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# Enhanced photocatalytic activity of hierarchical flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures



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## ABSTRACT

Preparation of flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures as photocatalysts was successfully obtained by a simple two-step solvothermal/hydrothermal method. The as-prepared sample consisted of the oriented aggregation of small CeO<sub>2</sub> nanoparticles supported on the self-assembled nanorods of hierarchical flower-like TiO<sub>2</sub>. Compared with pure CeO<sub>2</sub>, pure TiO<sub>2</sub> and commercial P25, the flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures exhibited markedly enhanced photocatalytic activity in the degradation of Rhodamine B (RhB) under UV light irradiation. The enhanced photocatalytic activity of flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures could be attributed to the improvement of charge separation derived from the coupling effect of TiO<sub>2</sub> and CeO<sub>2</sub> heterostructures.

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## 1. Introduction

The application of heterogeneous semiconductor photocatalysts in water treatment and environmental remediation has recently attracted extensive attention due to their effective utilization of solar energy, which is a natural abundant energy source [1]. Of all semiconductor photocatalysts employed in water treatment, anatase TiO<sub>2</sub>, with the band energy of 3.2 eV is found to exhibit a desirable photocatalytic activity under UV light irradiation. However, pure TiO<sub>2</sub> has a wide band gap and only exhibits photocatalytic activities in the UV range. Thus, designing coupled semiconductor heterojunction with matching band potentials and molecular architecture of semiconductors have been proved as the effective approaches to enhance photocatalytic activity. Nowadays, it shows that TiO<sub>2</sub> coupled with other materials, such as ZnO [2], ZnSnO<sub>3</sub> [3] and CeO<sub>2</sub> [4] and Cu<sub>2</sub>O [5], can enhanced the photocatalytic activity via improving the charge separation or photo-generated charges and extending the photoresponse region. Among the composite with TiO<sub>2</sub> as the major component, CeO<sub>2</sub> has been shown to be a promising candidate owing to the following reasons. Firstly, CeO<sub>2</sub>, due to its suitable band gap edge positions, has been successfully used in a variety of photocatalytic processes such as detoxification and hydrogen production [6,7]. Second, The redox couple of Ce<sup>3+</sup>/Ce<sup>4+</sup> and the high capacity to

store/release oxygen under oxidizing/reducing conditions of CeO<sub>2</sub> have gained additional importance in the application of heterogeneous catalysis [8]. As one type of promising architecture, hierarchical structures with a large surface area and abundant active sites have been investigated for a long time. For example, Huang et al. [9] reported that three-dimensional CeO<sub>2</sub>/TiO<sub>2</sub> nanowire was prepared by combining hydrothermal method and anodic electrodeposition. Liu et al. [10] reported that hierarchical hollow CeO<sub>2</sub>/TiO<sub>2</sub> nanocube was synthesized by a facile generic strategy. To our best knowledge, reports on the oriented aggregation of small CeO<sub>2</sub> nanoparticles assembled on the low-dimensional building blocks of hierarchical flower-like TiO<sub>2</sub> structures were quite few.

In this paper, we report a facile approach to prepare flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures. The CeO<sub>2</sub> nanoparticles oriented aggregation along the self-assembly nanorods of hierarchical TiO<sub>2</sub> structures can be clearly observed. The flower-like CeO<sub>2</sub>/TiO<sub>2</sub> photocatalyst showed high activity on the degradation of RhB. Many other heteroarchitectures materials with different morphology could be prepared by using this kind of environmentally friendly, cost-effective synthesis route.

## 2. Experimental

The flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures were successfully obtained by a simple two-step solvothermal/hydrothermal method. The detailed synthesis procedures are available in the

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supporting information.

### 3. Results and discussion

Fig. 1a depicted the XRD pattern of pure TiO<sub>2</sub>, pure CeO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures. The synthesized samples displayed composite materials corresponding to tetragonal anatase TiO<sub>2</sub> (JCPDS no. 21-1272) and a face centered cubic (FCC) fluorite structure (JCPDS no. 43-1002). The weak diffraction peaks of CeO<sub>2</sub>/TiO<sub>2</sub> heterostructure indicated that the crystallinities were reduced in comparison with single phase TiO<sub>2</sub>. This result may be attributed to lattice distortion induced by interfacial strain because of the different lattice parameters between CeO<sub>2</sub> and TiO<sub>2</sub> [11]. The defects may affect photocatalysis by effective capture of the photoexcited electrons, and thus inhibit the recombination of photoexcited electrons and holes. Fig. 1b showed the Raman spectra of the samples. The results showed the characteristic signals for the tetragonal phase of TiO<sub>2</sub> (anatase) around 142–143 cm<sup>-1</sup>, 196–198 cm<sup>-1</sup>, 395–396 cm<sup>-1</sup>, 514–515 cm<sup>-1</sup>, and 638–639 cm<sup>-1</sup> [12]. The band at 463 cm<sup>-1</sup> corresponds to the cubic phase of CeO<sub>2</sub> fluorite type phase [13].

Fig. 2a and b showed the SEM images of pure TiO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures, respectively. It was obvious that the CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures maintain the morphology of prepared TiO<sub>2</sub> except for a little shrinkage in size. The surface of the synthesized powder consisted of nano-size small particles. But the nanoparticles were clustered together, making it difficult to determine the size of individual nanoparticle. The flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures appeared hierarchical nanostructures self-assembled by nanorods, as shown in Fig. 2b. The nanorods were about 50 nm in width and 150 nm in length (Fig. 2c). The CeO<sub>2</sub> nanoparticles oriented aggregation along the self-assembly nanorods of TiO<sub>2</sub> can be clearly observed in Fig. 2c. The flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures was also characterized by HRTEM, as illustrated in Fig. 2d. As shown in Fig. 2d, the detected lattice spacing of 0.357 nm and 0.304 nm agreed with TiO<sub>2</sub> (101) and CeO<sub>2</sub> (111) plane spacing, respectively. The result was in total agreement with the observed XRD analysis.

The UV–vis spectra of pure CeO<sub>2</sub>, pure TiO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> were shown in Fig. 3a. The band gap ( $E_g$ ) of the synthesized photocatalyst was calculated by the following equation:  $E_g = 1240/\lambda_{\max}$ , where  $\lambda$  is the wavelength maximum. It was observed that pure TiO<sub>2</sub>, pure CeO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> showed a band gap edge at the wavelength of about 412 nm, 453 nm and 473 nm, respectively. Hence, the band gap of the pure TiO<sub>2</sub>, pure CeO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> was calculated to be 3.01 eV, 2.74 eV, and 2.62 eV. Fig. 3b showed the degradation curves of RhB on the commercial P25, pure CeO<sub>2</sub>, pure TiO<sub>2</sub>, the

mixture of CeO<sub>2</sub> and TiO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures. The results proved that the flower-like CeO<sub>2</sub>/TiO<sub>2</sub> showed enhanced photocatalytic activities in comparison with pure TiO<sub>2</sub>, pure CeO<sub>2</sub>, the mixture of CeO<sub>2</sub> and TiO<sub>2</sub> and commercial P25. The enhanced photocatalytic performance of CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures might be attributed to following factors. Firstly, the hierarchical structures make multiple reflections of light, allowing more efficient use of the light source. Moreover, the heterojunction effect can lead to enhanced charge separation and interfacial charge transfer efficiency. All the factors contributed greatly to the improved UV light catalytic activity.

The stability of photocatalyst is important for practical application. As shown in Fig. 3c, there was no obvious change in the photocatalytic activity after three cycles of photodegradation, implying the good stability of CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures.

Based on the above measurements and analyses, a possible mechanism for charge transfer and photocatalysis process can be proposed. The band edge positions of the conduction band and valence band of a semiconductor can be determined using the equation:  $E_{CB} = X - E_e - 0.5E_g$ , where X is the absolute electronegativity of the semiconductor (X is 5.81 eV and 5.56 eV for TiO<sub>2</sub> and CeO<sub>2</sub>, respectively) [14, 15].  $E_e$  is the energy of free electrons on the hydrogen scale (4.5 eV) and  $E_g$  is the band gap of the semiconductor. According to Fig. 3a, the band gap energies of CeO<sub>2</sub> and TiO<sub>2</sub> observed in this study were 2.74 eV and 3.01 eV, respectively, and the corresponding  $E_{CB}$  values were estimated to be -0.31 eV and -0.2 eV. As illustrated in Fig. 4, both TiO<sub>2</sub> and CeO<sub>2</sub> can be activated under UV light, which result in the form of photogenerated holes in the valence gap (VB) and electrons in their conduction band (CB). The activated electrons at CB gap of CeO<sub>2</sub> were transferred to the CB of TiO<sub>2</sub> through the interface, because the  $E_{CB}$  of TiO<sub>2</sub> (-0.2 eV) was more positive than that of CeO<sub>2</sub> (-0.31 eV). Similarly, VB holes (TiO<sub>2</sub>) could inject to the VB of CeO<sub>2</sub> by the control of the interface. It is more beneficial to accelerate the separation of photoinduced electron-hole pairs in TiO<sub>2</sub> and CeO<sub>2</sub>, resulting in the improvement of photocatalysis under UV irradiation.

### 4. Conclusions

In summary, flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures were synthesized by a simple two-step solvothermal/hydrothermal method. The flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures exhibited excellent photocatalytic activity under UV light irradiation, which was ascribed to the improvement of the separation for the photo-generated electron-hole pairs.

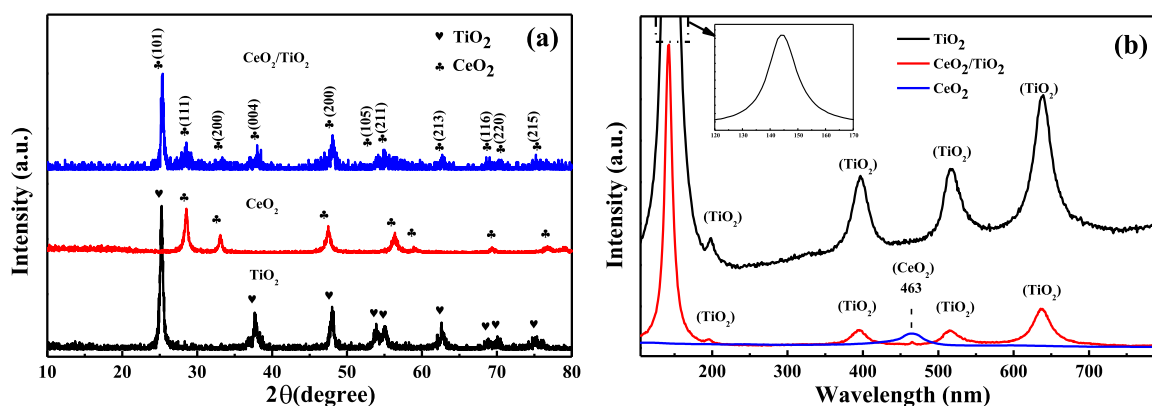


Fig. 1. XRD pattern (a) and Raman spectroscopy (b) of pure TiO<sub>2</sub>, pure CeO<sub>2</sub> and flower-like CeO<sub>2</sub>/TiO<sub>2</sub> heterostructures.

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