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Detection of trivalent-iron based on low-dimensional semiconductor metal oxide nanostructures for environmental remediation by ICP-OES technique

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Abstract

A large-scale synthesis of undoped low-dimensional semiconductor metal oxide nanostructures (ZnO nanoparticles, NPs) by simple wet-chemical method was performed using reducing agents at low temperature. The NPs were characterized in terms of their morphological, structural, and optical properties, and efficiently applied for the metal ions uptake. The detailed structural, compositional, and optical characterizations of the NPs were evaluated by powder X-ray diffraction pattern (XRD), Fourier-transform infra-red spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Electron dispersion spectroscopy (EDS), and UV–vis. spectroscopy, respectively which confirmed that the obtained NPs are well-crystalline undoped ZnO and possessed good optical properties. The ZnO NSs morphology was investigated by FESEM, which confirmed that the calcined materials were spherical shape in nano-level and growth in huge-quantity. The analytical efficiency of newly synthesized ZnO NPs was also investigated for a selective separation of trivalent iron [Fe(III)] prior to its determination by inductively coupled plasma-optical emission spectrometry (ICP-OES). The selectivity of ZnO NPs towards different metal ions, including Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), Zn(II), and Zr(IV), was studied. Data obtained from the selectivity study suggested that that ZnO NPs phase was the most selective towards Fe(III). The static uptake capacity of Fe(III) was found to be $\sim 79.80\ \mathrm{mg\ g^{-1}}$. Moreover, adsorption isotherm data also provided that the adsorption process was mainly monolayer on a homogeneous adsorbent surface.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; C. Optical properties; D. ZnO; E. Structural applications

1. Introduction

The development of simple, rapid and efficient methods has become of interest for monitoring metal ions in the environment. Several analytical methods have been applied to analyze metal ions in aqueous solutions, such as atomic absorption spectrometry [1], inductively coupled plasma-optical emission spectrometry (ICP-OES) [2], anodic stripping voltammetry [3], and ion chromatography [4]. However, analytical methods can not directly measure metal ions, in particular at ultra-trace concentration, in aqueous systems due to the lack of sensitivity and selectivity of these methods. Therefore, an efficient separation procedure is usually required prior to the determination of noble metals for sensitive, accurate and interference-free determination of noble metals [5]. Several analytical methods can be used for separation of analyte of interest, including liquid–liquid extraction [6], ion exchange [7], coprecipitation [8], cloud point extraction [9] and solid phase extraction (SPE) [10]. SPE is considered to be one of the most powerful techniques because it minimizes solvent usage and exposure, disposal costs, and extraction time for sample preparation. Several adsorbents have appeared because of the popularity of SPE for selective extraction of analytes, such as alumina [11], C18 [12], molecular imprinted polymers & cellulose [13], silica-gel [14,15], activated carbon [16,17] and carbon nanotubes [18,19].

The semiconductor nanomaterials have attracted potential interest due to their unique properties and potential applications

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in all branches of science and technology. Semiconductor nanostructure materials have attracted an extensive attention owing to their unique properties and potential applications [20-22], which have been recognized as promising nanomaterials. It is exhibited a controlled morphology and composed of a number of irregular phases with geometrically-coordinated codoped metals and oxide atoms, which stacked alternately along the axes [23–25]. For characteristic physical and chemical properties of nanomaterials, ZnO semiconductor has been also explored the significant attention due to their large-surface area and controlled sizes [26–28]. However, ZnO nanomaterials have also drawn an enormous interest towards itself owing to their extrinsic, remarkable and wonderful features in electrical, optical, thermal, and mechanical properties as compared to their un-doping materials. It is also essential for the facile synthesis of ZnO nanoparticles in order to achieve the exceptional quality of semiconductor structures. Advances in nanotechnology with innovative solid crystalline phases, semiconductor nanomaterial have been regulating a key-task in the fabrication and improvement of very precise, perceptive, accurate, sensitive, and stable crystalline adsorbent. The exploration for even miniature nanomaterials accomplished of nano-level imaging and controlled morphology, the doping materials (even physical) have lately expanded the spot-light of awareness of the scientist, mainly for control determination, owing to the amplifying essential for environmental safety and health care fields [29,30]. Semiconductor ZnO is the model materials for metal ions detection due to high crystalline surface areas and extensively employed as solid phase adsorbent for recognition, and quantification of various effective metal ions [31,32].

Finally, the objective of this study was to investigate the analytical potential of ZnO NPs phase as an adsorbent on the selectivity and adsorption capacity of trivalent-iron [i.e., Fe(III)] prior to its determination by ICP-OES. The selectivity of ZnO NPs towards different metal ions, including Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), Zn(II) and Zr(IV), was evaluated in order to study the effectiveness of ZnO NPs on the adsorption of selected metal ions. Based on the selectivity study, it was concluded that the selectivity of ZnO NPs phase was the most towards Fe(III). The static uptake capacity for Fe(III) was determined to be ~79.80 mg g^{-1}. Results of adsorption isotherm also confirmed that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. Adsorption data of Fe(III) were well fit with the Langmuir classical adsorption isotherm.

2. Experimental sections

2.1. Materials and methods

Stock standard solutions of 1000.0 mg L^{-1} Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), Zn(II), and Zr(IV) were purchased from Sigma-Aldrich (Milwaukee, WI, USA; http://www.sigmaaldrich.com). Zinc chloride, sodium hydroxide, and other chemicals were used of analytical and spectral purity grade. Doubly distilled deionized water was also used throughout experimental studies. The powder X-ray diffraction (XRD) prototypes were assessed with X-ray diffractometer (Rigaku X-ray difractometer, Mini-Flex 2; http://www.rigaku.com) equipped with Cu-K$_{\alpha}$1 radiation (λ=1.5406 nm) using a generator voltage of 40.0 kV and a generator current of 35.0 mA applied for the purposed. The $\lambda_{\max}$ (377.0 nm) of calcined ZnO nanostructures was evaluated with UV/visible spectroscopy (UVO-2960, LABOMED Inc.; http://www.labomed.com). FT-IR spectra were performed with a spectrophotometer (Spectrum-100 FT-IR; http://www.perkinelmer.com) in the mid-IR range, which was purchased from Bruker, USA. The XPS measurements were executed for ZnO NPs by a Thermo Scientific K-Alpha (KA1066 spectrometer, Germany; http://www.thermoscientific.com). Monochromatic AlKα X-ray radiation sources were used as excitation sources, where beam-spot size was kept in 300.0 μm. The spectra was recorded in the fixed analyzer transmission mode, where pass energy was kept at 200.0 eV. The scanning of the spectra was performed at pressures less 10^{-8} Torr. Morphology of undoped ZnO NPs was investigated on FESEM instrument (FESEM; JSM-7600F, Japan; http://www.jeol.co.jp). Elemental analysis of Zn NPs was investigated using EDS from JEOL, Japan. ICP-OES measurements were acquired by use of a Perkin Elmer ICP-OES (Model Optima 4100 DV, USA; http://www.perkinelmer.com). 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: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min^{-1}; auxiliary gas (Ar) flow, 0.2 L min^{-1}; nebulizer gas (Ar) flow, 0.8 L min^{-1}; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min^{-1}; integration time, 3 s; replicates, 3; wavelength range of mono-chromator 165–460 nm. Selected metal ions were measured at wavelengths of 228.80 nm for Cd(II), 238.90 nm for Co(II), 267.72 nm for Cr(III), 327.39 nm for Cu(II), 259.94 nm for Fe(III), 221.65 nm for Ni(II), 206.20 nm for Zn(II) and 343.82 nm for Zr(IV).

2.2. Samples preparation and procedure for metal ions uptake

Stock solutions of Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), Zn(II) and Zr(IV) were prepared in 18.2 MΩ·cm distilled deionized water and stored in the dark at 4.0 °C. For selectivity study, standard solutions of 5.0 mg L^{-1} of each metal ion were prepared and adjusted to pH value of 5.0 with acetate buffer. Then, each standard solution was individually mixed with 25.0 mg ZnO NPs. In this study, a fixed pH value of 5.0 was chosen for all metal ions in order to avoid any precipitation of other species, in particular for Fe(III). For example, Fe(III) usually forms a precipitation of $Fe(OH)_3$ with buffer solutions at pH value greater than 5.0. For the study of Fe (III) static adsorption capacity, standard solutions of 0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 50.0, 75.0, 125.0 and 150.0 mg L^{-1} were prepared as above, adjusted to the optimum pH value of 5.0 and individually mixed with 25.0 mg ZnO NPs. All mixtures were mechanically shaken for 1.0 h at room temperature.