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Template-Free Synthesis of Single-/Double-Walled TiO_2 Nanovesicles: Potential Photocatalysts for Engineering Application

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Significance *Single- and double-walled anatase TiO_2 nanovesicles have been, respectively, prepared by a template-free hydrothermal treatment of $Ti(SO_4)_2$ with H_2O_2 and urea. Photocatalytic degradation of Rhodamine B indicates that double-walled TiO_2 nanovesicles have an initial lower but a final higher photocatalytic efficiency than single-walled ones. All nanovesicles have significantly lower performance than commercially available P25 TiO_2. The enhanced capacity for UV light absorption and· OH radicals production, large specific surface area, and unique hierarchical hollow architectures contribute to the enhanced photocatalytic activity and improved feasibility of anatase TiO_2 nanovesicles for engineering applications.* *AIChE J*, 61: 1478–1482, 2015
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Multiwall/shell hollow nanostructures have spurred more and more interests owing to their superior properties with the advancement of nanoscience.[1–3] Multishelled TiO_2 hollow spheres present superior photocatalytic activity to sphere-in-sphere and nanoparticle samples because of the enhancement of light absorbance resulted from multiple reflections of UV light within the interior cavity.[2] However, the vast majority of existing studies focus on design and fabrication of simple TiO_2 hollow nanostructures with single wall/shell.[4,5] There are only a few reports on the preparation of multishelled TiO_2 hollow nanostructures based on template method.[2,6–8] For instance, Yao et al.[2] prepared multishelled TiO_2 hollow spheres by immersing porous polystyrene-divinyl-benzene spheres into the titania sol and subsequent postcalcination. Wang et al.[8] prepared shell-in-shell TiO_2 hollow spheres through hydrothermal treatment of TiF_4 and sucrose followed by removing carbonaceous cores and shells through calcination.

Although template method is the general way for preparing TiO_2 hollow nanostructures, it is subject to tedious procedures in surface modification, template removing, and postheat treatment for crystallization which is likely to consume more energy, reduce the specific surface area and even lead to the collapse of the hollow structures. Recent studies show that solution-phase chemical synthesis under hydrothermal conditions is not only effective for architecture control but also has great potential for large-scale production in terms of operation, cost, and throughput.[9,10] However, till now, it is still a challenge to prepare multiwall/shell TiO_2 hollow nanostructures by this method.

In this letter, a one-pot template-free method is presented for the first time to synthesize single- and double-walled anatase TiO_2 nanovesicles by hydrothermal treatment of $Ti(SO_4)_2$ with the assistance of H_2O_2 and urea. It is interesting to demonstrate that double-walled anatase TiO_2 nanovesicles have different photocatalytic activity from single-walled anatase TiO_2 nanovesicles at different stages of the degradation process. Anatase TiO_2 nanovesicles with unique hierarchical hollow structures not only enhance light harvesting capacity and offer large surface area for photocatalytic reaction but also are expected to overcome some practical problems encountered by particulate TiO_2 catalysts such as strong tendency of agglomeration and difficult postseparation and recycling.

Experimental details for the sample synthesis and characterization were described in Supplementary Material. XRD patterns of the products obtained at 2 and 16 h are shown in Supporting Information Figure S1a. All of the observed diffraction peaks can be well indexed to tetragonal anatase TiO_2 (JCPDS No. 21–1272). The sharper diffraction peaks

Additional Supporting Information may be found in the online version of this article.

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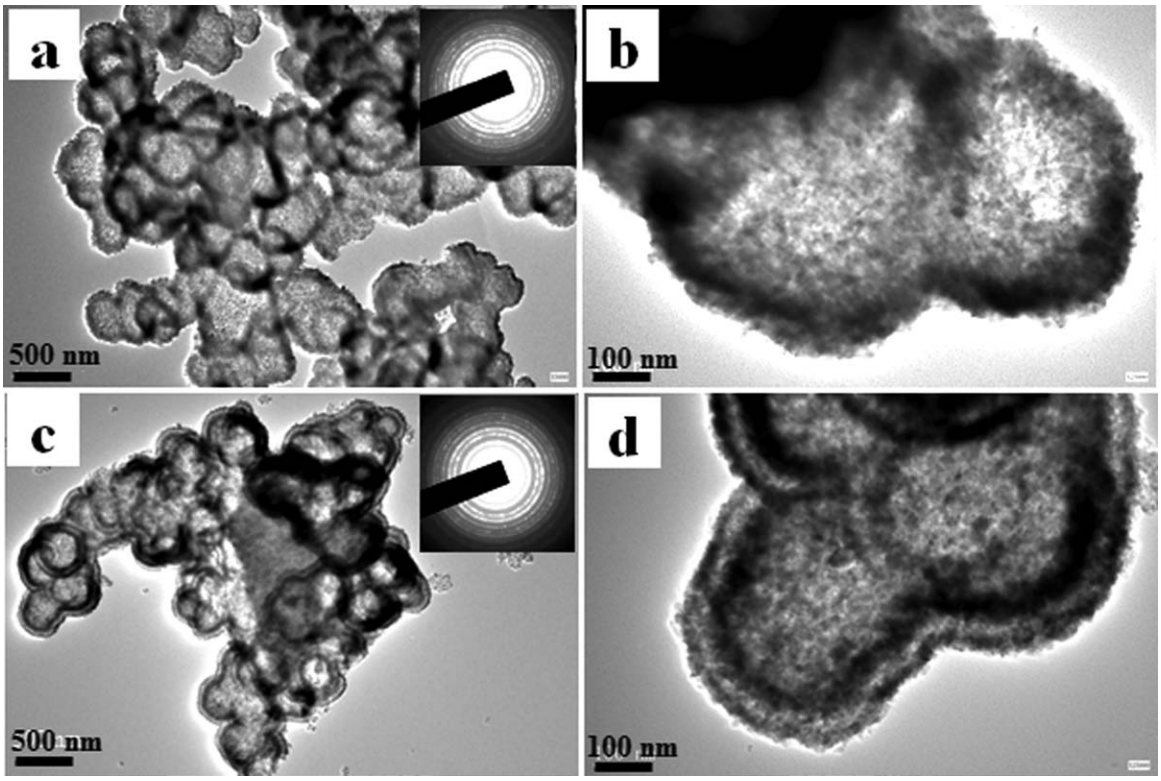

Figure 1. TEM images of anatase TiO_2 samples prepared by a hydrothermal treatment of $Ti(SO_4)_2$ with the assistance of H_2O_2 and urea for (a, b) 2 h and (c, d) 16 h. (The insets: SAED patterns of the samples).

with the increasing reaction time reveal the improvement of the crystallinity with bigger crystallite size. Nitrogen sorption experimental results in Supporting Information Figure S1b show that both of the samples have a type-IV isotherm with a hysteresis loop, indicating their mesoporous structure.[11] The BET surface area of the samples obtained at 2 and 16 h is 170.1 and 106.2 m^2/g with the average pore diameter of 3.76 and 7.59 nm, respectively, and the former displays a narrower pore size distribution than the latter.

TEM images in Figures 1a, b show that anatase TiO_2 sample obtained at 2 h displays single-walled vesicle-like nanostructures with sizes ranging from 400 to 500 nm, which are interconnected with each other to form larger aggregates at micrometer scale and are consistent with their FESEM observation (see Supporting Information Figures S2a, b). Actually, the nanovesicle wall with thickness of about 100 nm is composed of small nanoparticles with sizes of 15 nm. When the reaction time prolongs to 16 h, double-walled TiO_2 vesicle-like hollow nanostructures with sizes ranging from 400 to 500 nm can be clearly observed in Figures 1c, d, which is also in agreement with their FESEM results (see Supporting Information Figures S2c, d). The inner and outer walls with a spacing of 10–20 nm have a thickness of around 30 and 50 nm, respectively. Double-walled nanovesicles are also aggregated into larger particles at micrometer scale and assembled by nanoparticles with larger sizes (around 30 nm) than single-walled nanovesicles. SAED patterns of the two TiO_2 samples shown in the inset of Figures 1a, c are both ring-like, suggesting that they are polycrystalline.

The formation process of single- and double-walled anatase TiO_2 nanovesicles is shown in Supporting Information Figure S3. Ti^{4+} ions gradually hydrolyzed in the circumstance of H_2O_2 and urea aqueous solution and small nanoparticles were initially formed at 15 min, which gradually developed into metastable $H_2Ti_5O_{11}\cdot 3H_2O$ nanosheet assemblies at 30 min (see Supporting Information Figure S4a). At 1 h, more stable anatase $TiO_2/H_2Ti_5O_{11}\cdot 3H_2O$ core-shell nanostructures were formed (see Supporting Information Figure S4b). At this stage, low crystalline nanoparticles on the surface had direct contact with the surrounding solution and were first transformed to anatase crystalline layer through dissolution-recrystallization process, which were served as the nucleation seeds for subsequent recrystallization process. Poorly crystalline nanoparticles underneath the surface were dissolved gradually and recrystallized on the surface, leading to the inward evacuation and thus the formation of a core-shell structure.[12] At 2 h, the inner cores were completely dissolved and single-walled anatase TiO_2 nanovesicles were formed (see Figures 1a, b). However, the inner and outer surfaces of the wall have higher crystallinity than wall interior due to their direct contact with the surrounding solution. From 2 to 16 h, the relatively low crystalline nanoparticles located at the wall interior were dissolved and recrystallized on the wall surface because of the ripening effect, which led to the division of the wall into discrete regions and thus the formation of double-walled anatase TiO_2 nanovesicles at 16 h (see Figures 1c, d).

To evaluate the photocatalytic performances, anatase TiO_2 nanovesicles were used as the photocatalysts to degrade

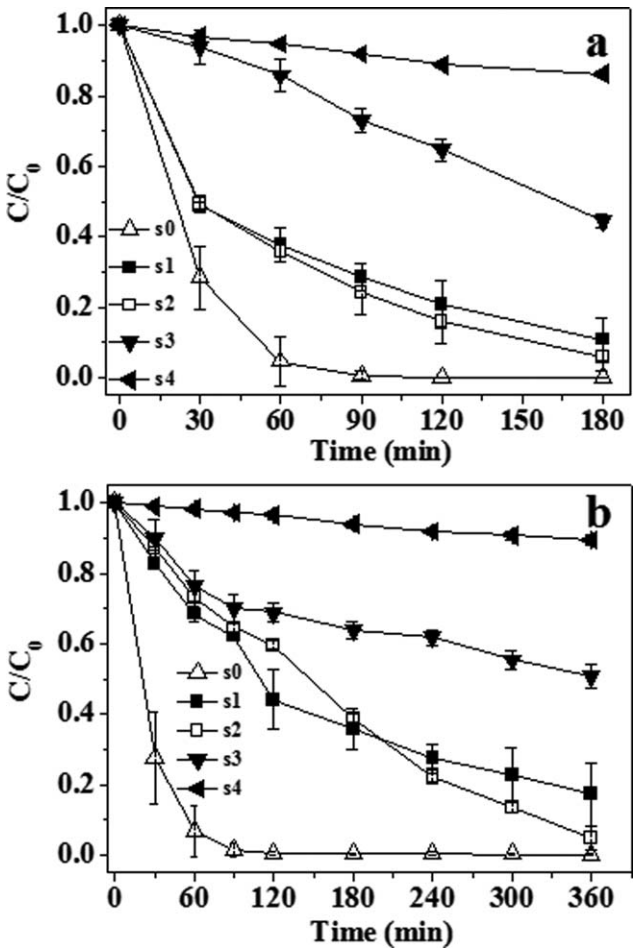

Figure 2. Photocatalytic degradation of RhB solution with an initial concentration of (a) 1×10^{-5} and (b) 2×10^{-5} mol/L under UV light irradiation in the presence of (s0) commercially available P25 TiO_2, (s1) single-walled anatase TiO_2 nanovesicles, (s2) double-walled anatase TiO_2 nanovesicles, (s3) commercial anatase TiO_2 nanoparticles, and (s4) in the absence of any photocatalyst. Each point represents the average value of four separate experiments derived from four batches of photocatalysts, and the vertical line represents the error range.

Rhodamine B (RhB) solution in the presence of UV light. Figure 2 plots the variation of the relative concentration of RhB aqueous solution with the irradiation time. The error bars represented by vertical lines indicate that the photocatalytic performance of the photocatalysts fluctuated within certain range. As shown in Figure 2a, after 180 min of illumination, the average RhB degradation ratio over single- and double-walled anatase TiO_2 nanovesicles and commercially acquired anatase TiO_2 nanoparticles can reach 89.2, 94.2, and 55.6%, respectively. When the initial concentration of RhB aqueous solution was increased from 1×10^{-5} to 2×10^{-5} mol/L, interestingly, single-walled anatase TiO_2 nanovesicles intially present higher photocatalytic efficiency than double-walled TiO_2 nanovesicles (see Figure 2b). With further extending the reaction time, the performance of the latter surpasses that of the former. The average degradation ratio of RhB over double-walled anatase TiO_2 nanovesicles can reach 95.0% after 360 min, which is much higher than that over single-walled anatase TiO_2 nanovesicles (82.7%) and the commercial anatase TiO_2 nanoparticles (49.3%), respectively, (see Figure 2b). A blank experiment was also conducted under UV light irradiation in the absence of any photocatalyst. The photolysis ratio of RhB with initial concentration of 1×10^{-5} and 2×10^{-5} mol/L is merely 13.7 and 10.6 %, manifesting that photocatalysts play a dominant role in the decomposition of RhB molecules.

It is interesting to find that double-walled anatase TiO_2 nanovesicles have different photocatalytic activity from single-walled anatase TiO_2 nanovesicles at different stages of the degradation reaction (see Figure 2b). Based on their adsorption curves (see Supporting Information Figure S5), more RhB molecules could be adsorbed and were finally degraded over single-walled anatase TiO_2 nanovesicles at the initial stage of the reaction because they have larger specific surface area than double-walled anatase TiO_2 nanovesicles (see Supporting Information Table 1), thus leading to their initially higher photocatalytic efficiency than that over double-walled anatase TiO_2 nanovesicles. However, double-walled anatase TiO_2 nanovesicles are able to produce more OH radicals than single-walled ones (see Supporting Information Figure S6) possibly because the former possesses higher crystallinity than the latter (see Supporting Information Figure S1a), which leads to lower recombination rate for electron-hole pairs on the former than on the latter. In addition, double-walled anatase TiO_2 nanovesicles have a lower internal diffusion resistance for RhB molecules (diameter: 1.6 nm, tending to aggregate and form dimmers with the increasing concentration)[13] than single-walled anatase TiO_2 nanovesicles because the pore size of the former (7.59 nm) was larger than that of the latter (3.76 nm) (see Supporting Information Table 1). Thus, double-walled anatase TiO_2 nanovesicles have a final higher photocatalytic effciency than single-walled anatase TiO_2 nanovesicles.

Single- and double-walled anatase TiO_2 nanovesicles exhibit superior photocatalytic activity to the commercial anatase TiO_2 nanoparticles. It can be rationally explained by the following aspects. First, TiO_2 nanovesicles have much larger specific surface area (see Supporting Information Table 1) and thus provide more active sites than the commercial anatase TiO_2 nanoparticles.[14] Second, the diffusion reflectance UV-vis absorption spectra indicate that single- and double-walled anatase TiO_2 nanovesicles exhibit superior light absorption capacity to the commercial anatase TiO_2 nanoparticles within the wavelength range from 200 to 335 nm (see Supporting Information Figure S7) because their interior cavity and shells with accessible mesopores allow the scattering and reflecting of the light within hollow structures, extend the distance that the light travels, and enhance the light harvesting.[15] In addition, single- and double-walled anatase TiO_2 nanovesicles are able to generate more OH radicals than the commercial anatase TiO_2 nanoparticles (see Supporting Information Figure S6). Thus, the as-prepared anatase TiO_2 nanovesicles offer more available photogenerated electrons and holes for the photocatalytic degradation of contaminants, leading to their enhanced photocatalytic performance in comparison with the commercial anatase TiO_2 nanoparticles.

Evonik P25 is also used as the benchmark for evaluating the prepared TiO_2 photocatalysts. RhB was nearly degraded completely over P25 at 90 min (see Figure 2: s0) under the same catalytic conditions. Although single- and double-walled anatase TiO_2 nanovesicles have a little bit lower photocatalytic efficiency than P25, their photcatalytic performaces are not that comparable because they have different composition. P25, which has a particle size of around 30 nm and specific surface area of 36.4 m^2/g (see Supporting Information Figure S8 and Table 1), consists of mixed phases (about 80% anatase and 20% rutile, see Supporting Information Figure S8a), whereas the as-prepared TiO_2 nanovesicles are pure anatase.

Actually, single- and double-walled anatase TiO_2 nanovesicles present some advantages over P25 not only in preparation but also in practical application. First, P25 is readily available and produced commercially at tons/h. It is prepared from titanium tetrachloride vapor in an oxyhydrogen flame hydrolysis at around 1000°C, whereas single- and double-walled anatase TiO_2 nanovesicles are synthesized via mild hydrothermal reaction at 170°C, which facilitates the operation and lowers the energy consumption for large-scale production. Meanwhile, single- and double-walled nanovesicles not only have hierarchical hollow structures assembled by small nanocrystallites, but also are interconnected to form much larger aggregates at micrometer scale. This structural characteristics make them not only inherit nanoscale properties such as large surface area and high activity but also be readily separated from solutions through initial gravity sedimentation followed by some other separation technologies. Life cycle assessment also indicates that RhB degradation ratio can still reach 81.0 and 82.8% over single- and double-walled anatase TiO_2 nanovesicles after five cycles (see Supporting Information Figure S9), indicating their good stability as photocatalysts.

In addition, the photocatalytic performance of single- and double-walled anatase TiO_2 nanovesicles can be further enhanced by improving their crystallinity and tuning their phase composition. For example, pure anatase phase can be transformed into mixing phases with certain ratio of anatase and rutile via postheat treatment. Through further optimization for process parameters, the as-prepared photocatalysts would have comparable photocatalytic performance with P25 and be more practical for large scale photocatalytic application.

In brief, single- and double-walled anatase TiO_2 nanovesicles were successfully fabricated via a simple hydrothermal treatment of $Ti(SO_4)_2$ with the assistance of H_2O_2 and urea. The evolution process reveals that anatase TiO_2 nanovesicles with single- and double walls are controllably transformed from $H_2Ti_5O_{11}{\cdot}3H_2O$ nanosheet assemblies using urea and H_2O_2 to tune the nucleation kinetics and dissolution-recrystallization process. Photocatalytic degradation of RhB demonstrates that double-walled anatase TiO_2 nanovesicles have an initial lower but a final higher photocatalytic efficiency than single-walled anatase TiO_2 nanovesicles at relatively higher RhB concentration. They both possess enhanced photocatalytic activity than the commercial anataste TiO_2 nanoparticles. Their unique hierarchial hollow structures facilitate postseparation and increase their feasibility for engineering applications. This work opens a new avenue to large-scale preparation of potential TiO_2 photocatalysts and expects their wide applications in environmental remediation.

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