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Au/graphene quantum dots/ferroferric oxide composites as catalysts for the solvent-free oxidation of alcohols

Xiaochen Wu [a], Shouwu Guo [a,*], Jingyan Zhang [b,**]

[a] Department of Electronic Engineering, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai, 200240 PR China

[b] State Key Laboratory of Bioreactor Engineering, Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science and Technology, Shanghai, 200237 PR China

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ABSTRACT

Nanocomposites of graphene quantum dots and Au nanoparticles (GQDs/Au) are immobilized on the Fe_3O_4 nanoparticles, forming $GQDs/Au/Fe_3O_4$ ternary composites. The as-prepared ternary composites exhibit superparamagnetic property rendering them easy to be isolated from the reaction mixture. More importantly, they show superb catalytic activity for solvent-free oxidation of VA and other alcohols that contain an aromatic benzyl group, to the corresponding aldehydes exclusively with air as oxidant. The great stability and selectivity of the $GQDs/Au/Fe_3O_4$ indicate that they might be applicable catalysts for the oxidation of aromatic alcohols.

1. Introduction

Owing to its convenience for separation and recovery through simple magnetic interaction, superparamagnetic Fe_3O_4 nanoparticles have been widely used in catalysis [1]. Also, Fe_3O_4 nanoparticles can be used as supporting matrices for nanosized catalysts [1,2]. We previously found that the composite of Au nanoparticles and graphene quantum dots (Au/GQDs) can catalyze the oxidation of veratryl alcohol (VA) to veratryl aldehyde or veratric acid with efficient conversion and excellent selectivity [3]. However, given the nanoscale size of the Au/GQDs, it is hard to recover them from the liquid reaction mixture except for using ultrahigh speed centrifugation. This limits somehow the practical applications of Au/GQDs as catalyst. To overcome the drawback of the hard separation and recovering of Au/GQDs from the VA oxidation reaction system, and to improve the recyclability, in this work, the Au/GQDs are immobilized on the Fe_3O_4 nanoparticles, obtaining the $Au/GQDs/Fe_3O_4$ composites with moderate magnetic property, which makes the recovery of the catalyst much convenient. In our previous work, the oxidation product was obtained through a complicated extraction procedure when VA oxidation was carried out in aqueous solution, which consumed large quantities of organic solvent and accumulates massive waste. Therefore, the catalytic activity of $Au/GQDs/Fe_3O_4$ composites in the oxidation of VA and other alcohols with air as oxidant without solvent is explored in this work, since some alcohols are liquid.

2. Experimental

Au/GQDs were prepared as described in our previous work [3,4]. Fe_3O_4 nanoparticles were prepared through a solvothermal procedure [5]. 300 mg of Fe_3O_4 were dispersed in a mixture of ethanol (60 mL), H_2O (1 mL) and $NH_3 \cdot H_2O$ (1.5 mL, 28 wt%), 195 μL of tetraethoxysilane and 780 μL of (3-aminopropyl) triethoxysilane were added quickly, mechanically stirred for 6 h to get the modified Fe_3O_4. 1 mg/mL of as-modified Fe_3O_4 nanoparticles was mixed with 0.15 mg/mL 100 mL of Au/GQDs under pH 4 and stirred for 1 h to get the $Au/GQDs/Fe_3O_4$.

In a typical procedure, 1.2 g of alcohol was added into an open round-bottomed flask and heated to the desired temperature (100 °C) until dissolved. 50 mg of $Au/GQDs/Fe_3O_4$ and 50 mg of K_2CO_3 were added under vigorous stirring, and kept under 100 °C for 36 h. The $Au/GQDs/Fe_3O_4$ were separated through magnetic absorption, the products were analyzed using GC–MS.

TEM (JEM-2010, Japan), FE-SEM (Zeiss ultra 55, Germany), XRD (D8-Advance, Bruker, Germany), vibrating sample magnetometer

* Corresponding author.
** Corresponding author.
E-mail addresses: swguo@sjtu.edu.cn (S. Guo), jyzhang@ecust.edu.cn (J. Zhang).

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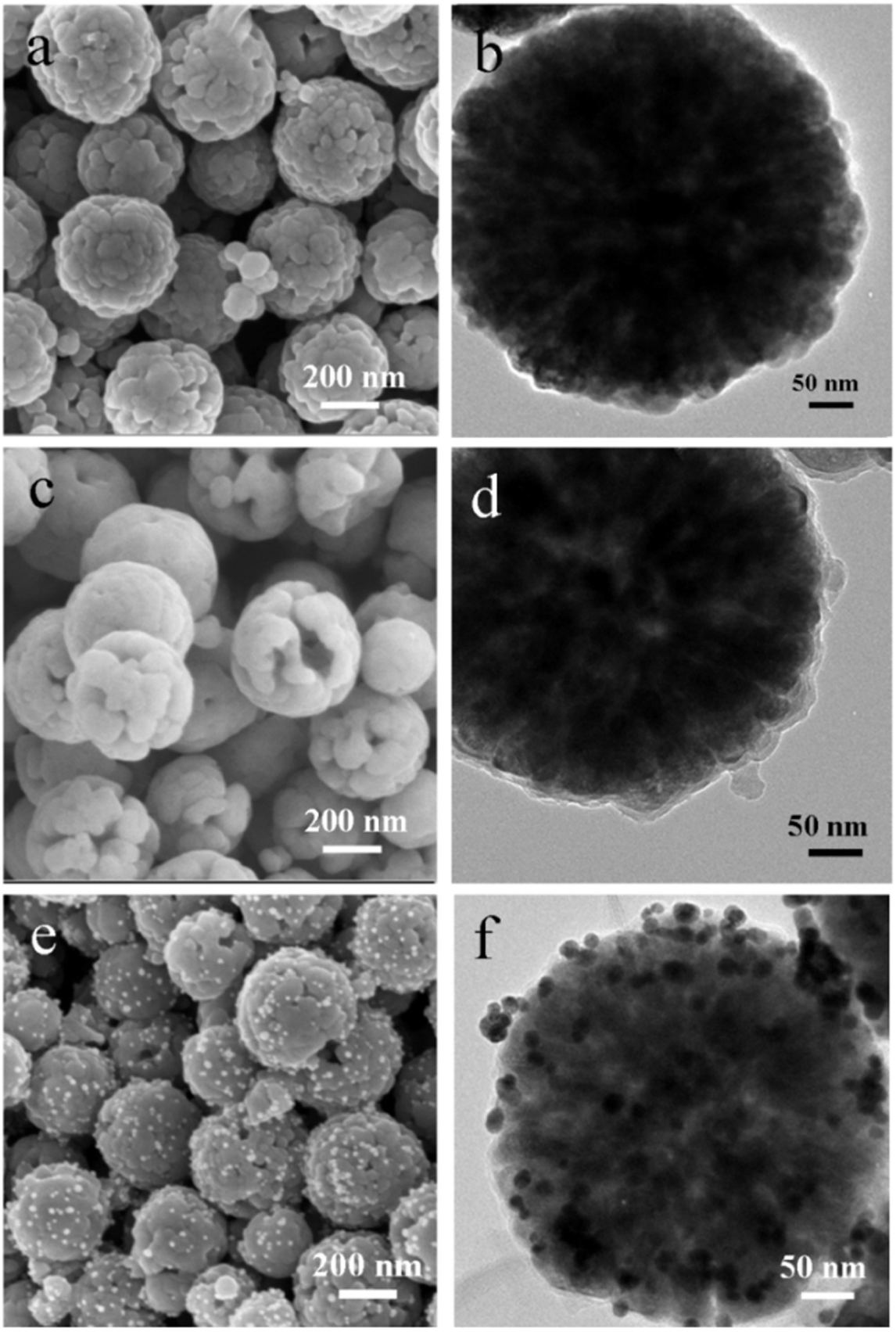

Fig. 1. SEM and TEM images of Fe_3O_4 nanoparticles (a, b), modified Fe_3O_4 nanoparticles (c, d), and Au/GQDs/Fe_3O_4 composites (e, f).

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