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Preparation, characterization of $Co_xMn_{1-x}O_2$ nanowires and their catalytic performance for degradation of methylene blue

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Abstract $Co_xMn_{1-x}O_2$ nanowires and microspheres ($0.15 \leqslant x \leqslant 0.5$) catalysts were synthesized, and their catalytic performance in oxidative degradation of methylene blue (MB) in water under oxygen air bubbles pumping was investigated. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM) and N_2 adsorption–desorption techniques were used to characterize the structure, morphology and S_{BET} of $Co_xMn_{1-x}O_2$ nanostructures. Nucleation–dissolution–recrystallization and reduction migration species mechanism was suggested for the growth of the nanowires. The effect of molar ratios of reactants and morphology of products were investigated in terms of MB degradation. The catalyst characterization was performed by mass spectra, chemical oxygen demand (COD), total organic carbon (TOC), the Langmuir and Freundlich isotherms. The results revealed the $Co_xMn_{1-x}O_2$ nanowires exhibited excellent catalytic efficiency for the degradation of MB than $Co_xMn_{1-x}O_2$ microspheres.

1. Introduction

Organic dyes have received particular attention as eminent environmental contaminants because of their non-biodegradability and carcinogenic impacts on humans (Priya et al., 2009). Among organic dyes, MB as a type of cationic dye is widely used in many fields such as dyeing, monitoring and printing. The hazardous effects of MB dye can be a cause for health problems, such as skin irritation, increased heart

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rate on inhalation and cancer (Choi et al., 2007). Many chemical processes were employed to treat dye from wastewater (Munaf et al., 1997; Aksu and Yener, 1998; Bertoncini et al., 2003; Khalid et al., 2004; Denizli et al., 2005). As one of them, manganese oxide has a great deal of attention to remove organic dye pollutants due to their reactivity with contaminants under environmentally relevant conditions (Chen et al., 2013; Remucal and Ginder-Vogel, 2014; Luo et al., 2015).

Metal dopant material oxide nanostructures are of interest in numerous industrial applications due to their unique and often advantageous properties (Cremades et al., 2014). In particular, the selection of transition metals inserted in the framework of manganese oxides can improve the properties of materials (Brousse et al., 2004; Zhang et al., 2004; Yin et al., 2011; Sawangphruk et al., 2012). The synthesis of metal incorporated nanocrystals has made great progress in the past few years (Heiligtag and Niederberger, 2013). The crystal growth of the nanostructures, an electrostatic interaction between two differently charged ions makes possible the incorporation of cobalt ion into the manganese oxide lattice and to cause the improvement of their catalytic activity with respect to olefin oxidation and degradation of RhB (Lee et al., 2007; Ahmed et al., 2013).

In this work, a one-step hydrothermal synthesis of $Co_xMn_{1-x}O_2$ nanowires was carried out through the reduction potassium permanganate with cobalt nitrate under hydrothermal process. The catalytic degradation of MB is investigated in a reflux reactor using $Co_xMn_{1-x}O_2$ nanowires under O_2-air bubble pumping. The effect of molar ratios of products was estimated in terms of the degradation, TOC and COD removal, catalytic stability, the Langmuir and Freundlich isotherms adsorption of catalysts surface and reaction rate constant were also determined.

2. Experimental method

2.1. Synthesis of $Co_xMn_{1-x}O_2$ nanowires

$Co_xMn_{1-x}O_2$ were obtained by an in-situ redox precipitation hydrothermal synthesis method. In a typical experiment, 1 mmol of $KMnO_4$ was added to an aqueous solution of 0.5 mmol $Co(NO_3)_2$ under magnetic stirring for 10 min. The homogeneous solution was transferred into a 40 mL Teflon-lined stainless steel autoclave, which was subsequently sealed at 140 °C for 18 h. After the desired time, the system was allowed to cool down naturally and the resulting precipitation was collected, washed several times with distilled water and absolute ethanol, centrifuged, and dried under vacuum at 60 °C for 12 h.

2.2. Measurements

The morphology and structures of the samples were characterized using a field emission scanning electron microscope (FEI Sirion, 200, Netherlands). The transmission electron microscopy (TEM) images were investigated using a Tecnai $G^2$20, Netherlands. A high-resolution transmission electron microscopic (HR-TEM) image was investigated by JEM-2010 FEF TEM at an acceleration voltage of 200 kV. XRD data were obtained on an X-ray diffractometer (Panalytical X' Pert Pro; Netherlands). The IR spectrum was recorded with an EQUINOX55, Bruker FT-IR spectrometer within the range 400–4000 cm^{-1}. EDAX Eagle III energy-dispersive micro-XRF (mXRF) spectrometer was employed by Agilent 6510 in positive ionization mode between mass ranges of 50 and 600 Da.

2.3. Test of the catalytic activity

The catalytic degradation of MB process was studied under in reflux route, magnetic stirring, oxygen air bubble pumping and room light (250 lux or 23foot-candle) in three-neck of ground glass. 1 mmol of catalyst powders were replaced in 150 mg/L of MB solution containing. At regular intervals, samples are taken from reactor and the catalytic powder was removed by centrifuging route. Total organic carbon (TOC) was examined by employing a Vario TOC Cube Elementar (Varian). The COD analysis of the degradation dye was obtained by following by potassium dichromate in 50% sulfuric acid solution at reflux temperature. UV–vis spectrophotometer of decomposition of dye was analyzed using a Varian Cary 50 Bio. The degradation rate of MB was estimated by $[D\% = (1 - A_t/A_o)/100]$ equation. The mass spectra were recorded by Agilent 6510 in positive ionization mode between mass ranges of 50–600 Da.

3. Results and discussion

The crystalline phase of $Co_xMn_{1-x}O_2$ nanowires was determined by XRD (Fig. 1(a)). Almost diffraction peaks indicated to tetragonal α-MnO_2 with lattice parameter of a = 9.7847

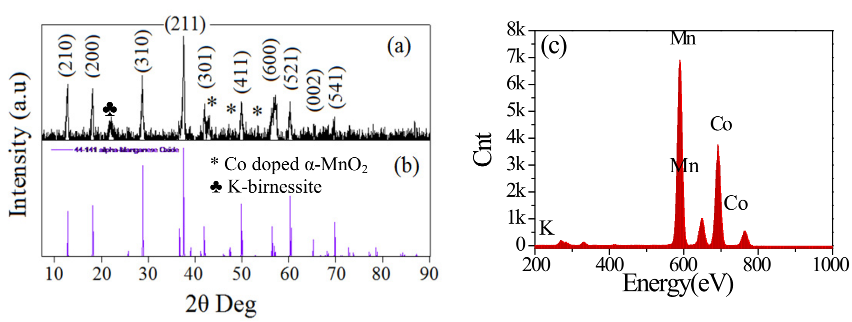

Figure 1 (a) XRD pattern, (b) the standard data from JCPDS card No. 44-0141 and (c) EDAX spectrum of the prepared $Co_xMn_{1-x}O_2$ nanowires.

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