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Preparation and photoluminescence properties of $MMoO_4$ (M = Cu, Ni, Zn) nano-particles synthesized via electrolysis

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ABSTRACT

Metal molybdate ($MMoO_4$, M = Cu, Ni, Zn) nano-particles were successfully synthesized by electrochemical method in a cation exchange membrane electrolytic cell with Na_2MoO_4 solution as anolyte, diluted hydrochloric acid (HCl) as catholyte, metal (Cu, Ni, Zn) as anode and stainless steel as cathode. The composition, morphology, structure, microstructure and photoluminescence property of the synthesized $MMoO_4$ were investigated and characterized. The results show that the photoluminescence spectra of electrolytic synthesized $MMoO_4$ have fine structures, which is markedly different from the existing research.

1. Introduction

Metal molybdate is a family of inorganic functional materials as important as metal tungstate [1,2], which has been widely used in many aspects, such as photoluminescence devices, microwave components, optical fibers, humidity sensors, magnetic devices, photocatalysts, electrocatalysts, supercapacitor materials, lithium batteries, fuel cells, solar energy conversion, corrosion protection, and so on [3–18]. As reported in typical examples, copper molybdate ($CuMoO_4$) was studied as photocatalyst for the oxidation of methane to methanol [19], that depended on the O 2p → Cu 3d excitation of $CuMoO_4$ under visible light. Shale/natural gas with methane as the primary component could be converted into shippable liquid methanol at the catalysis of $CuMoO_4$, which is a comparable technology to the technologies converting methane into liquid aromatic hydrocarbons [20]. $NiMoO_4$ was studied as supercapacitor material in recent research [21–23]. Phosphor properties of doped $ZnMoO_4$ were studied and used for light emitted diode application [24].

Several methods have been applied to synthesize metal molybdates in reports, including hydrothermal method, sol-gel method, microwave-assisted synthesis method, molten salt method, coprecipitation method, microemulsion-based synthesis, sonochemical method, polymerized precursor method, solid state reaction method and electrochemical synthesis [25–35]. Precursors for $MMoO_4$ synthesis are adapted to the adopted methods. To obtain $CuMoO_4$, soluble molybdates such as Na_2MoO_4, $(NH_4)_6Mo_7O_{24}\cdot 24H_2O$ and soluble copper salts such as $CuCl_2$, $CuSO_4\cdot 5H_2O$ were used in hydrothermal method [36–38] and sol-gel method [39]. MoO_3 as the molybdenum source and Cu or CuO as the copper source were used in the solid-state reaction [40]. To prepare $NiMoO_4$, soluble nickel salts such as $Ni(NO_3)_2\cdot 6H_2O$ and $Ni(CH_3COO)_2\cdot 4H_2O$, were used as the nickel source [41]. $Zn(CH_3COO)_2\cdot 2H_2O$ was used as the zinc source for the synthesis of $ZnMoO_4$[42].

In this paper, an electrochemical method was introduced to synthesize $MMoO_4$ (M = Cu, Ni, Zn) nano-particles. A cation exchange membrane electrolytic cell was established as illustrated in Scheme 1; pure metal (Cu, Ni, Zn) was used as the anode, stainless steel mesh as the cathode, and sodium molybdate solution as the anolyte, diluted chloride acid as the catholyte. A constant-voltage applied on the electrolytic cell, the cation (Na^+) in the anolyte

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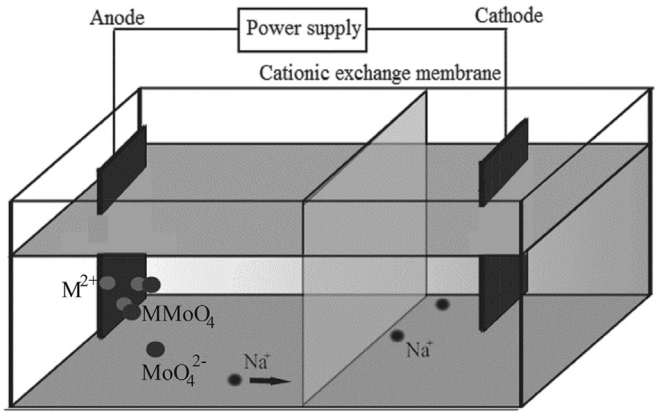

Scheme 1. Electrolytic cell with cation exchange membrane for electrochemical synthesis of $MMoO_4$ (M = Cu, Ni, Zn).

will move through the cation exchange membrane into the catholyte (HCl). The metal anode was dissolved into the anolyte as metal ion, which combined with MoO_4^{2-} in the anolyte to form the metal molybdate $MMoO_4$. Pure copper anode was used for $CuMoO_4$ synthesis, pure nickel anode for $NiMoO_4$ synthesis, and pure zinc anode for $ZnMoO_4$ synthesis.

2. Experimental

2.1. $MMoO_4$ (M = Cu, Ni, Zn) synthesis

$Na_2MoO_4 \cdot 2H_2O$ and HCl used in the present experiment were of analytical purity and as received without further purification. Copper, nickel and zinc foil (in 99.99% purity) were washed with acetone (C_3H_6O) and anhydrous ethanol (CH_3CH_2OH) before used as the anode. 100 mL 0.1 mol/L Na_2MoO_4 aqueous solution was used as the anolyte, and 100 mL 0.1 mol/L HCl as the catholyte. A 2 × 4 cm metal foil as the anode, stainless steel mesh as the cathode, and a DuPont™Nafion® PFSA NRE-212 membrane as the

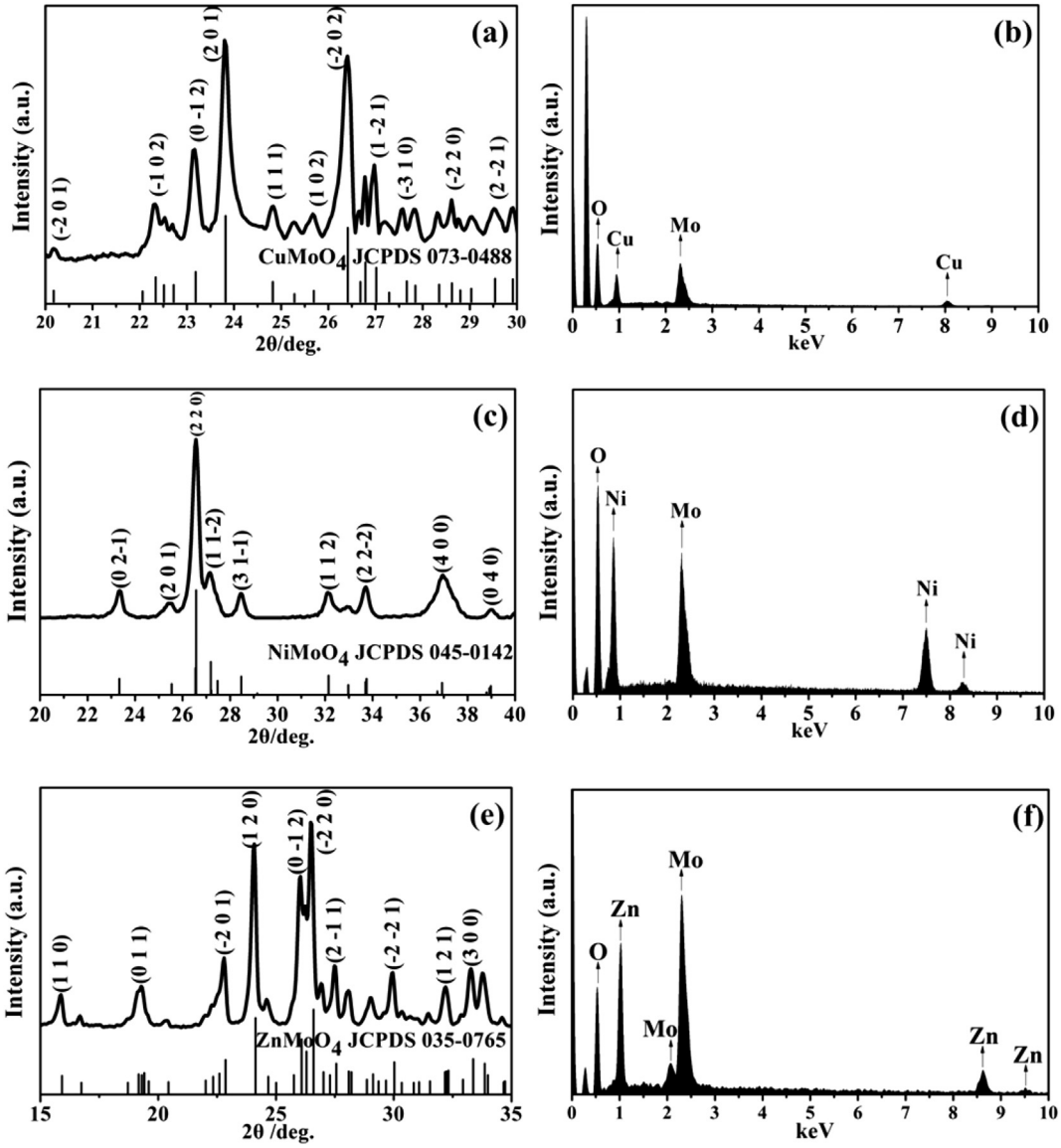

Fig. 1. XRD (a) and EDS (b) patterns of $CuMoO_4$; XRD (c) and EDS (d) patterns of $NiMoO_4$; XRD (e) and EDS (f) patterns of $ZnMoO_4$.