Separation and Purification Technology 149 (2015) 74–81

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Design of composite maghemite/hematite/carbon aerogel nanostructures with high performance for organic dye removal

Yi-Feng Lin *, Chia-Yu Chang

Department of Chemical Engineering, R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli 320, Taiwan, ROC

ARTICLE INFO

Article history:
Received 27 November 2014
Received in revised form 16 May 2015
Accepted 22 May 2015
Available online 22 May 2015

Keywords:
Fe_3O_4/α-Fe_2O_3
γ-Fe_2O_3/α-Fe_2O_3
Carbon aerogel
Nanorods
Mesoporous

ABSTRACT

Composite Fe_3O_4/α-Fe_2O_3 nanorods (180N) with a specific surface area of 16.2 m^2/g were successfully synthesized via a facile hydrothermal reaction at 180 °C. To increase the specific surface area, a mesoporous carbon aerogel (CA) with a large specific surface area was added to the hydrothermal reaction to form mesoporous Fe_3O_4/α-Fe_2O_3/CA structures (CA-180) with a specific surface area of 267.7 m^2/g instead of nanorods. The as-prepared 180N and CA-180 samples were further annealed at 400 °C to oxidize the Fe_3O_4 phase, resulting in the formation of composite γ-Fe_2O_3/α-Fe_2O_3 nanorods (400N) with a specific surface area of 27.7 m^2/g and mesoporous γ-Fe_2O_3/α-Fe_2O_3/CA structures (CA-400) with a specific surface area of 551 m^2/g. The CA-400 samples were further used to remove the dye Rhodamine B (RhB) from aqueous solution, and 98.2% of the RhB dye was removed using the CA-400 sample when the initial RhB concentration was 8 ppm. The as-prepared CA-400 sample exhibits strong potential for use in wastewater treatment applications, such as organic dye removal.

1. Introduction

One-dimensional (1-D) nanostructures such as nanowires [1–3], nanorods [4,5], nanotubes [6,7] and nanofibers [8,9] have drawn extensive research attention in recent years because of the novel properties that result from this special dimensionality [10]. A wide range of applications of 1-D nanomaterials have been investigated, such as field emitters [11,12], piezoelectric nanogenerators [13–15], solar cells [16,17], water-splitting systems [18], photocatalysts [19] and sensors [20,21]. Various important 1-D nanomaterials, such as ZnO [22], ZnS [23], CdS [11–14] and Si [24], have been successfully prepared through gas-phase or wet-chemistry approaches in recent years. Magnetic building blocks have been the subject of numerous studies because of their magnetic properties and their broad range of applications in many fields, including drug delivery [25], imaging [26], spintronic devices [27], recording devices [28], supercapacitors [29], photocatalysis [30] and the adsorption of heavy-metal ions [31]. Iron oxide is one such magnetic building block material. It has three different crystalline phases: magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). As a result, relevant 1-D iron oxide nanostructures such as nanorods [32,33], nanowires [34,35], nanoneedles [36] and nanotubes [37,38] have been successfully developed in recent years. Numerous applications of 1-D iron oxide nanostructures have been discussed, including field emitters [36], degradation catalysts [39], wireless manipulation devices [40] and sensors [41]. To the best of our knowledge, few previous studies have examined the application of 1-D iron oxide nanostructures as adsorbents for the dye RhB.

Carbon aerogels (CAs), one of mesoporous materials [42–44] and carbon materials [45,46], have been the subject of numerous studies because of their high specific surface area (400–1200 m^2/g), high porosity (greater than 80%), high mechanical strength, mesoporous structures (2–50 nm) and low cost [41]. A wide range of applications of CAs, including hydrogen storage materials [47], capacitors [48], supercapacitors [29], ion-exchange resins [49] and metal-ion adsorbents [50], have been previously studied. For metal-ion adsorption applications, CAs require an additional separation step, such as centrifugation, to remove them from solution. In our previous study, mesoporous Fe/CA structures were successfully prepared for use as As(V)-ion adsorbents [51]. The resulting as-prepared Fe/CA structures could be easily separated from the solution using an external magnetic field because of their ferromagnetic property, and further separation steps, such as centrifugation, were not needed.

Herein, Fe_3O_4/α-Fe_2O_3 nanorods (180N) were successfully prepared using a facile hydrothermal process at 180 °C, as shown in Scheme 1. The as-prepared 180N samples were further annealed at 400 °C under atmospheric conditions to form γ-Fe_2O_3/α-Fe_2O_3

* Corresponding author at: 200, Chungpei Rd., Chungli, Taoyaun, Taiwan, ROC.
E-mail address: yflin@cycu.edu.tw (Y.-F. Lin).

http://dx.doi.org/10.1016/j.seppur.2015.05.025
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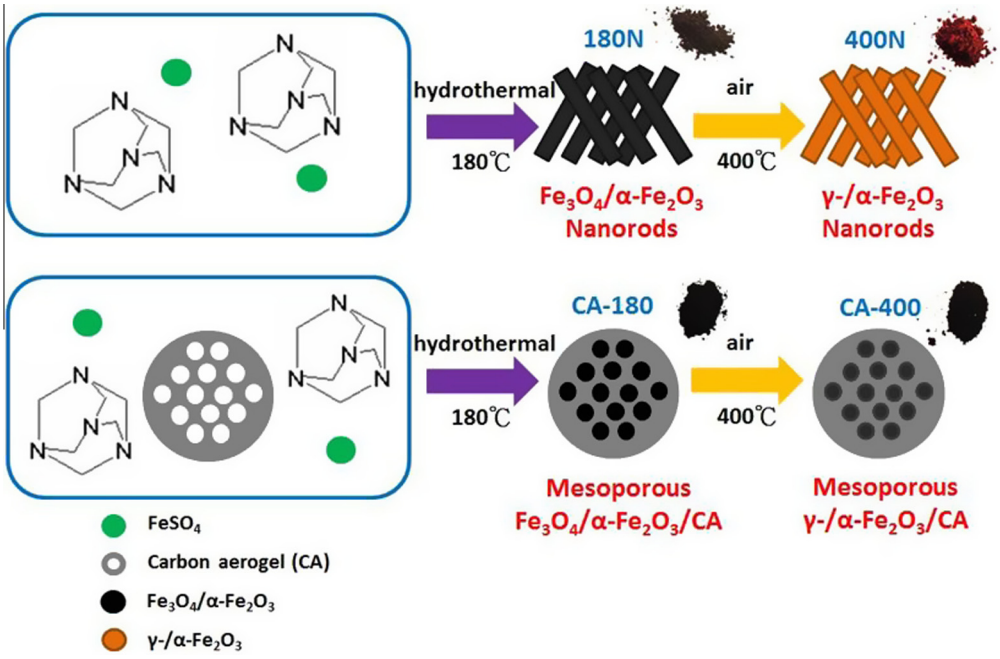

Scheme 1. Preparation of mesoporous iron oxide/carbon aerogel composite nanostructures.

nanorods (400N). However, the specific surface area of the as-prepared nanorod samples was quite small. As a result, we attempted to add a CA with a high specific surface area to the reactant solution to prepare mesoporous Fe_3O_4/α-Fe_2O_3/CA structures (CA-180). The specific surface area of the CA-180 samples was greatly increased compared to the 180N samples. The CA-180 samples were also further annealed at 400 °C to form mesoporous γ-Fe_2O_3/α-Fe_2O_3/CA structures (CA-400). We also investigated the ability of the four as-prepared samples (180N, 400N, CA-180 and CA-400) to adsorb RhB. The CA-400 samples exhibited better adsorption performances than the other three samples and good response to an external magnetic field, which indicates that the use of a magnetic field can replace the traditional centrifugal separation step used to remove adsorbents from solution, thereby reducing energy consumption. Furthermore, the CA-400 samples are also reusable for the adsorption of RhB dye, which makes them potentially useful for wastewater treatment, including organic dye removal.

2. Experimental

2.1. Chemicals

Ferrous sulfate ($FeSO_4$), hexamethylenetetramine (HMTA) and DI water were used to prepare the Fe_3O_4/α-Fe_2O_3 nanorods (180N) and γ-Fe_2O_3/α-Fe_2O_3 nanorods (400N). The synthesis of carbon aerogel (CA) was based on the procedure described in our previous report [52]; the specific surface area and average pore diameter of the CA were approximately 702 m^2/g and 10 nm, respectively. The RhB dye was dissolved in DI water to an initial concentration of 8 ppm.

2.2. Preparation of iron oxide and iron oxide/carbon aerogel structures

To prepare the Fe_3O_4/α-Fe_2O_3 nanorods (180N), $FeSO_4$ (ca. 1.67 g) and HMTA (ca. 0.84 g) were dissolved in 60 ml of DI water. After stirring for 2 h, the solution mixture was transferred to a 100-ml Teflon-lined autoclave for the subsequent hydrothermal reaction. The hydrothermal reaction was performed at 180 °C for 24 h. After cooling to room temperature, the product was washed with ethanol and then dried at 50 °C for 24 h. The 180N samples were further annealed at 400 °C under atmospheric conditions for 7 h to form the γ-Fe_2O_3/α-Fe_2O_3 nanorods (400N).

To prepare the mesoporous Fe_3O_4/α-Fe_2O_3/CA structures (CA-180), $FeSO_4$ (ca. 1.67 g) and CA (ca. 0.3 g) were added to 60 ml of DI water and stirred for 24 h. The resulting solution was centrifuged to obtain black powders, and the black powders were further dried at 50 °C for 24 h. The as-obtained black powders and HMTA (ca. 0.84 g) were added to 60 ml of DI water and stirred for 2 h. The solution was then transferred to a 100-ml Teflon-lined autoclave, and the autoclave was heated at 180 °C for 24 h. After cooling to room temperature, the product was washed with ethanol and then dried at 50 °C for 24 h. The CA-180 samples were

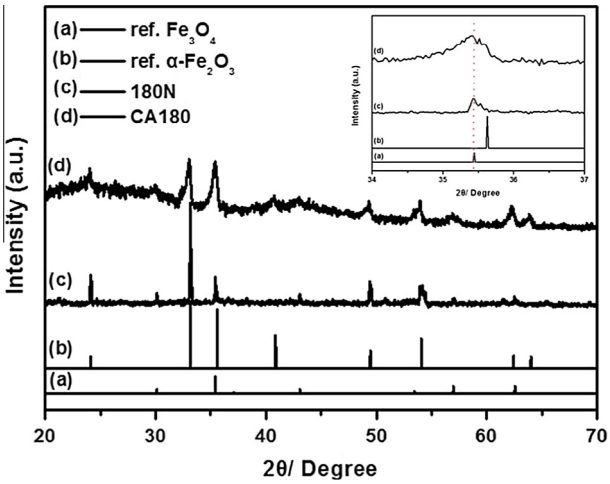

Fig. 1. XRD patterns of reference (a) Fe_3O_4, (b) α-Fe_2O_3 crystals, (c) 180N and (d) CA-180 samples. The inset shows the corresponding XRD patterns at the diffraction angles between 34° and 37°.