SiO₂/TiO₂ Double-Shell Hollow Particles: Fabrication and UV-Vis Spectrum Characterization

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ABSTRACT

Well-defined SiO₂/TiO₂ double-shell hollow particles (STDShPs) were successfully fabricated by a sol-gel method with avoiding the particle aggregations and the generation of freestanding TiO₂ particles. Comparing with the conventional solid TiO₂ particles, STDShPs showed a novel hollow structure, a much smaller TiO₂ grain size (9nm), and a larger specific surface area (113m²/g). In the UV-vis spectrum characterizations, STDShPs showed significant light harvesting capability in both UV- and visible-light range. STDShPs also showed stronger per-weight UV absorbance capability than solid TiO₂ particles and commercial TiO₂ photocatalyst P25, which could be attributed to their novel hollow structure—and thus the absence of light-inaccessible TiO₂ particles. Moreover, we analyzed the narrowed band-gap of STDShPs by the Brus' effective-mass model (EMM).

KEYWORDS

TiO₂; Hollow particles; double-shell

1. INTRODUCTION

Since 1972, when the activity of TiO_2 towards the electrochemical photolysis of water splitting was firstly found by Fujishima and Honda ^[1], the photoelectrochemical property of TiO_2 has been deeply studied. As a semiconductor, when a photon with energy equal to or greater than the band-gap of TiO_2 was absorbed by TiO_2 , an electron in the valence band would conduct an interband transition to the conduction band, and a positive charged hole would accordingly generate in its valence band ^[2, 3]. The formation of photogenerated charge carriers (electrons and holes) derives to the photocatalytic properties of TiO_2 . That is, the photogenerated electrons and holes diffuse to the surface of TiO_2 and react with the adsorbed molecular (H_2O , O_2 , etc.) to generate some high activity species (hydroxyl radicals, superoxide radical anions, etc.), and then initiate the organic degradation reaction ^[4- 6] or water splitting reaction ^[7, 8].

The photocatalytic property of TiO_2 is influenced by many factors, such as the crystalline structures ^[9, 10], particle size ^[11], doping elements ^[12, 13], surface area ^[14], etc. Especially, because of their size quantization effect and their large specific surface area, TiO_2 nanoparticles owned their advantages and competitiveness during photocatalytic applications with respect to the bulk TiO_2 ^[15]. Nevertheless, it was reported that this advantages of TiO_2 nanoparticles would be weakened by the particle agglomeration. Lin H. et. al. ^[16] measured the particle size distribution of TiO_2 nanoparticles in aqueous solution which was pre-treated by ultrasound and compared that with their primary particle size which determined by XRD measurements. The results indicated that the agglomeration did take place readily even in a short time. Even worse, the smaller the primary particles were, the faster they aggregated. Obviously, in the practical applications of TiO_2 nanoparticles, a considerable number of TiO_2 primary particles existing inside the secondary particles would be light-inaccessible. Recently, it was found the hollow structure

would likely to supply an effective solution for the technique bottleneck in the applications of TiO₂ nanoparticles. It has been reported that the hollow structure could not only supply a high specific surface but also enabled multiple diffractions and reflections of incident light ^[17]. Therefore, TiO₂ hollow particles could supply much larger area for light adsorption than that of normal solid TiO₂ particles and minimize the proportion of light-inaccessible TiO₂ particles. Kondo et al. ^[18] found that the catalytic activity of TiO₂ hollow spheres toward gaseous isopropyl alcohol decomposition under UV irradiation was 1.8 times higher than that of the conventional commercial P25 TiO₂ and the dye-sensitized solar cell (DSC) using an electrode of the TiO₂ hollow spheres represented a 2.5 times higher per-weight efficiency towards that of the conventional DSCs of TiO₂. However, such works were rarely reported and even less work referred to the UV-vis spectrum studies of TiO₂ hollow structure, the band gap information as well.

In this work, we designed a new TiO₂-based hollow particles-- SiO₂/TiO₂ double-shell hollow particles (STDShPs), and focused on their UV-vis spectrum characterizations. The motivation to combine both SiO₂ and TiO₂ in the shells of hollow particles was for sustaining the integration of the shells, since the TiO₂ shells normally showed low mechanical strength. In fact, an additional merit would also be brought by the composition of SiO₂ shell, as suppressing the growth of TiO₂ nanoparticles in size. It is worth noting that the particle aggregation and the generation of free-standing TiO₂ particles were well suppressed by optimizing the experimental parameters in the fabrication process of the STDShPs. In the UV-vis spectrum characterization, we focused on confirming the “light harvesting capability” brought by the hollow structure and comparing the UV-light absorption capability of STDShPs, as well as the band-gap, with that of home-made solid TiO₂ particles (s- TiO₂) and commercial Degussa P25.

2. EXPERIMENTS

2.1 Materials

CaCO₃ templates were from Yabashi Industries Co., Japan. Tetraethyl orthosilicate (TEOS, 95.0%), Ethanol (99.5%), Ammonia solution (28.0 and 25.0 %), Titanium (IV) Tetrabutoxide (TBOT, 95.0%), Acetonitrile (99.5%), and hydrochloric acid (HCl, 35 wt. %) were from Wako Pure Chemical Industries, Ltd. Japan. All the chemicals were used as received and without further purification. DI water was produced by RFD250NB distilled water system (Toyo Roshi Kaisha, Ltd. Japan). P25 TiO₂ powder was provided from Degussa Co., Germany.

2.2 Fabrication of hollow SiO₂ particles (HSPs)

Hollow SiO₂ particles (HSPs) were fabricated by a previously reported modified Stöber method ^[19]. In a typical process, 10 g CaCO₃ templates were dispersed into a solution containing 300 mL Ethanol, 36 mL water, and 30 mL 25.0 wt% ammonia solution. After 10 min ultrasonic treatment, the uniform CaCO₃ suspension was immediately transferred to a 25 °C thermostatic water bath. Thereafter, 8 mL TEOS was dropped in under vigorous stirring. After 3h, the reaction was terminated by the addition of excess amount of ethanol. Particles were filtrated and washed with ethanol for several times and then dried under vacuum at 100°C for overnight. The well dried powder was re-dispersed into 3M HCl and stirred for 2h to remove CaCO₃ templates. Finally, the obtained hollow particles were washed with distilled water for several times, and dried under vacuum at 100°C for overnight.

2.3 Fabrication of STDShPs

STDShPs were synthesized by a sol-gel method using the as-fabricated HSPs as the templates and TBOT as the precursor. Considering the much higher hydrolysis rate of TBOT

than that of TEOS, we used acetonitrile to accelerate the mass transfer rate of TBOT and their partial hydrolysates from solvent to the surface of HSPs^[20]. During the preparation process, 0.1 g HSPs were dispersed into a solution containing both acetonitrile and ethanol with a volume ratio of 1: 3. Then 0.63ml 28% ammonia solution was added to make the suspension basic. After a 30min ultrasonic treatment, the uniform suspension was transferred to a 25 °c thermostatic water bath, and then a mixture solution with TBOT, 15 mL Ethanol and 5 mL acetonitrile was dropped in under vigorous stirring. The reaction was allowed to sustain for 3 hr. The resultant products were centrifuged under 3000 rpm rotation speed and washed with water and ethanol for 3 times. Thereafter, particles were transferred into a vacuum oven and dried at 100 °c for 24 hr. For comparison, pure TiO₂ solid particles (s-TiO₂) were fabricated by a similar sol-gel method but without the appearance of HSPs. The crystallization (calcination) of TiO₂ was conducted at 600°C, with the heating rate of 5°C/min.

2.4 Characterizations

SEM images were taken on JSM- 7600F (JEOL Ltd.), and the acceleration voltage was set to 20 kV. XRD patterns were recorded by Ultima IV (Rigaku co.) with Cu K α radiation (40 kV, 40 mA), and the scan step was 0.02°. High resolution transmission electron microscopy (HRTEM) and electron diffraction characterizations were conducted on JEM-2000FX (JEOL Ltd.), and the acceleration voltage was set to 200 kV. The specific surface area of HSPs, STDSPs and s-TiO₂ solid particles was determined by the Brunauer-Emmett-Teller multiplayer nitrogen gas adsorption (BET) method on Belsorp-max-NS (Bel Japan Inc.). X-ray Fluorescence (XRF) analysis was conducted on EDX-7000 (Shimadzu Co. Ltd.). Zetasizer nano-ZS (Malvern Ltd.) was used to conduct the DLS measurements.

The UV-vis diffuse reflectance spectra was recorded by UV-3150 (Shimadzu Co. Ltd.). All the samples were weighed exactly for 0.5 g and then finely spread on the surface of pressed BaSO₄ (Wako Co., Ltd.) powder. During the measurements, the scanning wavelength range was between 300 and 800 nm, slit width was (20) nm, and the scanning speed was set as medium. The respective band gap of each sample could be calculated according to the formula (eq. 1) ^[21]

$$(h\nu F(R\infty))^{1/2} = A(h\nu - E_g) \quad (1)$$

where h, ν , A and F(R ∞) are Planck's constant, wavelength, proportional constant and Kubelka- Munk function, respectively ^[16]. In order to simplify the calculation, $(h\nu F(R\infty))^{1/2}$ was plotted against the h ν . A line was drawn tangent to the point of inflection on the (h ν - (h ν F(R ∞))²) curve, and the h ν value at the point of intersection of the tangent line and the horizontal axis is the band gap E_g value.

3. RESULTS AND DISCUSSION

3.1 Fabrication of SiO₂/TiO₂ double-shell hollow particles (STDShPs)

Figure 1a depicts a typical fabrication process of STDShPs, which generally includes two steps. In Step 1st, SiO₂ layers were constructed on the surfaces of CaCO₃ templates by a modified Stöber method ^[19]—making the hydrolysis and condensation over TEOS conduct under the catalyzing of NH₃. The CaCO₃ templates used in this work were approximate to ellipsoid and with the diameter of 600-700 nm, as seen in **Figure 1b**. After the formation of CaCO₃@SiO₂ core-shell particles, the HSPs were further obtained by HCl etching. In this course, HCl penetrated through SiO₂ shells and subsequently etched CaCO₃ templates by conducting the following reaction,

Obviously, void spaces would gradually formed inside $\text{CaCO}_3@\text{SiO}_2$ core-shell particles with the on-going penetration and etching process of HCl. To minimize the damage brought by HCl and CO_2 gas penetration to SiO_2 shells, HCl solution with a low concentration (3M) were used in this work. The SEM observation (**Figure 1c**) indicates particles treated by HCl solution for 2h well maintained the shape and size of CaCO_3 templates, while no fragments and broken particles generated. Furthermore, the high-magnification STEM image (insert of **Figure 1c**) confirms the hollow structure of HSPs, as the result of CaCO_3 templates being removed by HCl etching.

In Step 2nd, the as-fabricated HSPs were used as the templates for TiO_2 decorating to obtain SiO_2 - TiO_2 shells. TBOT was used as the precursor of TiO_2 and it underwent hydrolysis and condensation processes with the presence of water. Concerning the high reactive of TBOT, both the concentrations of TBOT and water were set on low level (1.5 and 0.9 vol. %). Considering NH_3 played as the catalyst for the hydrolysis and condensation reactions over TBOT, we observed the influence of the concentration of NH_3 to the morphology of resulting STDSHPs. As seen in **Figure 2a**, though the decoration of TiO_2 was significant when NH_3 was absent, the resulting composite hollow particles showed a server-aggregated morphology and numerous freestanding TiO_2 nanoparticles could be found. In order to suppress the aggregation and the generation of freestanding TiO_2 nanoparticles, a certain amount of NH_3 was added into the reaction system, while fixed the concentration of water (0.9 vol. %). As seen in **Figure 2b~d**, the dispersibility of resulting composite hollow particles was improved with increasing the concentration of NH_3 ($c(\text{NH}_3)$) from 69mM to 208mM. The size distribution curves in **Figure 2e** also demonstrates the improvement of particle dispersibility with increasing the concentration of NH_3 . As seen, two peaks (~1500 and ~5500nm) appeared in the distribution curve of the STDSHPs sample which was fabricated without the presence of NH_3 , indicating the occurrence

of severe aggregation. On contrary with the presence of NH_3 , only one peak could be observed in the range of 100~10000nm, while the peak gradually shifted to left (small size) with increasing $c(\text{NH}_3)$. Apparently, the uniformity of resulting STDSHPs was considerably improved, and even more importantly, the yield of aggregated STDSHPs significantly decreased with increasing the $c(\text{NH}_3)$ in reaction system. Especially when $c(\text{NH}_3)$ reached to 208mM, the average size of STDSHPs was calculated to 650nm, close to the size of a single STDSHP in the SEM observation (**Figure 2d**). On the other hand, the yield of free standing TiO_2 nanoparticles decreased with the increasing of NH_3 concentration, and there were less particles could be observed when the concentration of NH_3 was adjusted to 208mM (**Figure 2d**). The probable role of NH_3 in the reaction system was partly screening the negative surface charge of HSPs^[20] that made the surface more advantageous for the heterogeneous nucleation of TiO_2 (hydrates of TBOT also carried negative charges), rather than independently homogeneous nucleation to yield freestanding TiO_2 particles and caused particle aggregation thereafter^[22]. Moreover, though the decorating of TiO_2 became invisible in SEM image with the increasing of their uniformity (**Figure 2d**), the co-existence of SiO_2 and TiO_2 on shells could still be confirmed by point EDS spectrum, as seen in **Figure 2f**. In addition, this EDS spectrum also indicates CaCO_3 templates were thoroughly removed by 2h of HCl (3M) etching, as there is no peak can be assigned to Ca element.

The purpose of adding acetonitrile as a second solvent (other than ethanol) was to promote the decoration rate of TiO_2 on the surface of HSPs under such a low concentration of TBOT, H_2O and NH_3 . As seen in **Figure s1**, the shell of STDSHPs became much thicker with increasing the volume ratio of acetonitrile to ethanol (V_a/V_e) from 0 to 0.5, indicating the decoration rate of TiO_2 was effectively promoted by the addition of acetonitrile and showed a positive correlation

with the content of acetonitrile in the reaction system. This phenomenon shows a good agreement with that described in other report ^[20], and a probable reason is acetonitrile weakens the interaction between TBOT (and/ or its hydrates) and solvent—thus enhances the diffusion rate of TBOT (and/ or its hydrates) from bulk solution to the surface of HSPs to form thick TiO₂ shells. Nevertheless, it should not neglect the agglomeration which occurred when V_a/V_e was too high (0.5). Therefore, by considering the decorating efficiency of TiO₂ and the dispersibility of STDSPs synthetically, 1/3 is believed as the optimum value of V_a/V_e.

3.2 Structure characterization of STDSPs

Figure 3 shows XRD patterns of HSPs, STDSPs (calcined at 600°C) and home-made solid TiO₂ particles (s- TiO₂, calcined at 600°C) respectively. As seen, both the TiO₂ in STDSPs and s- TiO₂ were crystallized after calcination at 600°C. Meanwhile, all the X-ray diffraction peaks of these two samples could be well indexed to the standard XRD pattern of Anatase TiO₂ (JCPDS #21- 1272). Nevertheless, the diffraction peaks of the TiO₂ in STDSPs showed significant broaden phenomenon with respect to that of s- TiO₂. According to Scherrer formula (eq. 3)

$$D = \kappa \lambda / \beta \cos \theta \quad (3)$$

where the λ (nm), β (rad), θ (rad) are wavelength of the incident X-ray (Cu K α , 0.154 nm) radiation, full width at half maximum (FWHM) of the characteristic peak of TiO₂ and diffraction angle while κ (0.89), respectively. The TiO₂ grain size for STDSPs was calculated to 9nm, while 38nm for that of s-TiO₂. Obviously, TiO₂ particles showed strong interaction with the surface of HSPs during their decoration process, and their growth on size was effectively suppressed.

Figure 4a~c show TEM images of STDShPs (calcined at 600°C) under different magnifications. The low-magnification TEM image (**Figure 4a**) indicates the hollow structure of HSPs was maintained after the decoration of TiO₂, while the high-magnification TEM image (**Figure 4b**) indicates there were numerous TiO₂ nanoparticles adhered on the surface of HSPs. Considering the high density of TiO₂ decoration, the shell of STDShP could be seen as a composite shell including two sub-layers of SiO₂ (inner) and TiO₂ (outer). Moreover, the size of TiO₂ (primary) particles observed on the shell of STDShPs was about 5~12nm, showing good agreement with that calculated by XRD pattern (**Figure 4c**). Furthermore, both the diffraction rings and dots could be observed in electron diffraction pattern of STDShPs (**Figure 4d**), demonstrating the co-existence of amorphous SiO₂ and crystallized TiO₂ in the shells.

Figure 5 compares the nitrogen adsorption-desorption isotherms curves of HSPs, STDShPs and homemade s-TiO₂. The specific surface area for each sample was calculated to 176, 113 and 62 m²/g, respectively. It is clear that the specific surface area of the as-prepared STHPs possess nearly one folder larger than that of the s-TiO₂ particles, though it still lower than that of un-decorated HSPs. It's easy to understand the large specific surface area of STDShPs benefitted from their hollow structure brought by HSPs. Furthermore, the average size of TiO₂ secondary particles in the s-TiO₂ sample was calculated by the corresponding BET data. As a result, the secondary particles in s-TiO₂ was 181nm in their average size (see the calculation process in the supplementary information). Obviously, according to the TEM observation (**Figure 4a**), the size of TiO₂ secondary particles in STDShPs ($\leq$ the shell thickness) was far smaller than 181nm, though we cannot give a quantitative analysis yet. It is believed the small TiO₂ secondary particle size in STDShPs was attributed to the small primary particle (grain) size of the TiO₂ in STDShPs, which has been demonstrated by both XRD pattern and TEM

observation, as well as the immobilization effect of HSPs preventing the aggregation of TiO₂ particles. Therefore, two points should be taken into consideration to explain the large specific surface area of STDSHPs, as (1) STDSHPs maintained the hollow structure of HSPs—thus a lower density than solid particles; (2) the TiO₂ in STDSHPs were much smaller in both primary and secondary particle sizes than those in s- TiO₂.

3.3 UV-vis spectrum evaluation of STDSHPs

The UV-vis diffuse reflectance spectra of STDSHPs (calcined at 600°C) was measured and compared with that of HSPs, homemade s-TiO₂ particles (calcined at 600°C) and commercial available TiO₂-based photocatalyst P25 (**Figure 6a**). In the visible-light range (500~ 800 nm), the plot of STDSHPs overlaps with that of HSPs and showing a light absorbance fraction between 8% and 10 %. On contrary, the light absorbance fraction of homemade TiO₂ solid particles and P25 in that range is only 4% and 1%, respectively. The “light- harvesting capabilities” of hollow particles can be employed to explain this phenomenon, as the hollow structure allows the incident light conducting multiple diffractions and reflection internally or among particles—and thus reduces its chance of being reflected back ^[17, 18]. Nevertheless, the UV-vis spectrum of STDSHPs showed a similar trend with that of s-TiO₂ particles when the incident wavelength was below 500 nm, and started to show a strong light absorbance capability at the wavelength of about 400 nm. On contrary, HSPs showed much poorer UV absorbance capability. When the wavelength was 290 nm, the light absorbance fraction of STDSHPs reaches to 70%, which is higher than that of s-TiO₂ particles (68 %) but lower than that of P25 (75 %). Furthermore, if we presume the contained SiO₂ of STDSHPs possesses the same per weight light

absorbance capability with that in HSPs, the light absorbance fraction of the contained TiO₂ (f (TiO₂ in STDSHPs)/%) is calculated to 67.28% by the following equation

$$f(\text{TiO}_2 \text{ in STDSHPs}) = 70\% - m(\text{SiO}_2 \text{ in STDSHPs}) \cdot f(\text{HSPs}) / m(\text{HSPs}) \quad (4)$$

where $m(\text{HSPs})$ is 0.5g, $f(\text{HSPs})$ is 8% under 290 nm wavelength incident light and $m(\text{SiO}_2 \text{ in STDSHPs})$ is 0.17g from the XRF measurement. That is to say, when the wavelength of the incident light was 290 nm, the TiO₂ contained in STDSHPs is able to absorb as 99 % much light as that by s-TiO₂ solid particles and 90 % of that by P25, though the its weight was only 66 % of other two. Two facts should be taken into consideration for explaining the high light absorbance capability of the TiO₂ in STDSHPs, as (1) **those TiO₂ particles exists only in the shells of STDSHPs**, meaning all of them are accessible for the incident UV-light, (2) the “light-harvesting capabilities” are still effective in the UV range and therefore increases the ratio of absorbed light.

The band gaps of STDSHPs (calcined at 600°C), s-TiO₂ particles (calcined at 600°C) and P25 were determined as 3.14, 3.27 and 3.06 eV, respectively (**Figure 6b**). The narrow band gap of P25 can be attributed to the contained Rutile TiO₂ phase^[23], which has a narrower band gap (3.0 eV) than that of Anatase TiO₂. The band gap of homemade TiO₂ solid particles shows a good agreement with the reported value of Antase TiO₂^[24], while the band gap of STDSHPs shows a significant shifting ($\Delta E_g = 0.13$ eV). The size quantization effect of TiO₂ grains should be considered to explain the band gap shifting phenomenon. According to the Brus’ effective-mass model (EMM)^[16, 25-27], the band gap of semiconductor particles E_g^* (eV) can be expressed as a function of particle radius R (m), as

$$\Delta E_g = E_g^* - E_g \cong \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\epsilon R} \quad (5)$$

where ΔE_g (eV), E_g (eV), $\hbar$ (J s) are the band gap shift, the band gap of bulk semiconductor, the reduced Plank's constant, respectively. Herein, for TiO_2 , the effective mass of the electron m_e^* (kg) is in the range of 5- 13 m_e (the average value of 9 m_e was chosen in this calculation), and the effective mass of the hole m_h^* (kg) is equal to 2 m_e (m_e is the mass of an electron), e is the charge of electron (C), and ϵ ($\text{C}^2 \text{N}^{-1} \text{m}^{-2}$) is the electric permittivity TiO_2 varied between $23\epsilon_0$ to $184\epsilon_0$ (the average value of $103.5\epsilon_0$ was chosen in this calculation). According to the XRD results, the TiO_2 primary particle (grain) radius R (m) of STDSHPs is 4.5×10^{-9} , and 1.9×10^{-8} for s- TiO_2 . After substituting, the band gap shifting of TiO_2 in those two samples was calculated as -0.060 and -0.015 eV from the band gap of bulk anatase TiO_2 phase, respectively. Therefore, the band gap of TiO_2 in STDSHPs is about 0.045 eV narrower than that of homemade TiO_2 solid particles by means of theoretical calculation. It should be pointed out the dielectric permittivity of TiO_2 was fixed in the above calculation process. However, as reported by some researchers [28, 29], if TiO_2 composited with other materials, its dielectric permittivity would be varied by some factor such as the composition state, structure and morphology. Therefore, in this work, the changes of the TiO_2 dielectric permittivity should not be also neglected. Especially, if the dielectric permittivity of TiO_2 was decreased by composing with the SiO_2 , a material owns very low dielectric permittivity (about $3.9\epsilon_0$), the band gap shifting value would be further enlarged according to eq. 5. As a result, the difference of band gap between STDSHPs and s- TiO_2 particles would be possibly larger than 0.05 eV and be closer to the experimental value.

4. CONCLUSION

In this works, well-defined STDSHPs were fabricated by a sol-gel method with successful excluding the appearance of aggregation and free-standing TiO_2 particles. It was demonstrated

the TiO₂ in STDShPs had much smaller size (9nm) than that in the home-made s-TiO₂ particles, which was also obtained by a similar sol-gel method. Benefitting by the ultra-small size of TiO₂ and the hollow structure, STDShPs showed a considerably high specific surface area (113 m²/ g). In the UV-vis spectrum evaluation, STDShPs showed higher per-weight light absorbance capability for UV-light than that of s- TiO₂ particles and commercial P25 photocatalyst. This advantage of STDShPs could be attributed to the absence of light-inaccessible TiO₂ in the STDShPs and the “light- harvesting capabilities” brought by the hollow structure. Furthermore, the band-gap analysis indicated the narrower band-gap of STDShPs than that of s- TiO₂, though the TiO₂ in both of them were in Anatase crystallization type, and could be well explained by the the Brus’ effective- mass model.

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Captions:

Figure 1. (a) schematic diagram of the fabrication process of STDShPs; SEM images of CaCO_3 templates (b) and obtained HSPs (c); **insert of (c) is the high-magnification STEM image of HSPs.**

Figure 2. SEM images of STDShPs fabricated with the concentration of NH_3 in reaction system of 0 (a), 69mM (b), 138mM (c) and 208mM (d), while the concentration of water was fixed at 0.9 vol. %; (e) size distribution curves of STDShPs fabricated with different concentration of NH_3 ; (f) EDS point spectrum of STDShPs (the scanning position is assigned in (d)).

Figure 3. XRD patterns of STDShPs (calcined at 600°C), HSPs and s- TiO_2 (calcined at 600°C).

Figure 4. low- (a) and high-magnification (b, c) TEM image of STDShPs; (d) electron diffraction pattern corresponding to (b).

Figure 5. nitrogen adsorption-desorption isotherms curves of HSPs, STDSHPs and homemade s-TiO₂ particles.

Figure 6. (a) UV-vis diffuse reflectance spectra plots of STDSHPs (calcined at 600°C), homemade s-TiO₂ particles (calcined at 600°C), HSPs and P25; (b) corresponding $h\nu F(R_{\infty})^{\frac{1}{2}}$ curves of STDSHPs (calcined at 600°C), homemade s-TiO₂ particles (calcined at 600°C) and P25 for band-gap calculations.

Figure1

Figure 2

Figure3

Figure4

Figure5

Figure6

$\text{SiO}_2/\text{TiO}_2$ double-shell hollow particles (STDSPs)