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# Facile synthesis of various $\alpha$-$Fe_2O_3$ micro/nanostructures: Highlighting on the enhanced catalysis activities by formation of bowl-like $\alpha$-$Fe_2O_3$/Au composites

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ABSTRACT

Various $\alpha$-$Fe_2O_3$ micro/nanostructures referring to spherical-like, bowl-like, cubic, and discoid shapes have been fabricated by a facile hydrothermal method using sodium bicarbonate as surfactant and alkaline reagents, displaying superior Fenton catalytic performances for degradation of Rhodamine 6G. Because of abundant exposed crystal surfaces such as (110) and (104) on the surfaces of bowl-like $\alpha$-$Fe_2O_3$, the rapid degradation rate of 90.0% in 5 min is observed under the dark condition as the adding amount of $H_2O_2$ limiting to 300 μL. Significantly, the enhanced catalytic performances of bowl-like $\alpha$-$Fe_2O_3$/Au catalysts under natural light condition have been investigated and carried out by in situ reduction of well-distributed Au nanoparticles with average sizes of 3–6 nm. Due to the appropriate phase structures and heterogenous interface properties, the highest photo-Fenton catalytic activity with the degradation rate of 90.0% in 2 min can be obtained for $\alpha$-$Fe_2O_3$/$Au_{0.01}$ composites.

## 1. Introduction

Recently, there have been continuing research interests for the development of different functional oxide micro/nanomaterials with high specific surface area, tunable sizes and shapes, and significant characteristic responses in the practical applications, such as heterogeneous catalysis, water treatment, biomedical imaging, drug delivery, energy storage, and sensing [1,2]. Although a lot of efforts have been concentrated on the morphology and structure controls of various oxide architectures, the apparent diversity and adjustability of micro/nanostructures achieved by facile synthetic routes have become the main limiting factors for understanding the fascinating relationship between the structure and property of products [3,4]. Actually, the investigation of new synthesis technologies employed for tuning microcosmic parameters played a dominant role for the configuration evolutions of advanced materials.

Iron oxides, as the important kind of semiconductor materials combining prominent functionality with low cost, low toxicity, the elevated specific surface area, and a high yield, have evoked considerable concentration as promising materials in the fields of catalysts, sensors, in-vivo magnetic imaging agents, magnetic fluids, and lithium batteries [5–7]. In particular, $\alpha$-$Fe_2O_3$ micro/nanocrystals can be confirmed as good catalysts with remarkable surface effects in different reaction environments. The increase of surface active sites are mainly ascribed from the synergistic actions of small particle size, the volume fraction of surface states, the bonding and electronic states, and the surface atomic coordination [8]. $\alpha$-$Fe_2O_3$ micro/nanocrystals with a variety of morphologies including spherical particles, nanorods, nanobelts, nanoplates, nanowires, nanotubes, and cubic shapes have been extensively investigated by numerous synthetic methods such as co-precipitation, electrodeposition, hydrothermal and solvothermal reaction, sonochemical reaction, and microwave-assisted synthesis in catalyst field [9–11]. For instance, Yin and co-workers prepared a series of $\alpha$-$Fe_2O_3$ nanoparticles by a combination of co-precipitation and microwave drying technologies, exhibiting superior catalytic property for the ortho-methylation of phenol with methanol from 623 to 653 K [12]. Du and co-workers provided porous $\alpha$-$Fe_2O_3$ nanocubes that were derived from Prussian blue nanocubes for improving the catalytic efficiency of the degradation of Rhdamine B (RhB) [13]. Yu and co-workers synthesized $\alpha$-$Fe_2O_3$ hollow spheres with novel cage-like architectures and high surface area which were evaluated as good catalysts by photocatalytic decolorization of RhB aqueous solution at ambient temperature [14]. In general, the activity and selectivity of catalysts constituting of $\alpha$-$Fe_2O_3$ particles can provide with the advantages of high efficiency and long-term operation. The catalysis properties of $\alpha$-$Fe_2O_3$ products were depedent on the composition, structure, and size, as well

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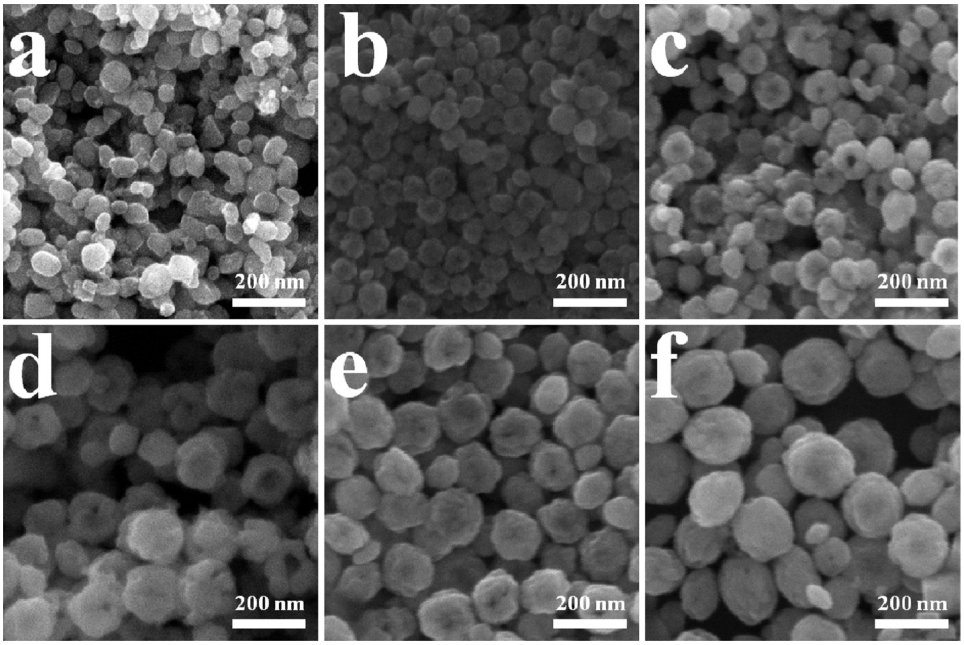

**Fig. 1.** SEM images of $\alpha$-$Fe_2O_3$ samples obtained under different reaction times: a–f, Sample.1–6.

as the surface exposed facet conditions. Until now, there have been an increasing attention on the influence of exposed facet on surface reactivity for catalysis process. For instance, Chen and co-workers proposed the mechanism study of redox mediator on $\alpha$-$Fe_2O_3$ exposed by different facets and the enhanced photocatalytic water oxidation behavior [15]. The available fabrication of $\alpha$-$Fe_2O_3$ micro/nanocrystals with tunable exposed facets and porous structure may open the door for further development of enhanced $\alpha$-$Fe_2O_3$ calalytic systems.

Fenton catalytic process has been verified to be a high-efficiency approach for activating $H_2O_2$ to generate hydroxyl radical (OH·) according to the radical (Weiss-Harber) mechanism, which has the second highest oxidant potential (about 2.7 eV) in nature and can completely oxidize organic compounds without light, heat, or electricity [16,17]. The design of $\alpha$-$Fe_2O_3$-based heterogeneous Fenton catalysts would be of great importance for promoting the catalytic performance due to the rapid formation of strongly oxidizing reactive oxygen species with high reactivity and non-selectivity influenced by the structure optimization, dissolved oxygen, inorganic ions, and pH value. It is found that the introduction of precious metals onto the surface of $\alpha$-$Fe_2O_3$ particles can alleviate the poor charge transport process and decrease the recombination of charge carriers through the tunable heterointerfaces in virtue of good catalytic activity, optical properties, and chemical properties [18–22]. Various inorganic heterostructures have been applied by introducing precious metals as the coating materials to inhibit charge recombination and make it possible for improving the catalytic activity. $\alpha$-$Fe_2O_3$/Au catalysts can generally show attractive catalytic properties on different chemical reactions and detections, such as CO catalytic oxidation, $NO_X$ catalytic reduction, and propylene epoxidation [23]. Moreover, $\alpha$-$Fe_2O_3$/Au micro/nanostructures with well-dispersed and shape-controlled Au nanoparticles can result in the enhancement of Fenton catalytic activity by suppressing the recombination and promoting the charge-transfer process of photogenerated electrons and holes at the photocatalyst/electrolyte interface under light irradiation [24,25]. On the other hand, the photo-induced electron ejection on the surface and the electron-transfer from Au to $H_2O_2$ can be commonly observed as Au atoms serving as the electron-donors or -acceptors under different environments, which is beneficial to the fast producing of OH· for oxidation application [26]. Meanwhile, $\alpha$-$Fe_2O_3$/Au heterostructures with a certain amount of Au deposition can probably induce the magnetic separation for recyclability, because of the phase transformation of iron oxides during the reduction of Au nanoparticles [27].

In this study, various $\alpha$-$Fe_2O_3$ microstructures with tunable spherical-like, bowl-like, cubic, and discoid shapes have been synthesized by a simple and effective hydrothermal approach. The formation mechanisms and Fenton catalytic properties for degradation of Rhodamine 6G (R6G) were also investigated as well as the effect of different exposed crystal surfaces of $\alpha$-$Fe_2O_3$ products on the catalytic activity. Furthermore, photo-Fenton catalytic systems of $\alpha$-$Fe_2O_3$/Au composites have been obtained by adjusting the facile in situ reduction process. By optimizing the phase composition and surface configuration, $\alpha$-$Fe_2O_3$/Au composites could exhibit excellent catalytic performance in photo-Fenton degradation of R6G.

## 2. Experimental section

### 2.1. Preparation of $\alpha$-$Fe_2O_3$ micro/nanostructures

As for the bowl-like $\alpha$-$Fe_2O_3$ products, 0.676 g of $FeCl_3{\cdot}6H_2O$ and 1.8 g of $NaHCO_3$ were added into 25 mL of ethanol solvent to form the transparent solution under vigorous magnetic stirring about 30 min. The obtained solution was then transferred into a Teflon-lined stainless-steel autoclave, and subsequently sealed and heated at 200 °C for 16 h in an oven. After cooling to room temperature naturally, the products were collected and dried at ambient temperature after centrifugation by washing with distilled water and ethanol for several times. Other $\alpha$-$Fe_2O_3$ micro/nanostructures can be obtained by adjusting the parameters including the concentration of $NaHCO_3$ and reaction time, respectively. Detailed synthesis parameters were summarized in Table S1.

### 2.2. Preparation of $\alpha$-$Fe_2O_3$/Au composites

In a typical process, 0.296 g of $\alpha$-$Fe_2O_3$ nanoparticles were dispersed in 40 mL of distilled water under magnetic stirring about 30 min. After adding 1 mL of Lysine and 0.2 mL of $HAuCl_4$ (0.01 M) into the mixing solution under strong magnetic stirring, 5 mL of $NaBH_4$ aqueous solution was dropped slowly into the reaction system within 30 min. Finally, the products were filtered, and washed with distilled water, and then dried in air at ambient temperature. Other $\alpha$-$Fe_2O_3$/Au composites can be prepared by changing the adding amounts of $HAuCl_4$ (0.01 M) as