Preparation of Au@TiO$_2$ yolk-shell nanocomposites for solar-light degradation of methylene blue

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Abstract. A novel synthetic approach has been developed to prepare Au@TiO$_2$ yolk-shell (Au@TiO$_2$-YS) structures using silica as a template with controllable size, shape, crystal phase. This approach shows a few unique features, including tunable TiO$_2$ shell thickness, high repeatability, low cost, and easy operation. The morphology, composition and the corresponding properties were characterized by several advanced techniques, such as TEM, XRD, and UV-vis spectroscopy. The Au@TiO$_2$-YS structures consist of Au NPs as cores and TiO$_2$ hollow spheres as shells. The Au NPs can be controlled in various diameters (e.g., 100 nm, 50nm, and 30 nm), while the TiO$_2$ shell can form cavities with diameters of 255 nm and the thickness of ~45 nm. The absorption peak of the product can be changed by adjusting the size of Au cores. In addition, the photocatalytic activities of the synthesized composites were systematically measured by degrading methylene blue (MB) under simulated solar light irradiation. The photocatalytic performance test reveals that the reaction kinetic constants of the Au@TiO$_2$-YS structures with different Au core sizes are superior to that of the TiO$_2$ hollow spheres (0.00521 min$^{-1}$). Among the yolk-shell structures, the YS-50 show highest kinetic constant (0.00704 min$^{-1}$), which is 1.35 times higher than that of pure TiO$_2$ hollow spheres. These findings provide an effective way for design and construction of TiO$_2$-based photocatalysts for solar-light degradation of organic pollutant.

1. Introduction
Titanium dioxide (TiO$_2$) nanoparticles have been attracted great attention due to the multifunctional properties of high oxidation activity, good chemical stability, non-toxic, low cost and easy manufacture [1-2]. Therefore, TiO$_2$, as a functional semiconductor material, is widely applied in numerous fields, such as solar cells, air purification, self-cleaning coatings, pigments, and water or gas treatment [3-5]. Particularly, the photocatalytic properties of TiO$_2$ have been extensively studied since discovered by Fujishima and Honda in 1972. However, pure TiO$_2$ nanomaterials always suffer from narrowly adsorbed wavelength (ultraviolet light) due to the wide bandgap (3.2 eV for anatase TiO$_2$), resulting in less than 10% of the utilization rate of solar energy [6]. In addition, the high recombination rate of electron-hole (e$^-$-h$^+$) pairs generated by photoexcitation restricts the photon yield of TiO$_2$ and greatly prevents the practical use.

In order to solve these problems, attempts have been made to modify TiO$_2$ to tune the spectral absorption range and reduce the recombination of photogenerated electron-hole pairs. Currently,
researchers mainly modify TiO$_2$ by noble metal doping, ion doping, and organic surface modification [7-10]. Among them, combining noble metal with TiO$_2$ has been attracted increasing attention [11]. Since this strategy cannot only significantly increase the separation rate of the electron-hole pairs but also enhance the electron transfer rate, thereby improving the photocatalytic efficiency [12].

Au nanoparticles (Au NPs) have been considered as an effective additive for surface modification in photocatalysis due to the high catalytic nature and transformable plasmon resonance properties. By adjusting the particle size, tunable light absorption can be achieved. Au-sensitized heterogeneous catalysts have been successfully applied in photovoltaic related fields, such as water splitting, degradation of organic contaminant, and conversion of organic compounds [13-15]. The types of the surface modification are diverse, including NPs surface doping, core-shell structure, and yolk-shell structure. In these methods, Au@TiO$_2$ yolk-shell catalysts were explored by several groups [16-17] and correspondingly high photocatalytic efficiency is obtained. The yolk-shell structure is a unique core-shell structure of the core@void@shell. It does not only increase the surface area of the TiO$_2$ shell, but also promotes electron consumption. Due to the unique and movable core and adjustable cavity structure, a series of unique features, such as low density, large space, large surface area, good loading capacity and versatility can be obtained. However, low-cost, general high-yield, and reproducible methods are still challenging to synthesize the yolk-shell structures with controlled size, composition, and shape.

In this study, we develop an effective synthetic approach to prepare Au@TiO$_2$ yolk-shell (Au@TiO$_2$-YS) structures using silica as a template with tunable TiO$_2$ shell thickness. It has the following characteristics: (1) a movable core that provides more active sites to sufficient contact with the reactant molecules; (2) the outer mesoporous shell protects Au NPs from agglomerating and corrosion by the reaction solution; (3) the synergy between the Au core and the TiO$_2$ shell reduces the recombination of electron-hole pairs, which strongly improves the photocatalytic efficiency. The morphology, composition, and optical properties of the products are characterized by advanced techniques such as TEM, XRD, and UV-vis spectroscopy, respectively. Finally, the photocatalytic properties of the product are tested by degrading methylene blue (MB) under simulated solar light irradiation.

2. Experimental section

2.1. Materials

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$·3H$_2$O, >99.9%), L-ascorbic acid (AA, 99%), sodium borohydride (NaBH$_4$, 99%), trisodium citrate (Na$_3$C$_6$H$_5$O$_7$, 99%), poly(vinylpyrrolidone) (PVP, 99%) were purchased from Sigma-Aldrich, respectively. Potassium iodide (KI, 99%) was purchased from Macklin. Tetrabutyl titanate (TBOT, ≥98.0%), tetraethyl orthosilicate (TEOS, 98%), hydroxy-propyl cellulose (HPC) were purchased from Sinopharm Chemical Reagent Limited Corporation. High purity water (18.25 M Ω·cm) was used in the whole experimental processes. All chemicals were obtained from commercial suppliers and used without further purification.

2.2. Synthesis of Au nanosphere particles

A two-step method was used to synthesize Au NPs, including (1) the preparation of seeds and (2) seed growth. 500 μl of 5 mM HAuCl$_4$ and 500 μl of 5 mM trisodium citrate were added to 19 ml of ultra-pure water. After mixing, 600 μl of fresh 0.1 M NaBH$_4$ was injected into the 20 ml of the mixture under vigorous stirring. The seed solution was stirred at room temperature for 2 hours for further use.

40 ml of 5 mM HAuCl$_4$ solution, 10 ml of 5%wt PVP, 4 ml of 0.2 M KI solution and 4 ml of 0.1M L-ascorbic acid solution were mixed with 142 ml of H$_2$O under vigorous stirring. Finally, a certain amount (40-1000 μl) of Au seed solution was added to the above growth solution. The resultant mixture was stirred for 30 min and aged for 12 hours at 30 °C.
2.3. Synthesis of Au@TiO$_2$-YS structures

A three-step method was adopted to synthesize Au@TiO$_2$-YS structures: (1) SiO$_2$ coating; (2) TiO$_2$ coating; (3) and SiO$_2$ etching and calcination. Firstly, the as-prepared Au suspension was mixed with 3.3 ml of ultrapure water, 23 ml of ethanol, 0.86 ml of tetraethyl orthosilicate (TEOS) and 0.62 ml of 28% ammonia solution. The mixture was stirred for 8h at room temperature to form Au@SiO$_2$ core-shell nanostructures, then collected by centrifugation and washed three times with ethanol.

The Au@SiO$_2$ nanocomposites were redispersed in a mixture composed of HPC (0.1 g), ethanol (20 ml), and ultrapure water (0.1 ml). After 30 min stirring, an ethanol solution of tetrabutyl titanate (TBOT, 1 ml in 5 ml of ethanol) was slowly injected into the mixture within 15 min. Afterward, the mixture was heated to 85 °C with stirring for 120 minutes under refluxing conditions. The precipitates contained Au@SiO$_2$-YS nanocomposites were collected using centrifugation, washed three times with ethanol.

Finally, the above Au@SiO$_2$-TiO$_2$ nanocomposites were dispersed in 20 ml of water. 1 ml of 2.5 M NaOH solution was added to the above-mentioned Au@SiO$_2$@TiO$_2$ suspension. After etching for 6 h, the Au@TiO$_2$ yolk-shell structure precursors were finally formed. After centrifugation and washed five times with ultrapure water and ethanol, the above Au@TiO$_2$ yolk-shell structure precursors were calcined in the air at 550 °C for 2 h to remove all organic compounds and crystallize the amorphous TiO$_2$.

2.4. Characterizations

TEM was performed on a JEOL JEM 2100F electron microscope operating at 200 kV to observe the composite morphologies. The compositions of the products were employed using Philips X’pert Multipurpose X-ray Diffraction System (MPD) equipped with graphite monochromatized Cu-Kα radiation (λ = 1.54 Å). UV-vis absorption spectra were recorded using a Shimadzu UV-2600 UV-vis spectrophotometer (Varian) with a 1 cm quartz cell.

2.5. Measurement of photocatalysis

The photocatalytic performances of the as-synthesized catalysts were measured by the photo degradation of MB under simulated solar light irradiation. A 300 W Xenon lamp (PLS-SXE300C) equipped with AM 1.5G total reflection filters was used to obtain simulated solar light to trigger the photocatalytic reaction. The lamp was placed above 15 cm away from the reactant solution meniscus and the luminance of the light source over the reactant solution was 0.7 W cm$^{-2}$. 20 mg of the as-prepared nanocomposites were added to 250 ml of 30 ppm MB solution and then magnetically stirred for 30 min in the dark to reach the adsorption-desorption equilibrium of the organic dye with the catalyst. 3 ml of the reaction solution was sampled at intervals of 15 min. The suspension was analyzed by recording the variations of the maximum (664 nm) absorbance of MB solution using a Shimadzu UV-2600 UV-vis spectrophotometer. The degradation efficiency of MB in the sample can be calculated by the following formula:

$$\text{Degradation efficiency} = \frac{C}{C_0} \times 100\%$$

Where $C_0$ is the initial MB absorbance at 664 nm and $C$ is the absorbance in the sample taken at different intervals. The reaction rate ($k$) could be estimated as a linear relationship between $\ln(C_0/C)$ and time ($t$):

$$kt = \ln(C_0/C)$$

3. Results and discussion

3.1. Transmission electron microscopic analysis

Figure 1 shows the TEM images of Au NPs with different sizes and the corresponding yolk-shell structures. The TEM images of Au NPs are shown in Figure 1 (a-c), revealing that the Au NPs are of uniform particle size with diameters of 100, 50, and 30 nm, respectively. Figure 1 (d-f) display the
typical TEM images of the Au@TiO$_2$-YS structures with the Au core sizes of 100, 50, and 30 nm (denoted as YS-100, YS-50, and YS-30), respectively. The thickness of the TiO$_2$ hollow shell is about 45 nm and the cavity size is approximately 255 nm.

![Figure 1](image1.png)

**Figure 1.** TEM images of Au NPs with different sizes and the corresponding yolk-shell structures. (a) 100 nm Au NPs, (b) 50 nm Au NPs, (c) 30 nm Au NPs, (d) YS-100, (e) YS-50, (f) YS-30.

3.2. Composition analysis

The XRD patterns of the as-synthesized Au@TiO$_2$-YS structures (red line) are shown in Figure 2. It can be seen that the peak centered at 25.2º can be indexed to anatase TiO$_2$ (101), while the diffraction peaks at 2θ = 38.3º, 44.6º, 64.7º, 77.8º, and 81.84º, can be assigned to (111), (200), (220), (311) and (222) plans of Au NPs. In comparison, the TiO$_2$ hollow sphere (TiO$_2$-HS) structures are also prepared and the XRD pattern is shown in this figure (black line). It can be seen that the XRD pattern of TiO$_2$-HS structures displays a major peak (101) at 2θ = 25.2º, which is consistent with the diffraction peaks of anatase TiO$_2$. For Au@TiO$_2$-YS structures, no other peaks associated with impurities are observed, which indicates the preparation of high purity products.

![Figure 2](image2.png)

**Figure 2.** XRD of TiO$_2$-HS and Au@TiO$_2$-YS.

3.3. Optical property analysis

UV–vis absorption spectra of TiO$_2$-HS structures and Au@TiO$_2$-YS structures with different sizes of Au cores are shown in Figure 3. The absorption peak of TiO$_2$-HS structures is centered at 286.5 nm. Compared with the TiO$_2$-HS structures, an intense UV absorption band in Au@TiO$_2$-YS structures
shows a small red-shifts (from 292.5 nm for YS-30, 321.5 nm for YS-50 to 298.5 nm for YS-100), which is ascribed to electrons promotion of TiO$_2$ from the valence band to the conduction band and SPR of Au NPs [18]. In addition, absorption peaks corresponding to Au NPs (with 575 nm for YS-30, 588.5 nm for YS-50) appear. However, the absorption peak corresponding to Au NPs for YS-100 is extremely weak, perhaps attributed to the inhomogeneous polarization of the particle in the electromagnetic field and associated retardation as well as multiple excitation effects to confine the free electrons within the metal core [19-20]. In any case, due to the presence of Au NPs, the absorption peak of TiO$_2$ has been modified that enlarges the spectral absorption range.

Figure 3. UV-visible absorption spectra of TiO$_2$-HS and Au@TiO$_2$-YS.

3.4. Photocatalytic activity
The photocatalytic properties of Au@TiO$_2$-YS structures are evaluated by photo degradation of MB under simulated solar light irradiation. MB solution with the photocatalyst was stirred in dark conditions for 30 minutes to achieve the absorption-desorption equilibrium of MB on the sample surfaces. Figure 4a shows the photo degradation efficiencies of MB with different photocatalysts under simulated solar light irradiation. In comparison, the photocatalytic activity of as-synthesized TiO$_2$-HS structures is measured under the same conditions. It can be seen that the photocatalytic performances of the Au@TiO$_2$-YS structures are superior to that of the TiO$_2$-HS structures. The as-prepared TiO$_2$-HS structures show only 46.53 % of degradation efficiency in 120 min, while YS structures exhibit higher degradation rates. The best degradation rate (57.59% in 120 min) can be observed from the YS-50. Figure 4b displays the reaction rate constant (k) as a function of light exposure time. And the rate constants (the slopes of the profit lines) of the degradation reaction for the catalysts (YS-100, YS-50, and YS-30) are 0.00579, 0.00704 and 0.00656 min$^{-1}$, respectively. In comparison, the rate constant of the as-prepared TiO$_2$-HS structures is 0.00521 min$^{-1}$. It can be found that YS-50 show highest kinetic constant, which is 1.35 times higher than that of pure TiO$_2$-HS structures.

The noble metal core plays an important role in the photocatalytic properties of the semiconductor by changing the distribution of electrons. The Fermi levels of Au and TiO$_2$ reach equilibrium when the yolk-shell structures are formed. Due to the high work function of Au (5.1 eV), the photo-generated electrons can transfer from the conduction band of TiO$_2$ to Au, resulting in the formation of the Schottky barrier and band bending. Thus, more holes can be kept on the TiO$_2$ shell and the recombination rate can be effectively decreased. In addition, compared to core-shell structures, the
yolk-shell structure can provide more reaction sites due to the presence of the inner and outer surface. Based on these two factors, the yolk-shell structure can strongly enhance the photocatalytic activities [21-22].

![Figure 4](image)

**Figure 4.** (a) Photocatalytic efficiency of different photocatalysts under simulated sunlight irradiation; (b) Apparent rate constant of different photocatalysts under simulated sunlight irradiation.

4. Conclusions

In summary, the Au@TiO$_2$-YS structures are synthesized by a facile method with tunable TiO$_2$ shell thickness, the cavity diameter, and Au core size. The yolk-shell structures show tunable absorption bands based on different Au core sizes. Moreover, Au@TiO$_2$-YS structures exhibit higher photocatalytic activities toward MB under solar light irradiation compared to the as-synthesized TiO$_2$-HS structures. The YS-50 show highest kinetic constant (0.00704 min$^{-1}$), which is 1.35 times higher than that of TiO$_2$-HS structures (0.00521 min$^{-1}$). The enhanced mechanism can be attributed to the increased reaction sites on the inner and outer surface of the TiO$_2$ hollow shell and the formation of the Schottky barrier at the interface of Au and TiO$_2$. The novel synthesis strategy can be beneficial for the design of TiO$_2$-based photocatalysts.

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References

[1] Xiang G, Wu D and He J 2011 Chem. Commun. 47 11456-11458
[2] Yu H, Shang L, Bian T, et al 2016 Adv. Mater. 28 5140-5140
[3] Primo A, Marino T, Corma A, et al 2011 J. Am. Chem. Soc. 133 6930-6933
[4] Tian Y, Tatsuma T 2005 J. Am. Chem. Soc. 127 7632-7637
[5] Lu J, Zhang P, Li A, et al 2013 Chem Commun. 49 5817-5819
[6] Lee J, Mubeen S, Ji X, et al 2012 Nano Lett. 12 5014-5019
[7] Tahir M, Amin N A S 2013 Appl. Catal. A: Gen. 467 483-496
[8] Anandan S, Ikuma Y, Niwa K 2010 Solid State Phenom. 162 239-260
[9] Rajh T, Nedeljkovic J M, Chen L X, et al 1999 J. Phys. Chem. B. 103 U321
[10] Michaelis A, Kudelka S, Schultzje JW 1996 Mrs Proc. 451
[11] Chen X, Liu Li, Yu P Y, et al 2011 Science 331 746-750
[12] Chen J T, Hsu C S 2011 Polym. Chem. 2 2707-2722
[13] Primo A, Corma A, García H 2011 Phys. Chem. Chem. Phys. 13 886
[14] Pu Y C, Wang G, Chang K D, et al 2013 Nano Lett. 13 3817
[15] Kochuveedu S T, Jang Y H, Dong H K 2014 *Chem. Soc. Rev.* **45** 8467-8493
[16] Bian Z, Zhu J, Cao F, et al 2009 *Chem Commun.* **25** 3789-3791
[17] Lee I, Joo J B, Yin Y, et al 2011 *Angew. Chem. Int. Ed.* **50** 10208-11
[18] Zhou N, Wang X, Hu Z 2013 *Chem. Lett.* **42** 1079-1081.
[19] And S L, Elsayed M A 1999 *J. phys. chem. B.* **103** 8410-8426
[20] Tom R T, Sreekumaran Nair A, Singh N, et al 2003 *Langmuir.* **19** 3439-3445
[21] Mcfarland E W, Tang J 2003 *Nature.* **421** 616-618
[22] Du J, Qi J, Wang D, et al 2012 *Energy Environ. Sci.* **5** 6914-6918