

可移动金核的二氧化钛空心球合成及光催化性质

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Hollow Spheres with Moveable Au Nanoparticles in Core and Titanium Oxide Shell: Synthesis and Photocatalytic Activity

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Abstract: Uniform hollow Au@TiO₂ core shell spheres with moveable Au nanoparticles were synthesized based on templating against Au@carbon spheres. The diameter of the shell of the Au@TiO₂ spheres could be controlled by adjusting the Ti(OC₄H₉)₄ hydrolyzing reaction time or the ratio of Ti(OC₄H₉)₄ to Au@carbon spheres, and the shell thickness of the core-shell spheres can be varied from 25 nm to 40 nm. As prepared hollow Au@TiO₂ core-shell spheres display enhanced photocatalytic activity in the initial stage of photocatalytic degradation of methylene blue compared with pure hollow TiO₂ spheres and the commercial photocatalyst TiO₂(P-25).

Key words: core-shell; titanium oxide; photocatalytic activity; hollow sphere

In recent years the preparation of core-shell composite particles and hollow spheres has attracted much interest due to the wide variety of optical, electrical and photochemical properties, low dielectric constant materials, controlled drug release, or catalyst systems^[1-9]. Because semiconductor-metal composites have been suggested for a wide variety of applications, a lot of work have been devoted to enhance the efficiency of photocatalytic activity by deposition of metal on

semiconductors^[10]. Among such nanocomposite structures, the Au/TiO₂ core-shell structure has attracted attention^[11,12] to various applications of TiO₂ and the inert nature in the bulk state of the gold. However, when gold is very highly dispersed on supports, it exhibits a surprisingly high activity for several reactions, both in the liquid and in the gas phase. Moreover, Au/TiO₂ core-shell nanostructures may lead to enhanced optical and catalytic properties because of

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the fabrication of a gold core and TiO₂ shell as well as new chemical activities owing to the electron transfer between photo excited TiO₂ and gold^[13]. There has been some work on the synthesis and functionality of Au/TiO₂ core-shell nanostructures. For instance, Rodriguez et al.^[14] reported the adsorption and reaction of SO₂ on TiO₂/Au. Baiker and co-worker successfully applied gold nanoparticles as catalysts to improve a series of metal oxide catalytic activity^[15]. Gedankens group^[12] synthesized TiO₂@carbon core-shell composite nanoparticles and evaluated their photocatalytic activities. Recently, our group has synthesized hollow sub-microspheres with movable Au nanoparticles and excessive Pt nanoparticles in core and silica as shell^[16]. To the best of our knowledge, synthesis of hollow core-shell spheres with moveable noble metal particle as core and a functional material as shell has been rarely studied.

In this paper, Au@TiO₂ hollow nanospheres with moveable Au nanoparticles were synthesized by coating TiO₂ on Au@carbon core-shell spheres and then by removal of the carbonaceous matter via calcination. The photocatalytic activity of this kind of Au@TiO₂ hollow spheres with moveable Au nanoparticle inside was compared with the commercial P-25 and pure TiO₂ hollow spheres.

1 Experimental

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

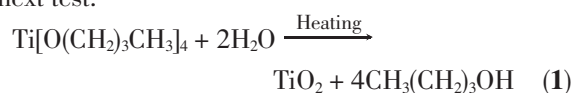
1.1 Synthesis of Au/carbon spheres under hydrothermal conditions

Nearly monodisperse Au@carbon spheres were prepared as described previously via hydrothermal method^[17,18]. In a typical synthesis, 2.5 g glucose was dissolved in 40 mL deionized water to form a clear solution under vigorous stirring, and then 1.2 mL HAuCl₄ (10 mmol·L⁻¹) was added to this solution dropwise with vigorous stirring for about 10 minutes to form a canary solution. Then all solutions were transferred into a 50 mL Teflon-sealed autoclave and maintained at 160 °C for 20 h. Through altering the ratio of HAuCl₄ to glucose, it

is possible to control the size of Au particles in the core, which could subsequently affect the photocatalytic activities of the final hollow spheres, each of which has a moveable Au core and nanoporous TiO₂ as shell.

1.2 Synthesis of hollow spheres with moveable Au nanoparticles core/nanoporous TiO₂ shell

The black products were isolated by centrifugation, cleaned by three cycles of centrifugation, washing with distilled water and alcohol respectively, and then dried at 80 °C for more than 4 h to form brown powders. About 0.1 g fresh prepared Au/carbon core-shell spheres were dispersed in 25 mL glycol with the aid of ultrasonication to form a homogeneous suspension, and then 500 μL 0.1 mmol·L⁻¹ Ti(OC₄H₉)₄ Tetrabutyltitanate was added to the suspension under continuous ultrasonication for about 0.5 h. Subsequently all solutions were subject to reflux at 140 °C under continuous stirring for about 8 h. In the middle of reflux process, 1.2 mL nitrate acid (0.1 mol·L⁻¹) was slowly dripped down the solution, to promote the Ti(OC₄H₉)₄ hydrolyzing according to equation 1. And then the products were calcined at 600 °C from the room temperature with a heating rate of 1 °C·min⁻¹ to remove the carbon shell. Thereafter the final products were collected through three cycles of centrifugation, washing and redispersion in alcohol and in water before the next test.



1.3 Characterization of photocatalytic activity

Newly prepared 20 mg·L⁻¹ methylene blue solution at pH value of 6.2 mainly contains azo-type structure, showing drastic and stronger photoabsorption in the range of wavelengths from 550 to 700 nm (Fig.6a). The UV source is a 100 W Hg lamp (output mainly at 360 nm) that placed 20 cm on the top of the solution. The amount of all reaction agents was controlled to be identical except for special explanation. Three kinds of solutions contained 0.1 g TiO₂ hollow spheres, P-25 and Au@TiO₂ hollow spheres with movable Au dispersed in 50 mL methylene blue solution (1×10⁻⁷ mol·L⁻¹) were subjected to 100 mL vitreous round-bottom flasks under illumination of 100 W Hg lamp, respectively.

1.4 Characterization

The final products were examined by XRD, SEM, TEM, and EDS respectively. XRD analysis was performed on a Rigaku(Japan) D/max-rA X-ray diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation($\lambda=0.15418$ nm), high voltage: 40 kV, current: 30 mA, at a scanning rate of $0.05^\circ \cdot \text{s}^{-1}$ and in 2θ of $15^\circ \sim 70^\circ$. Transmission electron microscope(TEM) was performed on a Hitachi(Tokyo, Japan) H-800 transmission electron microscope(TEM) at an accelerating voltage of 200 kV, and high-resolution transmission electron microscope(HRTEM) (JEOL-2011) operated at an acceleration voltage of 200 kV. And the EDS was also characterized by high-resolution transmission electron microscope(HRTEM) (JEOL-2011) operated at an acceleration voltage of 200 kV. UV-Vis spectra were recorded on a Shimadzu UV-240 spectrophotometer at room temperature.

2 Results and Discussion

2.1 Characterization of the moveable Au nanoparticles core/nanoporous TiO_2 shell

Fig.1 shows a representative XRD pattern of the as-synthesized hollow nanospheres. The diffraction peaks unmarked can be indexed to a cubic body-centered tetragonal structured TiO_2 with cell constant $a=0.3782$ nm, which is in good agreement with the value in the literature(PDF No.841285). The diffraction peaks with marked asterisk can be indexed as a cubic face-centered structured for Au with cell constant $a=0.408$ nm(PDF No.040784).

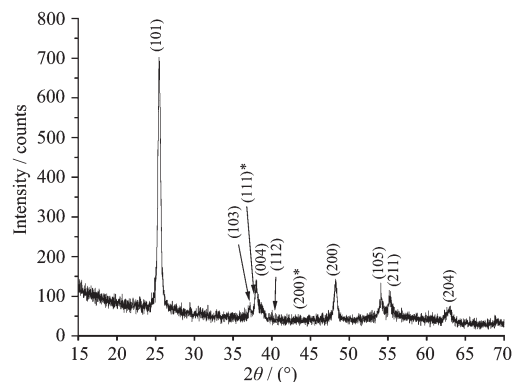


Fig.1 XRD pattern of Au@ TiO_2 hollow spheres with moveable Au nanoparticle core. asterisk (*) denotes the diffraction peaks of Au

The whole procedure was also characterized by transmission electron microscopy(TEM) (See Fig.2a-2f). Fig.2a,b show that the synthesized Au@C core-shell particles by hydrothermal process are with an average size of 350 nm and every individual carbon sphere contains a Au nanoparticle with a size of 30~40 nm at the center. Fig.2c,d show that Au@carbon core-shell particles coated with TiO_2 nanoparticles have an average size of 50 nm. Fig.2e,f clearly demonstrate that the hollow Au@ TiO_2 spheres with moveable gold nanoparticle cores can be obtained after carbon is removed. The strong contrast between the dark edge and flocculent center indicates that the particle is hollow and with porous structures on the shell. The obvious black dot in the interior is the speckle of Au nanoparticle, which is not in the center as before, indicating that the Au particle core becomes moveable after calcination.

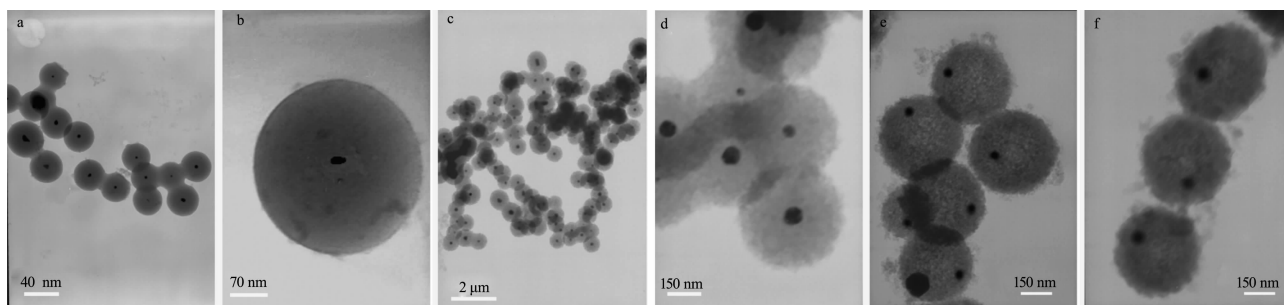


Fig.2 TEM images of (a) Au particles coated with carbon; (b) single Au@C sphere with the smooth surface; (c), (d) Au@C@ TiO_2 double shell structures and magnified image, showing the coarse surface; (e) and (f) Au@ TiO_2 hollow spheres after removal of carbon by calcination

Energy-dispersive X-ray analysis taken on the chosen plane area shown in Fig.3 clearly indicates that

the sample contains Au and Ti elements, indicating the black particle on the image indeed is encapsulated Au

nanoparticle. Scanning electron microscopy (SEM) images in Fig.4a,b show that the particles are indeed in a form of spherical shape and all the surface of the particles are rough and contain a lot of nanofiber-like particles, which are densely piled up to form the nanoporous surface structure.

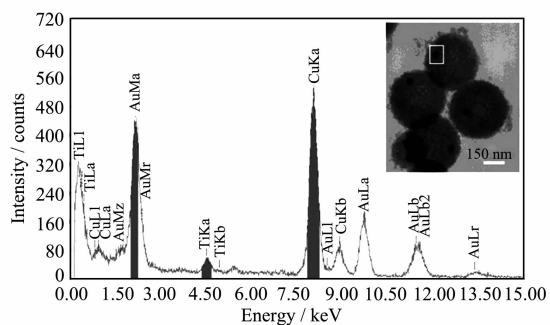


Fig.3 EDS spectra taken on the selected area as shown in insert.

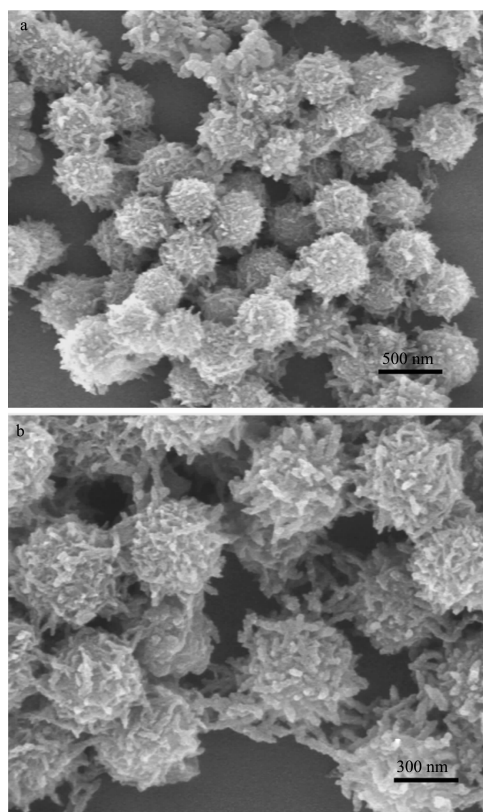
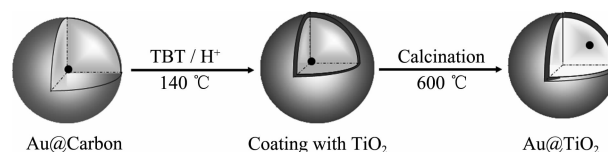


Fig.4 (a) SEM image of Au@TiO₂ hollow spheres and (b) a magnified image of Au@TiO₂

The Au@TiO₂ hollow spheres containing moveable Au nanoparticle can be prepared by a two-step process which can be schematically illustrated in Scheme 1. Similarly, pure TiO₂ hollow spheres without Au nanoparticles can be directly prepared by simply

coating TiO₂ on carbon spheres and then removing the carbonaceous matter by calcination as shown in Fig.5.



Scheme 1 Formation process of Au@TiO₂ hollow nanospheres, each of which has a movable Au nanoparticle core inside.

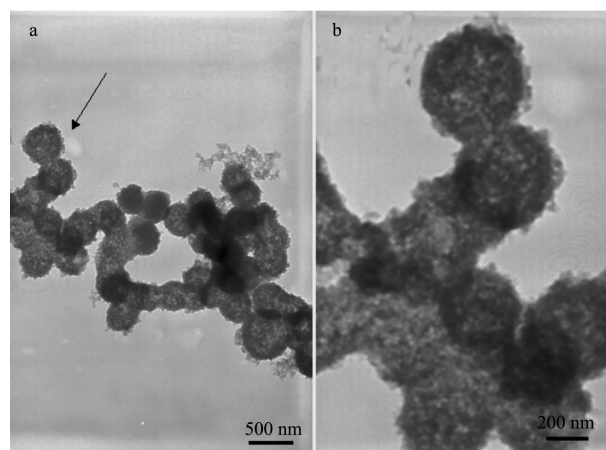
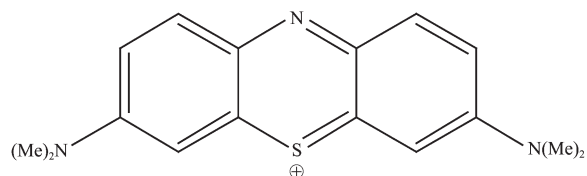


Fig.5 TEM images of (a) TiO₂ hollow spheres and (b) a magnified TiO₂ hollow spheres for areas indicated by the arrow.

2.2 Catalytic properties of Au@TiO₂ hollow spheres with moveable Au nanoparticles

In order to evaluate the photocatalytic activity of the moveable Au core/TiO₂ shell spheres, photocatalytic degradation rate of methylene blue has been measured. The results are shown in Fig.6. The methylene blue dye structure is shown in Scheme 2 below:

From Fig.6, it is obvious that Au@TiO₂ hollow spheres with moveable Au nanoparticles have shown better photocatalytic performance than that of the P-25 and the pure TiO₂ hollow spheres during the first three minutes (Fig.6a). However, after 3 minutes, the Au@TiO₂ hollow spheres with moveable Au nanoparticles show almost identical photocatalytic performance as that for



Scheme 2 Structure of methylene blue

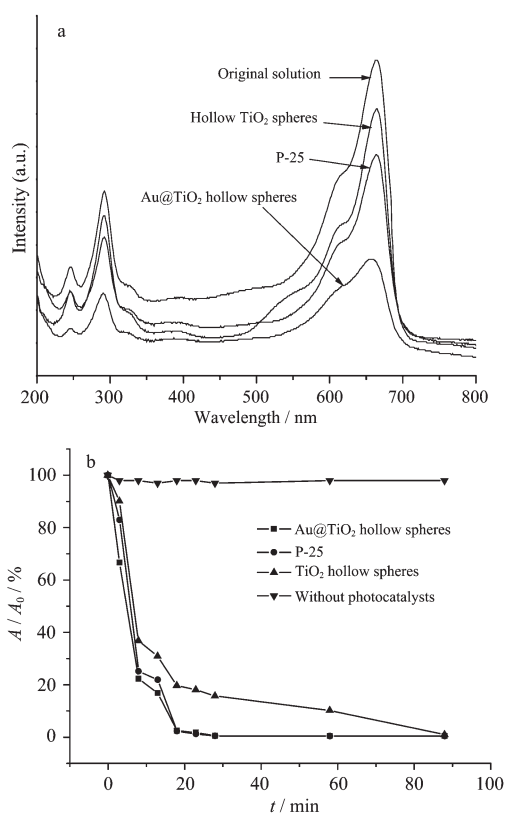


Fig.6 (a) UV-Vis absorption spectra of original mixed solution; P-25, hollow spheres and Au@TiO₂ hollow spheres irradiated after three minutes (b). Time dependent photocatalytic degradation rate of methylene blue in the absence of any photocatalyst, and in the presence of P-25, hollow TiO₂ spheres, Au@TiO₂ hollow spheres

the P-25, but still better photocatalytic ability than the pure hollow TiO₂ hollow spheres without gold encapsulation.

3 Conclusion

In summary, Au@TiO₂ hollow spheres with moveable Au nanoparticles in the core were synthesized by templating against Au@carbon core-shell sphere synthesized from hydrothermal process. The diameter of the shell of the Au@TiO₂ hollow spheres could be controlled by adjusting hydrolysis reaction time of Ti(OC₄H₉)₄, the concentration of Ti(OC₄H₉)₄ and the amount of the Au@carbon spheres. As-prepared Au@TiO₂ hollow spheres with moveable Au nanoparticles inside show enhanced performance in the initial stage of photocatalytic degradation of methylene blue compared

with pure hollow TiO₂ spheres and the commercial photocatalyst TiO₂ (P-25), however, after 3 minutes, the Au@TiO₂ hollow spheres with moveable Au nanoparticles could only show identical photocatalytic performance as that of P-25.

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