Chemical Engineering Journal 347 (2018) 953–962

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Hierarchical MgFe-layered double hydroxide microsphere/graphene composite for simultaneous electrochemical determination of trace Pb(II) and Cd(II)

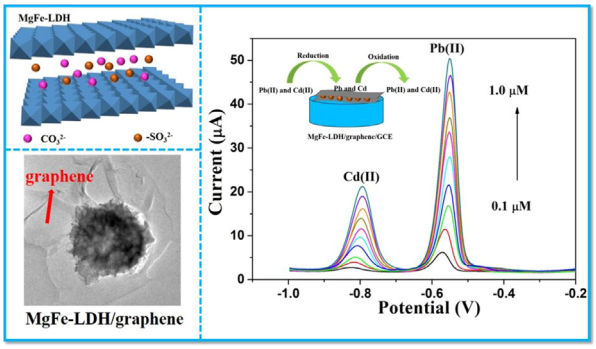
Yue Ma[a,b], Yongchuang Wang[a,b], Donghua Xie[a,b], Yue Gu[a,b], Xinle Zhu[c], Haimin Zhang[a], Guozhong Wang[a], Yunxia Zhang[a,*], Huijun Zhao[a,d]

[a] Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Centre for Excellence in Nanoscience, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China
[b] University of Science and Technology of China, Hefei 230026, PR China
[c] Safety Assessment Department, China Institute of Veterinary Drug Control, Beijing 100081, China
[d] Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, Queensland 4222, Australia

HIGHLIGHTS

- The hierarchical MgFe-LDH/graphene composite was synthesized.
- The individual and simultaneous detection of Cd(II) and Pb(II) were studied.
- Low detection limit, high sensitivity and broad linear range were realized.
- The proposed sensor was successfully applied for the determination of Cd(II) and Pb(II) in real samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hierarchical
MgFe-LDH/graphene
Cd(II)
Pb(II)
Simultaneous detection

ABSTRACT

Heavy metal contamination has been demonstrated to possess the severe threats toward the whole ecosystems and public security even at trace levels. Therefore, it is essential to exploit an ultrasensitive technique to determine the levels of heavy metal ions. In this work, hierarchical MgFe-layered double hydroxide (MgFe-LDH) microspheres have been successfully immobilized on the graphene nanosheets surface via a facile one-step hydrothermal route. Benefiting from the synergistic effects associated with high specific surface area, strong affinity of hierarchical MgFe-LDH architecture toward heavy metal ions, good electrical conductivity and effective electron transfer efficiency of graphene, the resulting composite (denoted as MgFe-LDH/graphene) is explored as an electrochemical sensor for simultaneous detection of Pb(II) and Cd(II) in aqueous medium. As a consequence, MgFe-LDH/graphene modified electrode exhibits low detection limit of 5.9 nM for Cd(II) and 2.7 nM for Pb(II), which are dramatically lower than the respective values of 3 ppb (27 nM) and 10 ppb (48 nM) in domestic water permitted by the World Health Organization (WHO). Meaningfully, the proposed electrochemical sensor shows specific recognition capability to Pb(II) and Cd(II), excellent reproducibility in repetitive measurements as well as feasibility in real water analysis.

* Corresponding author.
E-mail address: yxzhang@issp.ac.cn (Y. Zhang).

https://doi.org/10.1016/j.cej.2018.04.172
Received 27 February 2018; Received in revised form 20 April 2018; Accepted 24 April 2018
Available online 26 April 2018
1385-8947/

1. Introduction

With the rapid development of global industrial activities, heavy metal pollution has been evolved into a prominent environmental problem all over the world. Heavy metal ions, particularly Cd(II) and Pb (II), are alarming contaminants to environmental safety and public health due to their high toxicity even at low concentrations, non-biodegradability, and tendency of accumulation in the body via the food chain [1–9]. Hence, it is of vital importance to develop a feasible technique for detection of heavy metal ions from the viewpoint of environmental monitoring and human health concerns. With the increase of public awareness of environmental protection, diverse analytical techniques, such as atomic absorption spectroscopy [10,11], inductively coupled plasma optical emission spectroscopy [12–14], Raman spectrometry [15,16], spectrofluorimetry [17–20] and spectrophotometry [21] have been widely established for the detection of heavy metal ions in industrial wastewater and drinking water. In spite of high sensitivity and accuracy of these methods, they are not appropriate for on-site measurements on account of cumbersome and sophisticated apparatus, complicated pretreatment procedures and tedious analysis time. By contrast, electrochemical technique has received increasing attention in the analytical field due to its fascinating features such as simple handling, rapid response, low limit of detection (LOD), superior sensitivity and favorable selectivity [22–31].

Over the past decades, various materials such as inorganic, organic and bio-materials have been utilized to construct the electrochemical sensors for the determination of heavy metal ions. Nevertheless, most electrode materials suffer from some inherent limitations, e.g. low surface areas and poor electrical conductivity. Therefore, considerable efforts have been devoted to exploring advanced materials with well-defined structural design to improve the electrochemical sensing performances. As we all know, the sensitivity of electrochemical sensors is highly associated with the accumulating ability of modified electrode materials toward the target heavy metal ions. In this sense, layered double hydroxides (LDHs) are regarded as excellent candidates owing to flexible ion-exchangeability and tuneable compositions [32,33]. Particularly, surface hydroxyl groups and various interlayer anions of LDHs endow them with strong affinity to specific heavy metal ions, consequently contributing to enhanced electrochemical active sites [34–36]. Unfortunately, single LDHs usually possess rather poor electrical conductivity, which inhibits their potential applications in electrochemical sensing fields.

To overcome such limitation, one effective and feasible strategy has been proposed based on the rational integration of LDHs with conductive carbon materials. Among various carbon materials, graphene with a two-dimensional structure has been widely used in the environmental and energy fields on account of good electrical conductivity, large specific surface area, and excellent chemical/electrochemical stability [37–42]. On the one hand, ultrathin graphene nanosheets provide a platform for the rapid diffusion of electrolyte, facilitating the interfacial charge transfer during the electrochemical reaction. On the other hand, the incorporation of LDHs can effectively prevent the agglomeration of graphene and thereby is beneficial for full exposure of the electrode surface. Meanwhile, graphene is usually involved in abundant oxygen-containing functional groups, which are advantageous for preconcentrating heavy metal ions. Consequently, it is highly expected that hierarchical MgFe-LDH/graphene hybrid materials can greatly enhance the electrochemical detection toward heavy metal ions.

Based on the above considerations, in this work, a flower-like MgFe-LDH/graphene hierarchical architecture has been successfully prepared through a facile one-step hydrothermal route. The morphological and structural characteristics of the as-fabricated MgFe-LDH/graphene composite are systematically investigated through diverse characterization methods. The electrochemical sensing performances of the developed sensor, including sensitivity, LOD, linear range and selectivity, are investigated in detail by square wave anodic stripping voltammetry (SWASV). Furthermore, the repeatability and reproducibility study as well as real water sample analysis are also carried out to further evaluate the accuracy and reliability of the proposed sensor toward determination of Pb(II) and Cd(II).

2. Results and discussion

2.1. Morphological and structural characterization

The morphologies and structural details of the as-synthesized MgFe-LDH/graphene composite are investigated via field emission scanning electron microscope (FE-SEM) observation. As can be seen from Fig. 1a, the resulting composite displays a three-dimensional hierarchical structure, in which flower-like MgFe-LDH microspheres are composed of numerous ultrathin nanoflakes interlaced with each other. A closer observation reveals that MgFe-LDH microspheres are imbued with a layer of graphene voile. It should be mentioned that the crystallization

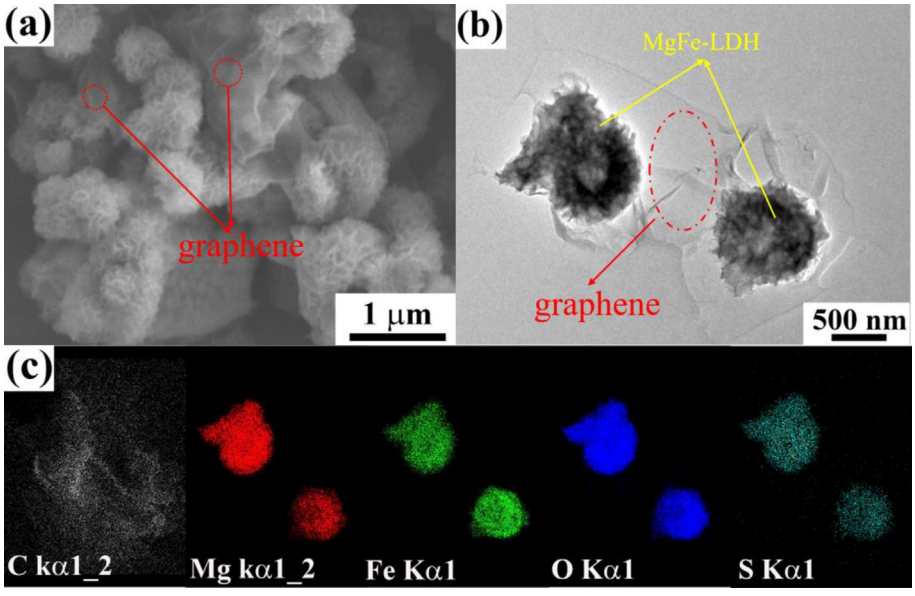


Fig. 1. (a) SEM image of MgFe-LDH/graphene composite; (b) and (c) TEM image of MgFe-LDH/graphene and the corresponding element mappings.