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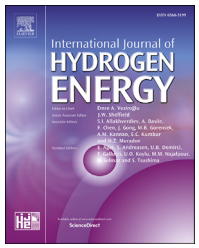

Pd nanoparticles immobilized on magnetic carbon dots@Fe_3O_4 nanocubes as a synergistic catalyst for hydrogen generation

Yali Guo, Jing Qian, Anam Iqbal, Lilan Zhang, Weisheng Liu, Wenwu Qin *

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

In this work, a cube-like Pd/carbon dots@Fe_3O_4 (Pd/C-dots@Fe_3O_4) hybrid material has been successfully prepared through a facile ultrasonic assisted chemical reduction method, and used as a highly efficient catalyst for the hydrolytic dehydrogenation of $NaBH_4$ in alkaline media. It is found that the small Pd nanoparticles (NPs) are uniform and well dispersed on the surface of C-dots@Fe_3O_4 nanocubes (NCs). Benefiting from the advantages of the unique cube-like structure, the super conductivity of carbon dots (C-dots) and the synergistic effect between Pd NPs and C-dots@Fe_3O_4 support, Pd/C-dots@Fe_3O_4 NCs exhibits the highest catalytic performance among all the as-prepared samples. The possible reaction mechanism is discussed. Furthermore, the effects of reaction temperature, $NaBH_4$ concentration and NaOH concentration on the catalytic activity of Pd/C-dots@Fe_3O_4 NCs are studied. Besides, the magnetic properties of Pd/C-dots@Fe_3O_4 NCs can achieve effective momentum transfer with the assistance of the external magnetic field, and a higher catalytic activity is observed for Pd/C-dots@Fe_3O_4 NCs in self-stirring mode than in magnetic-stirring mode. This novel catalyst also exhibits good stability and can be easily separated by a magnet, showing great potential for renewable energy applications.

Introduction

With the aggravation of world energy crisis, the development of clean, sustainable energy resources has attracted increasing attentions [1]. Hydrogen is considered to be one of the most promising candidates for future energy, owing to its high energy density and abundant sources [2–6]. The search for safe and efficient hydrogen storage materials is still a big challenge for establishing a hydrogen-based energy system [7]. After decades of efforts, various hydrogen storage materials have been considered, including alcohols, formic acid, hydrazine, ammonia borane and chemical hybrid systems [8–10]. Among various storage materials, sodium borohydride ($NaBH_4$) has been extensively investigated and regarded as a promising chemical hydrogen storage material due to its high hydrogen storage capacity (10.8 wt%), low molecular weight (37.83 g mol^{-1}), nontoxicity, good stability in alkaline solutions, and possible regeneration capacity [11–13]. Typically, hydrogen stored in $NaBH_4$ can be released through

* *Corresponding author*. Fax: +86 931 8912582.
E-mail address: qinww@lzu.edu.cn (W. Qin).
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thermolysis [14] and hydrolysis [15–19], among which catalytic hydrolysis of $NaBH_4$ seems to be the most effective route and generally gives a fast rate for hydrogen release under mild reaction conditions.

To date, a variety of catalysts, such as metal nanoparticles (NPs) [20], metal oxides [21,22], and multicomponent metallic systems [23–25] have been demonstrated to accelerate the hydrolysis reaction. However, owing to high surface energy, these catalysts usually suffered serious aggregation during the reaction, leading to a significant loss of catalytic activity [26]. To solve this problem, various support materials such as carbon black [27], graphene oxide [28,29], silica [30], and polymer [31,32] have been used for immobilizing the bare nanomaterials to improve their stability.

Carbon dots (C-dots), as a new class of carbon nanomaterials, have received much attention because of their excellent photostability, favorable biocompatibility, low toxicity, and super conductivity [33–36]. The abundant functional groups on the surface of C-dots give them as an excellent support for the stabilization of catalyst and the enhanced catalytic activities of the original materials [37]. So far, some groups have reported metal (Au [38], Ag [39], Pd [40], Cu [41], and AuAg alloys [42]) NPs@C-dots hybrid materials. Although the use of C-dots as support material can effectively disperse the metal NPs, however, the separation of such catalysts from the reaction medium is difficult during the filtration or centrifugation process. Therefore, the development of new catalysts with magnetically separable capacity is highly desirable.

In the present work, combining the merits of C-dots, active metal NPs, nanostructures and magnetic properties, we design a facile ultrasonic assisted chemical reduction method to fabricate Pd/C-dots@Fe_3O_4 to form a cube-like structure. The as-obtained Pd/C-dots@Fe_3O_4 NCs are characterized and employed as a catalyst for hydrogen generation from $NaBH_4$ solution, and the relationship between the structure and the catalytic activities is investigated. The magnetic momentum transfer properties of the catalyst and the possible reaction mechanism are also discussed. Furthermore, the effects of reaction temperature, $NaBH_4$ concentration, NaOH concentration, and stability of catalyst for the hydrolysis of $NaBH_4$ have been systematically studied.

Experimental section

Chemicals

All the chemicals used in the experiments were analytical grade and were used without further purification. $FeSO_4 \cdot 7H_2O$ (analytical grade), NaOH (≥96%) and KNO_3 (≥99%) were obtained from Tianjin Guangfu Reagent Company. $NaBH_4$ (≥96%) were purchased from Sinopharm Chem. Reagent Co., Ltd. Palladium chloride ($PdCl_2$) was supplied from Energy Chemical. o-Phenylenediamine (o-PD, ≥98%) was bought from Mclean reagent company.

Materials

Synthesis of palladium nanoparticles immobilized on C-dots@Fe_3O_4 NCs (Pd/C-dots@Fe_3O_4 NCs).

C-dots, Fe_3O_4 NCs and C-dots@Fe_3O_4 NCs were prepared according to the previous reports, and the details are described in Sections 1.1–1.3 of the Supporting Information [43–45]. In a typical procedure, 1 mg of the prepared C-dots@Fe_3O_4 NCs was dispersed in ultrapure water (10 mL) by

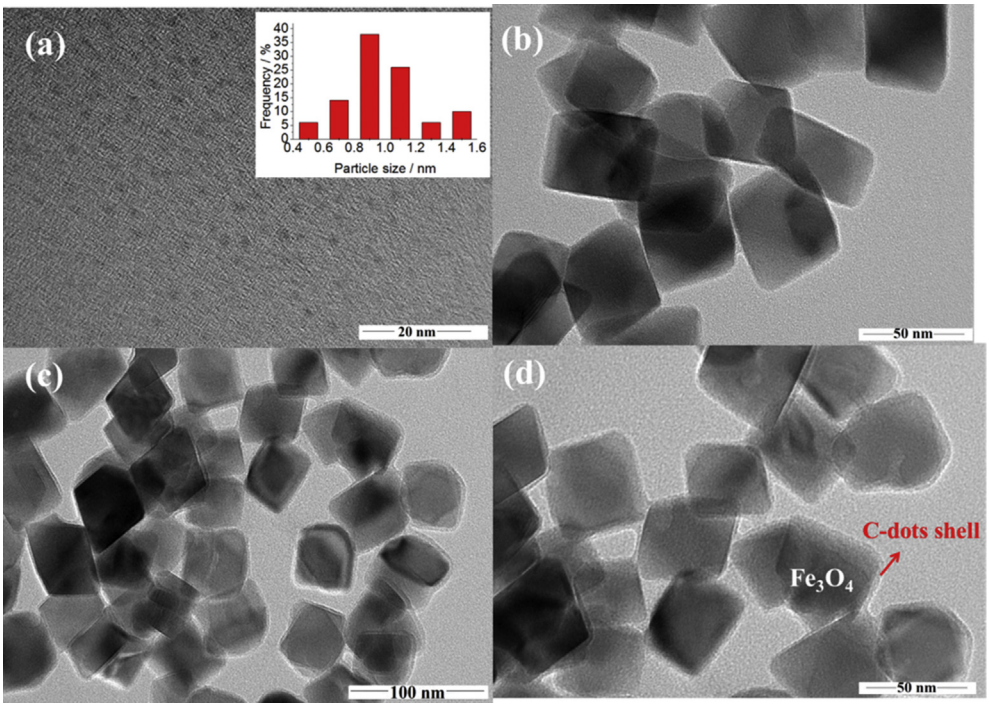

Fig. 1 – TEM images of (a) C-dots, (b) Fe_3O_4 NCs and (c, d) C-dots@Fe_3O_4 NCs.