



# Controllable location of Au nanoparticles as cocatalyst onto TiO<sub>2</sub>@CeO<sub>2</sub> nanocomposite hollow spheres for enhancing photocatalytic activity



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## ABSTRACT

Visible-light-driven photocatalysis as a green technology has attracted a lot of attention due to its potential applications in environmental remediation. Although TiO<sub>2</sub> is the most popular photocatalyst, the lack of visible light utilization and a low efficiency of electron-hole separation should be overcome. Therefore, Au nanoparticles (NPs) as cocatalyst were controllably loaded between the double-shell or into CeO<sub>2</sub> shell (as photocatalyst and oxygen buffer) and then a novel visible-light-driven TiO<sub>2</sub>@CeO<sub>2</sub> nanocomposite was prepared, using functionalized polystyrene spheres, sol-gel, hydrothermal reaction, and calcination. The presence of TiO<sub>2</sub> shell, Au NPs and CeO<sub>2</sub> shell were confirmed by EDX and electron energy loss mapping analysis. Under visible-light irradiation, the photo-degradation rate constant *k* (min<sup>-1</sup>) was in the order of TiO<sub>2</sub>@Au@CeO<sub>2</sub> (0.026) > TiO<sub>2</sub>@CeO<sub>2</sub>/Au (0.021) > TiO<sub>2</sub>@CeO<sub>2</sub> (0.014) > CeO<sub>2</sub> (0.0091) > TiO<sub>2</sub> (0.0046) > P25 (0.0034). Compared with P25, TiO<sub>2</sub>@CeO<sub>2</sub>, and TiO<sub>2</sub>@CeO<sub>2</sub>/Au, the visible-light photocatalytic activity of TiO<sub>2</sub>@Au@CeO<sub>2</sub> for the photo-degradation of organic pollutant and photo-reduction of Cr(VI) were the highest. This result was attributed to the combination of TiO<sub>2</sub> and CeO<sub>2</sub>, the double-shelled and sandwiched nanostructure and the addition of Au NPs as electron trap site and surface plasmon resonance-sensitizer, which could reduce the recombination of the electron-hole and induce the visible light absorption. The major obstacle of heterogeneous photocatalysis could be resolved. The photo-degradation rate of 95% was achieved by TiO<sub>2</sub>@Au@CeO<sub>2</sub>, which exhibited an increase of 63% compared to Degussa P25 TiO<sub>2</sub>. The photo-degradation activity of TiO<sub>2</sub>@CeO<sub>2</sub>/Au was improved by Au NPs loaded on outer shell of TiO<sub>2</sub>@CeO<sub>2</sub>/Au but limited by their stability. This work confirmed the importance of controllable location of the noble metals as cocatalysts.

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## 1. Introduction

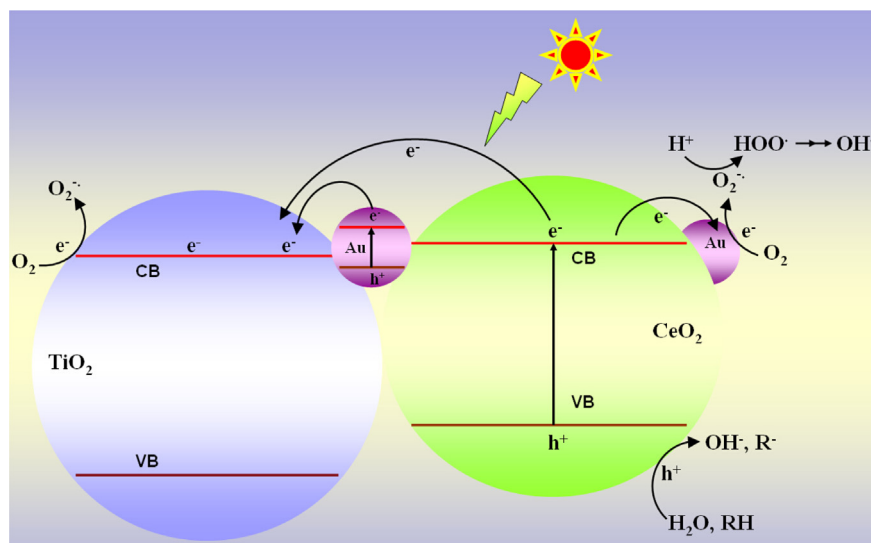
In recent years, photocatalytic degradation as an efficient and environment-friendly technology for organic pollutant removal has been attracted extensively attention [1–5]. Many metal-oxide photocatalysts have enabled great advances in the decomposition of pollutants under light irradiation [6–9]. Recently, it has been realized that the structure and morphology of the photocatalysts have significant effects on the photocatalytic activity [10–12]. As an efficient structure of metal oxide-based photocatalyst, hollow sphere has been used for its unique large surface area, low density, and efficient light-harvesting [13,14]. The surface plasmon resonance

(SPR) of Au nanoparticles (Au NPs) supported on semiconductors results in strong photo-absorption in the visible region which can be advantageous to improve photocatalytic activity [15]. Therefore, it is necessary to develop a new hollow sphere with supported Au NPs as a light-driven photocatalyst. However, the influence of Au NPs location site on the photocatalytic activity is unknown.

Among various inorganic oxide catalysts, CeO<sub>2</sub> has attracted extensive interest due to its high thermal stability, oxygen storage capacities, and easy conversion between Ce(III) and Ce(IV) oxidation states. Specifically, CeO<sub>2</sub> can act as an oxygen buffer by releasing/restoring oxygen, which plays an important role in many oxidation reactions [16–19]. As one of the most important metal oxides and semiconductors, titanium dioxide (TiO<sub>2</sub>), especially anatase TiO<sub>2</sub>, has been used for photocatalysis, lithium-ion batteries, and solar cells. [20–22]. After CeO<sub>2</sub>-doping, the light absorption property and photo-degradation performance of TiO<sub>2</sub> are improved. Therefore, TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites with various

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**Scheme 1.** Charge transfers in  $\text{TiO}_2@Au@CeO_2$  composites.

morphologies have been used for photocatalysis, including core-shelled spheroids [23,24], nanosphere arrays [25,26], nanofibers [27], films [28,29], and nanoparticles [30–33]. Coupling of the band-gap excitation of  $\text{TiO}_2$  (or  $\text{CeO}_2$ ) and the SPR of Au NPs in  $\text{Au}/\text{TiO}_2$  (or  $\text{Au}/\text{CeO}_2$ ) sample, solar light can be effectively utilized [34,35]. Furthermore, the structure of double-shelled hollow spheres can accelerate efficiently the separation and transfer of photon-induced electrons and holes as well as increase the efficiency of the photocatalysis process [15,36–39]. Therefore, hollow sphere for  $\text{TiO}_2@Au@CeO_2$  and  $\text{TiO}_2@CeO_2/Au$  nanocomposite is proposed by the paper, furthermore to discover the important of controllable location of Au NPs.

Using polystyrene spheres (PS) as sacrificial templates, the nanoparticles of  $\text{TiO}_2$ , Au and  $\text{CeO}_2$  are coated successively onto PS. The resulted  $\text{PS}@TiO_2@Au@CeO_2$  and  $\text{PS}@TiO_2@CeO_2/Au$  nanocomposites are calcined at elevated temperature, and then double-shelled  $\text{TiO}_2@Au@CeO_2$  and  $\text{TiO}_2@CeO_2/Au$  hollow spheres are obtained. As electron trap site and SPR-sensitizer, Au NPs in the  $\text{TiO}_2@Au@CeO_2$  or  $\text{TiO}_2@CeO_2/Au$  can reduce the recombination of the electron-hole separation. Moreover, the visible light absorption of  $\text{TiO}_2@Au@CeO_2$  and  $\text{TiO}_2@CeO_2/Au$  hollow spheres can be increased by the coexistence of Au NPs, and then the major obstacle of heterogeneous photocatalysis can be resolved. The work intensifies the fundamental of understanding the controllable location of noble metals as cocatalysts for enhancing photocatalytic activity (Scheme 1).

## 2. Experimental section

### 2.1. Reagents and chemicals

Tetrabutyl titanate (TBOT, 99%) was purchased from J&K Chemistry Co. Ltd. ( $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ , 99.8%) was purchased from Aladdin Chemistry Co. Ltd. G-glucose ( $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ , 99%), urea ( $\text{H}_2\text{NCONH}_2$ , 99%), sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ , 98%), trisodium citrate dihydrate ( $\text{C}_6\text{H}_{12}\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ , 99%), and ethanol ( $\text{C}_2\text{H}_6\text{O}$ , 99.7%) were purchased from Guangzhou Xilong Chemistry Technology Co. Ltd and used without additional purification. Tetrachloroauric (III) acid hydrate ( $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ , 99%), methyl acrylate ( $\text{C}_4\text{H}_6\text{O}_2$ , 98%) and styrene ( $\text{C}_8\text{H}_8$ , 99%) were purchased from Shanghai Sinopharm Chemistry Co. Ltd and used without additional purification. Distilled water was used in the catalyst preparation and subsequent catalytic tests.

### 2.2. Synthesis of $\text{CeO}_2$ nanoparticles

1 g of glucose and 0.22 g of urea were dissolved in 10 mL of deionized water to form a clear solution and 0.1 g of  $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$  was added to above solution. The mixture was transferred to Teflon-lined stainless steel autoclaves and heated to  $160^\circ\text{C}$  for 20 h. The resulting nanoparticles was washed three times with ethanol and dried in vacuum at  $60^\circ\text{C}$  for 6 h. Finally, heated with a rate of  $5^\circ\text{C}/\text{min}$  and maintained at  $600^\circ\text{C}$  (i.e., calcination temperature) for 6 h in static air. The  $\text{CeO}_2$  nanoparticles were finally obtained.

### 2.3. Synthesis of $\text{TiO}_2@CeO_2$ , $\text{TiO}_2@CeO_2/Au$ , and $\text{TiO}_2@Au@CeO_2$ hollow spheres

$\text{PS}@TiO_2$  nanocomposite (0.05 g) was added into the ethanol solution (50 mL) under vigorous stirring for 15 min, and the mixture was named as solution A. Glucose (1 g) and urea (0.22 g) were dissolved in deionized water (10 mL) and  $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$  (0.1 g) was added to above solution. The resulting mixture was kept for 15 min under stirring and the mixture was named as solution B. The solution B was added drop by drop into the solution A under vigorous stirring for 15 min. Then, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to  $160^\circ\text{C}$  for 20 h. The resulting nanoparticles was washed three times with ethanol and dried in vacuum at  $60^\circ\text{C}$  for 6 h. Finally, heated with a rate of  $5^\circ\text{C}/\text{min}$  and maintained at  $600^\circ\text{C}$  (i.e., calcination temperature) for 6 h in static air. The  $\text{TiO}_2@CeO_2$  hollow spheres were finally obtained.

For comparison, the  $\text{TiO}_2@CeO_2/Au$  and  $\text{TiO}_2@Au@CeO_2$  hollow spheres were also prepared by the similar experimental procedure. The difference was the addition of the prepared Au NPs (5 nm, 0.20 mM, 3 mL) under stirring for 2 h, but the adding sequences were different (see Scheme 2). Au NPs were added into solution B and mixed with  $\text{CeN}_3\text{O}_9$  for  $\text{TiO}_2@CeO_2/Au$ . After Au NPs were adsorbed onto  $\text{PS}@TiO_2$ ,  $\text{CeN}_3\text{O}_9$  in the solution B was added for  $\text{TiO}_2@Au@CeO_2$ .

### 2.4. Characterization

The morphology of nanocomposite samples was observed on S-4800 scanning electron microscopy (SEM) instrument (Hitachi, Japan). Transmission electron microscopy (TEM) images were recorded on JEM-2100 (HR) microscope (JEOL, Japan) operated at

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