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Citric acid assisted synthesis of manganese tungstate nanoparticles for simultaneous electrochemical sensing of heavy metal ions

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ABSTRACT

Manganese tungstate nanoparticles (NPs) were successfully synthesized via a simple and cost effective citric acid assisted solution combustion method. Rietveld refinement of PXRD pattern indicates the formation of pure wolframite phase of manganese tungstate. Transmission electron microscope (TEM) analyses confirm the spherical shaped nanoparticles with average particle size ranging from 12 to 26 nm. The ultra-light combustion derived manganese tungstate NPs exhibits mesoporous nature with the estimated band gap 2.9 eV. The synthesized NPs were found to be an excellent electrode modifier for the simultaneous detection of Pb(II), Cd(II), Cu (II) and Hg(II) ions at nanomolar (nM) concentration. The present electrochemical sensor exhibits wide linearity of 10 – 500 nM with limit of detection based on 3σ method is 3.3, 3.5, 2.9 and 3.1 nM for Pb(II), Cd(II), Cu(II) and Hg(II) respectively. Additionally, room temperature photoluminescence emission spectrum exhibits an intense band at 445 nm that can be attributed to $^1A_1$ ground-state to the high vibration $^1T_2$ energy levels of distorted [WO_6] octahedral groups.

1. Introduction

Over the past few years, due to their ultrafine structures and unprecedented properties, metal oxide nanomaterials have been receiving intensive research attention. Among various kinds of metal oxides, transition metal tungstates of the form MWO_4 (M = Fe, Co, Ni, Cu, Zn, and Cd) have wide applications in different interdisciplinary fields owing to their distinctive physicochemical properties allied with dimensions in the nanometer regime [1–4]. As a member of transition metal tungstates, $MnWO_4$ with wolframite phase has been attracted extensive research interests due to its novel applications in molecular imaging [5], photocatalysis [6], multiferroic [7], electrochemical [8] and humidity sensors [9]. Also, it has important electrochromic properties with long lasting structural stability.

Owing to its extensive applications in various domains of science and technology, $MnWO_4$ has been synthesized by variety of synthetic methods including hydrothermal synthesis [10], solid state approach [11], coprecipitation [12], sonochemical method [13] and microwave assisted sol–gel synthesis [14]. However, the above synthetic routes have many shortcomings such as multistep process, long reaction time, high calcination temperatures and requirement of special experimental arrangements. For this reason, there is a significant requirement to develop a novel synthetic protocol that permits the rapid and inexpensive preparation of nanoscale materials with desired phase pure compositions. Solution combustion synthesis (SCS) is an alternative technique which can be used to synthesis metal oxides in nano scale regime, which is a simple, time and energy saving process compared to other methods, especially for the synthesis of phase pure mixed metal oxides. The additional advantages of SCS are that the large specific surface areas and the well-developed porosity caused by gas evolution during combustion process leads to tailored properties in the resulting materials [15]. To this end, we have applied SCS method to synthesize various mixed metal oxides with nano scale range in our previous reports such as, selective synthesis of meta stable scheelite and stable wolframite $CdWO_4$ nanoparticles [16] and nanocrystalline monoclinic-$BiVO_4$ photocatalyst for H_2 evolution [17].

In recent years, development of sensitive and selective detection method of heavy metals with a cost-effective and handy protocol is of paramount important. Since heavy metal ions are non-biodegradable, presence of trace amount will cause serious health disorders in human beings, thus measurement of these metal ions at diminutive concentration level is required [18]. Although, many analytical methods

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such as UV–Vis spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectroscopy (XFS) and atomic absorption spectroscopy (AAS) are employed commonly, however they required fairly expensive instrumentation and expert personnel to perform the analysis. Quite the reverse, the electrochemical sensing method provides an alternative to the above said analytical methods, as it is simple, low cast and requires short analytical time with high sensitivity and selectivity [19]. Recent reports have shown that nanostructured metal oxides as electrode modifiers display good activity towards electrochemical sensing of heavy metal ions due to their high surface activity, chemical inertness, thermal stability, catalytic efficiency, strong adsorption ability and large surface-to-volume ratio [20,21]. Despite many reports have been found for electrochemical sensing of toxic metals using metal oxides as electrode modifier, there are merely a few publications on simultaneous determination of Pb(II), Cd(II), Cu(II) and Hg(II) ions in real sample matrices. For instance, Rudra Kumar et al. demonstrated the electrochemical sensing of toxic metal ions using graphene oxide/nickel tungstate (RGO/$NiWO_4$) nanocomposite synthesized by hydrothermal method followed by calcination and pyrolysis in air and nitrogen atmosphere at 600 °C for two hours [22], Xiong et al. employed RGO–Fe_3O_4 nanocomposite stripping voltammetric and mutual interference analysis of heavy metal ions [23] and Lee et al. demonstrated toxic metal sensing in soil and tap water using RGO decorated tin nanoparticles [24]. However, the above methods involve complex and multi step process for the synthesis of electrode modifier. In this context, it is important to develop materials of low cost, chemically inert and environmentally benign.

Here, we present a simple and cost effective solution combustion synthesis of manganese tungstate in nano size scale with the assistance of citric acid as fuel. Rietveld refinement of powder X-ray data has been carried out using 'General Structure Analysis System' (GSAS) to obtain the unit cell parameters and crystal structures. The major innovation of this study is that the use of synthesized nanoparticles as glassy carbon electrode (GCE) modifier in the simultaneous quantification of Pb(II), Cd(II), Cu(II) and Hg(II) ions. Our results suggest that $MnWO_4$ nanoparticles could be used effectively to improve the sensitivity and selectivity of electrode.

2. Experimental

2.1. Materials

In this study, analytical grade manganese nitrate tetra-hydrate, citric acid and hydrogen peroxide were obtained from Aldrich Chemicals. Tungsten metal powder (Fine powder 99 +) was obtained from MERCK chemicals and used as precursors without further purification. In our experiments, precursor solution-A has been prepared by dissolving 0.819 g $Mn(NO_3)_2{\cdot}4H_2O$ and 1.142 g citric acid (Ox/f = 1:3) in 2 mL NH_4OH solution (25%). Solution-B was prepared by dissolving 0.6 g of tungsten metal powder in 5 mL H_2O_2. Then solution-B was slowly added to the solution-A under constant stirring to obtain homogenous reactant solution in a beaker. The obtained precursor solution was kept in a furnace maintained at 500 ± 10 °C, the solution boils to give a voluminous mass which was calcined to give pure $MnWO_4$ NPs for 30 min at same temperature.

2.2. Preparation of $MnWO_4$ NPs modified electrode

The bare glassy carbon electrode was polished using alumina slurry (1.0 μm, 0.3 μm and 0.05 μm) prior to modification to remove the adsorbed impurities. Then 5 mg of as-prepared $MnWO_4$ nanoparticles were dispersed in 5 mL of double distilled water and sonicated for about 30 min to get homogenously dispersed solution. Then, 5 μL of the dispersed solution was drop coated onto the pretreated bare glassy carbon electrode and dried at ambient temperature. Further, the $MnWO_4$ NPs modified electrode was used as the working electrode for metal ions quantification.

2.3. Electrochemical measurements

Electrochemical measurements were performed on CHI 6194B [CH Instruments, Texas, USA] at room temperature in an electrochemical quartz cell of volume 10 mL-capacity with a standard three electrode system where $MnWO_4$ modified GCE as working electrode, platinum wire as auxiliary electrode and Ag/AgCl as reference electrode.

Electrochemical measurements of Pb(II), Cd(II), Cu(II) and Hg(II) ions were performed using electrochemical techniques such as cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) in the potential range − 1.2 TO 0.5 V with an amplitude of 0.01 V and pulse width of 0.05 s. The $MnWO_4$ NPs modified electrode was immersed into the cell containing 0.1 M KCl, acetate buffer solution (pH 5) and target metal ions which were stirred for 3 min to pre-concentrate the metal ions at open circuit potential. Then, the pre-concentrated metal ions were reduced at a reduction potential of − 1.2 V and subsequently stripped off from the electrode surface into the bulk of the electrolytic solution by sweeping the potential in the opposite direction after 30 s of equilibration time.

2.4. Characterization

The as synthesized samples were characterized using X-ray powder diffractometer (PANalytical X'pert PRO MPD) equipped with graphite-filtered Cu-Kα radiation source (α = 1.541 Å), the 2θ ranges from 10° to 80° in steps of 0.02°. Morphologies and microstructures of $MnWO_4$ NPs were characterized by scanning electron microscope (JEOL-JSM-6490 LV) and transmission electron microscope (TEM, JEOL JEM-2100). N_2 adsorption-desorption isotherms and the Brunauer–Emmett–Teller (BET) specific surface area of the as-prepared samples were acquired by using a gas sorption analyzer (Quantachrome Corporation NOVA 1000) operated at 77 K. Fourier transform infrared (FT-IR) spectra were measured using a Bruker Alpha-P spectrometer (ATR mode, diamond crystal, 400–4000 cm^{-1}). UV–vis UV-Vis diffuse reflectance spectroscopy (DRS) was performed on a Shimadzu 3101 UV–Vis spectrophotometer. Photoluminescence (PL) study was carried out on a Perkin-Elmer LS-55 luminescence spectrometer using Xe lamp at room temperature.

3. Results and discussion

In the present combustion reaction system, for the low-cost synthesis of $MnWO_4$ nanoparticles, citric acid has been used as complexing agent as well as fuel. Citric acid forms water soluble manganese citrate complexes (CA:Mn^{2+} = 1:2) in presence of NH_4OH solution [25]. This manganese citrate solution facilitates the homogenous mixing of precursor ions in the combustion reaction. Peroxotungstic acid was used as precursor solution for tungsten ions, which was prepared by dissolving tungsten metal powder in H_2O_2 solution at 60 °C. The following reactions may takes place.

$$Mn(NO_3)_2{\cdot}4H_2O + 2\,C_6H_8O_7 + 6\,NH_4OH \rightarrow [Mn\,(C_6H_8O_7)_2]\,(NH_4)_4 + 10\,H_2O + 2\,NH_4\,NO_3$$

$$W_{(s)} + 4H_2O_2 \rightarrow WO_2\,(O_2)\,(OH_2) + 3H_2O$$

$$[Mn\,(C_6H_8O_7)_2]\,(NH_4)_4 + WO_2\,(O_2)\,(OH_2) + xO_2 \rightarrow MnWO_4 + 12\,CO_2 + 17H_2O + 2N_2$$

3.1. Refinement and crystal structure of $MnWO_4$ nanoparticles

Rietveld refinement of experimentally obtained diffraction pattern was carried out using GSAS (General structure analysis system) software to determine the phase composition and crystal structure of the