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Selective detection of toxic Pb(II) ions based on wet-chemically prepared nanosheets integrated CuO–ZnO nanocomposites

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ABSTRACT

The present study describes a selective detection methodology for hazardous metal ions based on low-dimensional nanosheets (NSs) integrated CuO–ZnO composite materials. A large-scale synthesis of NSs by wet-chemical process is performed using alkaline reducing agents at higher pH medium. The prepared NSs are characterized in terms of their morphological, structural and optical properties, and efficiently applied for the toxic metal ions detection. The detailed structural, compositional, and optical characterization of NSs are evaluated by XRD, FT-IR, XPS, EDS, and UV–vis spectroscopy, which confirmed that the obtained NSs are well-crystalline CuO–ZnO and possessed good optical properties. The CuO–ZnO NS morphology is investigated by FE-SEM, which confirmed that the NS possesses microstructure shape and growth in large-quantity. The analytical application of CuO–ZnO NSs is studied for a selective extraction of toxic lead-divalent [Pb(II)] ions prior to its determination by inductively coupled plasma-optical emission spectrometry (ICP-OES). The selectivity of doped NSs phase is investigated for eight different metal ions, including Cd(II), Cu(II), Hg(II), La(III), Mn(II), Pb(II), Pd(II), and Y(III) under similar experimental conditions. From the selectivity study, it is confirmed that the composite CuO–ZnO NS phase is the most toward Pb(II) ions according to the magnitude of distribution coefficient (K_d) values, such as Pb(II) > Y(III) > Cd(II) > La(III) > Hg(II) > Cu(II) > Mn(II) > Pd(II). The uptake capacity for Pb(II) is experimentally calculated to be $\sim$82.66 mg g^{-1}.

1. Introduction

Lead poison is one of the major problems that concerned in human health and biological living systems [1]. Di-valent lead ions are absorbed mainly via respiration as well as ingestion system from the unhealthy lead-containing environments. There are increasing attention in adsorption, absorption, catalysis, ion-sieves, and rechargeable materials. Lead poisoning in human health is affected, when blood lead-level reaches to 10.0 μg/dL or more [2,3]. However, children are particularly very sensitive to this Pb(II) poisoning because of their weak growing central nervous system [4]. Although few natural sources are concerned for Pb(II) existence, such as soil-erosion, volcanic emissions, mining, and industrial activities delivered about 90% of Pb(II) into environment, where lead-containing dust particles are significantly polluted the air as well as soils [5,6]. The worldwide use of Pb(II) containing gasoline and fuels has regularly eradicated from the source of Pb(II) pollutant in air in many countries. Conversely, Pb(II) is still extensively used and pervasively caused the environmental contamination from activities that range from production and use of car batteries, paints and pigments, and glazed earthenware as well as soldering and piping in water distribution systems [7]. As such, the childhood Pb(II) poisoning has become one of the world great problems [8]. Heavy-metals are one of the most toxic groups of water pollutants and considered to be harmful in the environment. Pb(II) has become an eco-toxicological hazard of prime interest due to their toxicity, accumulation in living organisms and persistent in nature, even at low concentrations [9–11]. The typical concentration of Pb(II) in natural water lies between 2.0 and 10.0 ng mL^{-1}, whereas the upper limit recommended by World Health Organization (WHO) is less than 10.0 ng mL^{-1} [12]. Concern over this problem, it has conducted to the improvement of sensitive and competent techniques for monitoring toxic metal ions in the environment. Various analytical methods have been employed to assess the concentration level of toxic metal ions in aqueous medium, such as atomic absorption spectrometry (AAS), ICP-OES, cyclic voltammetry as well as anodic stripping voltammetry (ASV), and ion chroma-

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tography (IC) [13–17]. However, metal ions, in particular at ultra-trace concentration, it could not be directly measured in aqueous systems by analytical methods due to the lack of sensitivity and selectivity of these methods. Therefore, an efficient separation or adsorption method is usually required prior to the detection of toxic metal ions for sensitive, accurate and interference-free determination [18]. There are various analytical techniques for extraction of analyte of interest prior to their detection by an appropriate analytical technique, including liquid–liquid extraction [19], ion exchange [20], co-precipitation [21], cloud point extraction [22], and solid-phase extraction (SPE) [23,24]. SPE is considered to be one of the most popular methods because it reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Because of the popularity of SPE for selective extraction of analytes, several adsorbents have appeared, such as alumina [25], C18 [26], molecular imprinted polymers [27], cellulose [28], silica-gel [29], activated carbon [30] and carbon nanotubes [31].

Doped nanostructure materials have attracted a broad interest due to their unique properties and immense potential applications [32–36]. Semiconductor nanomaterial has been recognized as a promising host nano-substance for transition materials. It is exhibited a stable morphological structure composed a number of regular phases with geometrically-coordinated metals and oxide atoms alternately along the axes [37–39]. Transition-metals doped in semiconductor materials have concerned profound research attempt for their exceptional and outstanding optical and structural properties, and versatile applications [40–43]. Recently, an extensive improvement has been made on transition metal-oxides codoped ZnO-based nanomaterials actuated by both fundamental sciences and potential advanced technologies [44]. The doped semiconductor nanomaterials display promising uses as transistors [45], UV photo-detectors [46–49], sensors [50–56], field emission electron sources [57,58], metal-ions detection [59,60], nanostructure materials [61,62], nano-scale power generators [63,64], and many other functional devices [65–71]. Hydrothermal route is also a competent method that controlled the energy states of ZnO, which can be further developed by the changing in doping concentrations of transition-materials. Nanostructure metal oxides have attracted considerable attention owing to their potential applications in fabricating nano-scale electronics, electro-analytical, selective detection of metal ions, opto-electronics, biological devices, nanocomposites, electron field emission sources for emission displays, biochemical detections, and surface enhanced Raman properties, etc. [72–77]. It is also fascinated a broad-interest owing to their exceptional optical and structural properties as well as potential applications. It is displayed a regular morphological nanostructure, which composed of regular phases with geometrically-coordinated metals and oxide atoms along with the axes. Semiconductor nanostructure materials have concerned significant research efforts for its exceptional and outstanding properties as well as versatile applications [78–82]. In last decade, transition-metal doped materials have been widely studied as promising anodes for *Laser-induced-Breakdown-Spectroscopy's* [83,84]. Among them, transition metal oxide has attracted much interest due to their high surface area, large capacity, highly-stable, non-toxic, economical approach, and facile synthesis. It is a p-type semiconductor material with a band-gap energy ranging from 1.21 to 1.5 eV [85–87], which is studied for various applications in photo-thermal [88], photo-conductive [89,90], magnetic [91], and super-conductor devices [92–94], etc. Various efforts have been focused toward the fabrication of nano-structured to develop their performance in currently existing applications. It is also considered as one of the promising artificial mediators owing to their properties and functionalities [95–100]. Because the electrochemical properties of CuO can be greatly affected by morphologies, intensive research has focused on the controlled preparation of various CuO nanostructures over the two decades [101–104,13,105,106]. However, it is still a great challenge to achieve high-rate capability and crystallinity in pure doping nanostructures. It is well recognized that a smaller size of CuO can lead to higher capacity and higher rate capability as a dopant, which reduced the over potential and allowed faster reaction kinetics to detect the metal ions [107,16,108–110,18]. Therefore, the synthesis of CuO nanostructures with ultrafine size is a promising approach to obtain improved large-surface area and high-aspect-ratio in pure CuO nanostructures. Due to significant properties of semiconductors, the doped nanomaterials are attained a considerable attention in terms of controlled growth of crystalline material in huge quantity. Various growth techniques have been employed including vapor–liquid–solid growth [111], epitaxial-growth [20], vapor–solid growth [21], wet-chemical methods [22], and electro-spinning [23]. The aim of this investigation was to evaluate the utility and the analytical efficiency of CuO–ZnO NSs phase as adsorbent in terms of selectivity and adsorption capacity of toxic Pb(II) ion prior to its determination by ICP-OES. The selectivity of NSs phase toward eight metal ions, including Cd(II), Cu(II), Hg(II), La(III), Mn(II), Pb(II), Pd(II) and Y(III), was investigated in order to evaluate the effectiveness of NSs on the extraction of selected metal ions. Data obtained from the selectivity study, it is observed that the NS phasea are the most selective toward toxic Pb(II) in comparison towards other metal ions. The adsorption capacity for toxic Pb(II) is experimentally found to be $\sim$82.66 mg g^{-1}. Results of adsorption isotherm are also confirmed that the adsorption process is mainly monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites.

2. Experimental sections

2.1. Materials and methods

Mercuric nitrate [$Hg(NO_3)_2$], lanthanum nitrate [$La(NO_3)_3$], palladium nitrate [$Pd(NO_3)_2$], yttrium nitrate [$Y(NO_3)_3$], copper chloride [$CuCl_2$], zinc chloride [$ZnCl_2$], sodium hydroxide [NaOH], and all other chemicals were used of analytical grade and obtained from Sigma–Aldrich (Milwaukee, WI, USA). Stock standard solutions of 1000.0 mg L^{-1} [Cd(II), Cu(II), Mn(II) and Pb(II)] were also obtained from Sigma–Aldrich. All reagents used were of high purity and spectral purity grade, and doubly distilled deionized water was used throughout. The λ_{max} ($\sim$303.2 nm) of calcined CuO–ZnO heterostructures was evaluated with UV/vis spectroscopy (UVO-2960, LABOMED Inc.). FT-IR spectra were performed with a spectrophotometer (Spectrum-100 FT-IR) in the mid-IR range, which was purchased from Bruker, USA. The powder X-ray diffraction (XRD) prototypes were assessed with X-ray diffractometer (Rigaku X-ray difractometer, Mini-Flex 2) equipped with Cu Kα1 radiation (λ = 1.5406 nm) using a generator voltage ($\sim$40.0 kV) and a generator current ($\sim$35.0 mA) applied for this purposed. Morphology of doped CuO–ZnO NSs was investigated on FE-SEM instrument (FESEM; JSM-7600F, Japan). Elemental analysis of NSs was investigated using EDS from JEOL, Japan. The XPS measurements were executed on a Thermo Scientific K-Alpha KA1066 spectrometer (Germany). Monochromatic Al Kα X-ray radiation sources were used as an excitation source, where beam-spot size was kept in 300.0 μm. The spectra were recorded with the fixed transmission mode, where pass-energy fixed at 200.0 eV. The scanning of the spectra was performed at pressures less 10^{-8} Torr. ICP-OES measurements were done by using the Perkin Elmer ICP-OES model Optima 4100 DV, USA. The ICP-OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP-OES spectrometer was used with following parameters: