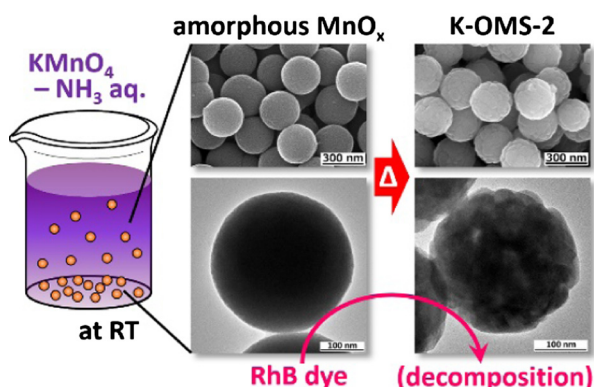Regular Article

Monodisperse manganese oxide nanoparticles: Synthesis, characterization, and chemical reactivity

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GRAPHICAL ABSTRACT

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ABSTRACT

Highly monodisperse amorphous manganese oxide (MnO_x) nanospheres with diameter of ca. 300 nm have been obtained from ammonia aqueous solution of $KMnO_4$ at room temperature. The amorphous MnO_x nanospheres successfully converted to monodisperse K-OMS-2 (cryptomelane) and K-OMS-2/ Mn_2O_3 nanoraspberries through calcination process at 600 and 800 °C, respectively. Analyzing the structure of such amorphous MnO_x has been a challenge because fewer reports are available to examine amorphous structure. Thus, shape, crystallinity, and structure of the amorphous and crystalline MnO_x nanostructures were characterized in detail by X-ray diffraction (XRD), thermogravimetry/differential thermal analysis (TG/DTA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and energy dispersive spectroscopy (EDS). We discussed a plausible formation mechanism of amorphous MnO_x nanospheres based on the investigations. The obtained MnO_x nanostructures have been demonstrated to possess oxidative degradation ability of Rhodamine B (RhB) under acidic aqueous condition without any additives such as chemical oxidizing agents and UV and/or visible light irradiation. RhB degradation rate of amorphous MnO_x nanospheres was about one hundred times faster than that of K-OMS-2 nanoraspberries.

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1. Introduction

Manganese oxide (MnO_x) materials have attracted much attention because they have been utilized in comprehensive applications due to their unique magnetic property [1,2], catalytic

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activity [3,4], and high energy density [5–7]. MnO_2 materials which are low cost and environmentally friendly compounds form various octahedral molecular sieve (OMS) structures. OMSs with mixed-valent manganese (Mn^{3+} and Mn^{4+}) frameworks consist of MnO_6 octahedra which are linked at edges and corners. OMSs are classified by their tunnel structures such as 1×1 tunnels (OMS-7, pyrolusite), 1×2 tunnels (OMS-4, ramsdellite), 2×2 tunnels (OMS-2; hollandite, cryptomelane, coronadite, or manjiroite with Ba^{2+}, K^+, Pb^{2+}, or Na^+ in the tunnel, respectively), 2×3 tunnels (OMS-6, romanechite), or 3×3 tunnels (OMS-1, todorokite) [8,9]. The diversity of MnO_x in atomic structure results in diversity of physicochemical properties of MnO_x materials.

OMS-2 has been particularly studied in OMS family with applications in catalysis [10] gas sensor [11], energy storage [12], and energy conversion [13]. The cations in tunnel structures are exchangeable, which result in modification of fascinating properties of OMS-2 materials [14,15]. A considerable number of synthetic methodologies of OMS-2 type materials have been reported; for example, sol-gel [16–18], hydrothermal [19–22], reflux [23,24], catalytic [25], co-solvent [26], chemical reduction [27,28], and sonochemical methods [29]. Additionally, amorphous MnO_x has recently emerged as a new family of MnO_x materials [30–36]. Amorphous MnO_x can convert to OMS-2 and other crystalline MnO_x materials by chemical or heat treatment and they show promising catalytic properties.

The development of synthetic method of monodisperse colloidal nano- and micro-particles has been a significant goal of colloidal science for a long period [37,38]. Colloidal particles with uniform size have found various applications such as catalyst [39], masks in lithography [40], filters and switches [41], optical sensors [42], drug delivery [43], bio-diagnostics [44], photonic materials [45], surface enhanced Raman scattering (SERS) [46], removal of heavy metals [47], and other devises. The material of monodisperse colloids has been limited to silica and polymer spheres whereas the majority of their applications, because of the easiness in preparing these materials. Recently, several efforts of synthesis of monodisperse MnO_x particles have also been reported [48–52]. However, they need high temperature with autoclave, capping agents, and/or complicated multi-step synthetic procedure. In this study, we report amorphous MnO_x nanospheres which are obtained after standing an ammonia aqueous solution of $KMnO_4$ at room temperature. Highly monodisperse nanospheres grow in one-step without addition of any protective agent. Monodisperse OMS-2 which contains potassium ions in the tunnels (K-OMS-2) and K-OMS-2/Mn_2O_3 nanoraspberries are successfully obtained by calcination of amorphous MnO_x nanospheres. The synthesized nanostructures show oxidative degradation ability toward Rhodamine B (RhB) in an acidic aqueous solution without chemical oxidants and photo-irradiation. Interestingly, amorphous MnO_x nanospheres enable ultra-rapid decomposition of RhB compared with K-OMS-2 nanoraspberries.

2. Experimental section

2.1. Materials

Potassium permanganate ($KMnO_4$), ammonia solution (NH_3, 28.0–30.0%), hydrochloric acid (HCl), and Rhodamine B (RhB) were purchased from Wako Pure Chemical Industries, Ltd. They were used without purification in this study.

2.2. Synthesis of monodisperse MnO_x samples

All procedures were carried out under aerobic condition. An ammonia solution (95 mL) was poured into a 100 mL plastic beaker (AS ONE Corporation). $KMnO_4$ (0.125 g) was dispersed in the ammonia solution. The solution was stirred with a Teflon-coated stir bar (AS ONE Corporation) for 10 min to dissolve $KMnO_4$. After stopping the stirring, the plastic beaker was sealed with a polyvinylidene chloride wrap (Saran Wrap, Asahi Kasei Home Products Corporation) and then the solution was stood for 24 h at room temperature (ca. 25 °C) in the dark. Formed brown precipitate was transferred to a polypropylene centrifuge tube (Eiken Centrifuge Tube, EIKEN CHEMICAL CO., Ltd.) and washed with distilled water 4 times by centrifugal separation and dried in vacuo. The obtained particles were crushed and grounded into a powder using an agate mortar. The powder was calcined in air using electrical furnaces (AS ONE Corporation).

2.3. Characterization

Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and thermogravimetry/differential thermal analysis (TG-DTA) were respectively performed using a Hitachi S-4800 type II (accelerating voltage, 15–25 kV), a MiniFlex II (X-ray source operated at 450 W), a Shimadzu KRATOS-AXIS Nova spectrometer (X-ray source operated at 15 kV), and a Rigaku TG-DTA8120. The powder samples were spread on a sample mounting plate for XRD measurement. The measured binding energies by the XPS were referenced to the C 1s line at 284.8 eV. In transmission electron microscopy (TEM), the obtained particles were dispersed in distilled water by ultrasonication for a few seconds, and the dispersion was dropped on carbon-coated copper grids (elastic carbon film ELS-C10, Okenshoji Co., Ltd.). The specimens were then dried at ambient pressure. TEM, high-resolution TEM (HRTEM), and TEM-energy dispersive spectroscopy (TEM-EDS) observations were performed using a JEOL JEM-2100F (acceleration voltage, 200 kV). Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were performed using a JASCO FT/IR-4100 and a JASCO NRS-1000, respectively. FTIR samples were prepared using a JASCO Tablet Master.

2.4. Oxidative degradation of RhB

A HCl aqueous solution (pH 2, 47.5 mL) was poured into a 100 mL plastic beaker with a stirrer bar. A stock aqueous solution of RhB (2.5 mL, 2.0×10^{-4} M) was added to the acid water. 50 mg of amorphous MnO_x nanospheres or K-OMS-2 nanoraspberries was dispersed to the acid aqueous solution of RhB. At given intervals, an appropriate amount of the suspension was taken out and filtered to remove the MnO_x particles before analysis. To determine the change of RhB concentration in the filtered solution, a UV–Vis spectrometer (JASCO, V-660) was used.

3. Results and discussion

A deep purple solution consisting of $KMnO_4$ dissolved in ammonia aqueous solution was stood without stirring at room temperature and deep brown precipitates formed in the solution. SEM images of the precipitates obtained at 24 h of standing time are shown in Fig. 1a and b. Interestingly, highly monodisperse nanospheres with diameter of ca. 300 nm and smooth surface were observed. The surface structure of the nanospheres became slightly rough after calcination at 600 °C (Fig. 1c and d) and 800 °C (Fig. 1e and f), resulting in formation of monodisperse raspberry-like nanoparticles.

The crystal structure of the nanoparticles was investigated by measuring the XRD. The XRD pattern of as-prepared nanospheres did not show any clear and intense signal, which clearly indicates the nanospheres are amorphous (Fig. 2a). However, extremely