °C.

Figure 6. TEM images of final C@TiO₂ yolk-shell nanostructures: (a) C@TiO₂, (b) C@TiO₂-HCl-600, (c) C@TiO₂-HCl-700, (d) C@TiO₂-HCl-750 and (e-f) C@TiO₂-HCl-800.

Figure 7. XRD patterns of final C@TiO₂ yolk-shell nanostructures. (a) C@TiO₂, (b) C@TiO₂-HCl-600, (c) C@TiO₂-HCl-700, (d) C@TiO₂-HCl-750 and (e) C@TiO₂-HCl-800.

Figure 8. (a) UV-vis absorption spectra changes showing degradation of RhB using the C@TiO₂-HCl-750 catalyst, (b) photocatalytic degradation behavior of RhB under UV light irradiation and (c) semilogarithmic plot versus time in the presence of different photocatalysts: blank experiment (no catalyst) (■), commercial P25-TiO₂ (○), C@TiO₂ (▲), C@TiO₂-HCl-700 (▽), C@TiO₂-HCl-750 (◆), and C@TiO₂-HCl-800 (◁). (d) Cycling test results of RhB degradation with C@TiO₂-HCl-750 under UV light irradiation for 30 min.