



One-pot synthesis of layered double hydroxide hollow nanospheres with ultrafast removal efficiency for heavy metal ions and organic contaminants

Mahfuza Mubarak^{a, b}, Hyokyung Jeon^a, Md. Shahinul Islam^b, Cheolho Yoon^c, Jong-Seong Bae^d, Seong-Ju Hwang^b, Won San Choi^e, Ha-Jin Lee^{a, b, *}

^a Western Seoul Center, Korea Basic Science Institute, 150 Bugahyun-ro, Seou daemun-gu, Seoul, 03759, Republic of Korea

^b Department of Chemistry and Nano Science, Ewha Womans University, 52 Ewhay eodae-gil, Seou daemun-gu, Seoul, 03760, Republic of Korea

^c Seoul Center, Korea Basic Science Institute, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea

^d Busan Center, Korea Basic Science Institute, 30 Gwahaksandan 1-ro 60beon-gil, Gangseo-gu, Busan, 46742, Republic of Korea

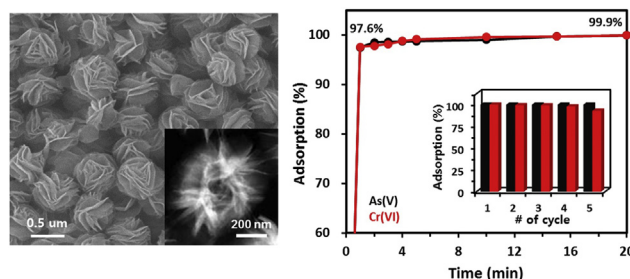
^e Department of Chemical and Biological Engineering, Hanbat National University, 125 Dongseodaero, Yuseong-gu, Daejeon, 34158, Republic of Korea



HIGHLIGHTS

- MF-LDH and MF-LDO hollow nanospheres were prepared by one-step thermal method.
- MF-LDH and MF-LDO showed ultrafast removal efficiency for As(V) and Cr(VI).
- MF-LDO purified contaminated water up to drinking water level within 20 min.
- Gold nanoparticles were successfully introduced into MF-LDO hollow nanosphere structure.
- Au-MF-LDO completely reduced 4-nitrophenol to 4-aminophenol within 5 min.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 September 2017

Received in revised form

2 March 2018

Accepted 5 March 2018

Available online 6 March 2018

Handling Editor: Shane Snyder

Keywords:

Layered double hydroxides

Nanosphere

Adsorption

Heavy metal ions

Catalyst

ABSTRACT

Herein, Mg/Fe layered double hydroxide (MF-LDH) hollow nanospheres were successfully prepared by a one-step thermal method. After the thermal treatment of MF-LDH nanospheres at 400 °C, the MF-LDH was converted into the corresponding oxide, Mg/Fe layered double oxide (MF-LDO), which maintained the hollow nanosphere structure. The MF-LDO hollow nanospheres exhibited excellent adsorption efficiency for both As(V) and Cr(VI), showing 99% removal within 5 min and providing maximum removal capacities of 178.6 mg g⁻¹ [As(V)] and 148.7 mg g⁻¹ [Cr(VI)]. Moreover, it met the maximum contaminant level requirements recommended by World Health Organization (WHO); 10 ppm for As(V) and 50 ppm for Cr(VI) in 10 and 20 min, respectively. Furthermore, Au nanoparticles were successfully introduced in the MF-LDO hollow nanospheres, and the products showed a conversion rate of 100% for the reduction of 4-nitrophenol into 4-aminophenol within 5 min. It is believed that these excellent and versatile abilities integrated with a facile synthetic strategy will facilitate the practical application of this material in cost-effective wastewater purification.

© 2018 Elsevier Ltd. All rights reserved.

* Corresponding author. Western Seoul Center, Korea Basic Science Institute, 150 Bugahyun-ro, Seou daemun-gu, Seoul, 03759, Republic of Korea.

E-mail address: hajinlee@kbsi.re.kr (H.-J. Lee).

1. Introduction

The supply of safe and clean drinking water is essential to humans and other lifeforms. Water pollution mainly occurs when pollutants are directly or indirectly discharged into bodies of water without adequate treatment. The contaminants accumulated from industrial effluents and agricultural wastes contain health hazardous chemicals, such as heavy metals and organic pollutants, which pose serious risks to human health and ecological systems. In particular, arsenic and chromium are heavy metal ions that are highly toxic to the human body, and long-term exposure to arsenic and chromium are responsible for skin, liver and lung cancer, kidney damage and anaemia (Naujokas et al., 2013; Kieber et al., 2002; Islam et al., 2017). Due to their serious virulence, the WHO (World Health Organization) defines the acceptable level as 10 ppb for the maximum concentration of arsenic and 50 ppb for chromium in safe drinking water (USEPA, 2003; WHO, 2008).

In recent years, many conventional techniques have been developed for the removal of heavy metal ions from wastewater, including adsorption, chemical precipitation, chemical redox reactions, electrochemical treatments, membrane processes, and ion exchange (Islam et al., 2017; Tchobanoglous et al., 2003; Al-Shannag et al., 2015; Admassie et al., 2015; Sounthararajah et al., 2015; Vijayakumar et al., 2015). Among the aforementioned methods, adsorption is considered to be one of the most economical and effective techniques owing to its simplicity, ease of operation and cost effectiveness (Wen et al., 2017). This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations. Since the effectiveness and efficiency is the core of the adsorption technique, high surface area and active adsorption sites are necessary for the adsorbents (Zeng et al., 2015; Guo et al., 2014).

Layered double hydroxides (LDHs, $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[(A^{n-})_x/n]^{x-} \cdot mH_2O$) in the form of anionic clays have attracted increasing attention for the adsorption of anionic inorganic and organic pollutants thanks to their layered structure, high surface area, porous structure and interlayer ion exchange (Abellan et al., 2015; Zubair et al., 2017). Easily prepared LDHs, such as MgAl-LDH, CaFe-LDH, and ZnAl-LDH, have been widely applied as adsorbents for various organic dyes and heavy metal ions due to their high adsorption capacity, low-cost and non-toxicity (Shan et al., 2015; Wu et al., 2012; Li et al., 2014). In particular, spherical LDH microparticles with porous structures have attracted significant attention for their structural stability and high surface area, which are essential factors enhancing their removal capabilities for water pollutants (Li et al., 2014; Sun et al., 2015; Lei et al., 2017a, 2017b; Lin et al., 2015). To control the morphology and porosity in the LDH structure, hydrothermal methods have been employed in aqueous media using surfactants (Sun et al., 2015), sacrificial templates or urea as a precipitating agent (Li et al., 2014; Lei et al., 2017a, 2017b; Lin et al., 2015). The porous LDH particles have been applied as adsorbents for anionic organic dyes and heavy metal ions. Despite enhancing the adsorption efficiency for pollutants, several considerable problems remain, such as the toxicity of the surfactants, multiple steps for the synthesis and the performance limit for heavy metal removal. Therefore, developing a simple, nontoxic, low-cost synthetic strategy with some unique features towards excellent remediation performance is still a great challenge.

In this work, Mg/Fe-LDH hollow nanospheres with high specific surface area were synthesized by a simple ethylene glycol-mediated thermal method using only two metal precursors, Mg^{2+} and Fe^{3+} . After calcination at 400 °C for 1 h, the Mg/Fe-LDH was oxidized to Mg/Fe layered double oxide (LDO) retaining the hollow sphere shape, which could rapidly purify water contaminated by heavy metals to drinking water standards. In addition to the heavy

metal adsorption tests, excellent catalytic performance for the reduction of 4-nitrophenol by introducing Au nanoparticles into the LDO nanosphere structure was also observed.

2. Materials and methods

2.1. Materials

Magnesium acetate tetrahydrate ($Mg(OAc)_2 \cdot 4H_2O$, 98%), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, 99.99%), potassium dichromate ($K_2Cr_2O_7$, 99.99%), ethylene glycol ($C_2H_6O_2$, 99.9%), iron (III) sulfate hydrate ($Fe_2(SO_4)_3 \cdot xH_2O$, 97%), chloroauric acid ($HAuCl_4$, 99.99%), sodium borohydride ($NaBH_4$), 4-nitrophenol, sodium chloride ($NaCl$, 99.5%), sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$, 99.5%), potassium phosphate (KH_2PO_4 , 99%), sodium sulfate (Na_2SO_4 , 99%), and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, 99%) were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without further purification.

2.2. Synthesis

Mg/Fe-LDH hollow nanospheres were synthesized by a simple one-step thermal method. First, $Mg(OAc)_2$ (1 g, 4.7 mmol) was dissolved in 40 mL of ethylene glycol. Separately, $FeCl_3$ (0.095 g, 0.35 mmol) was dissolved in 10 mL of ethylene glycol and added dropwise to the $Mg(OAc)_2$ solution under stirring at room temperature. After stirring for 4 h, the solution was transferred to a Teflon-lined autoclave bomb and heated at 200 °C in an electric oven for 8 h. The final product was cooled to room temperature and then washed three times with ethanol and DI water. The white MF-LDH hollow nanospheres were obtained after drying overnight at 80 °C. The MF-LDO hollow nanospheres were obtained by heat treatment of MF-LDH at 400 °C for 1 h in a muffle furnace.

Au nanoparticle (AuNP) embedded-MF-LDO (Au-MF-LDO) was prepared to test the catalytic ability for the reduction of 4-nitrophenol to 4-aminophenol. MF-LDO nanospheres (20 g) were dispersed in 20 mL of DI water by ultrasonic treatment for 5 min. An aqueous $HAuCl_4$ solution (10 mL, 1 mg mL^{-1}) was added dropwise to the MF-LDO suspension under stirring, and then $NaBH_4$ (0.1 mL, 10 mM) was added to the solution. After further stirring for 10 min, the Au-MF-LDO was collected by centrifugation and washed with DI water three times.

2.3. Characterization

The MF-LDH and MF-LDO hollow nanospheres were comprehensively characterized using field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL) and field emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL). Powder X-ray diffraction (XRD) analysis was carried out using a Rigaku D/Max-2000/PC diffractometer (Cu $K\alpha$ radiation, 298K). The Brunauer–Emmett–Teller (BET) surface areas and the Barrett–Joyner–Halanda (BJH) pore-size distributions were measured using an accelerated surface area and porosimetry system (Micromeritics ASAP 2010, USA). Fourier transform infrared (FT-IR) spectra were recorded on a Varian 800 FT-IR instrument (Scimitar Series), and X-ray photoelectron spectroscopy (XPS) studies were performed using a K-ALPHA+ (Thermo Scientific, UK) system with an aluminum anode (Al $K\alpha$, 1486.6 eV) at 12 kV and 72 W. Thermogravimetric analysis (TGA) was performed using a TGA N-1000 (Scinco, Korea) at a heating rate of 5 °C/min under flowing nitrogen, and ζ -potential measurements were performed on a Zeta-potential & particle size Analyzer ELSZ-2000 (Otsuka Electronics) at room temperature in water. UV–vis absorption spectra were recorded on

Download English Version:

<https://daneshyari.com/en/article/8851642>

Download Persian Version:

<https://daneshyari.com/article/8851642>

[Daneshyari.com](https://daneshyari.com)