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Endowing manganese oxide with fast adsorption ability through controlling the manganese carbonate precursor assembled in ionic liquid

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ABSTRACT

Manganese oxides with desired structure are controllably obtained through annealing $MnCO_3$ precursors with required structures. The structures of $MnCO_3$ precursors are determined by a "mesocrystal formation" process in an ionic liquid system of a choline chloride/urea (CU) mixture. Without addition of surfactants, only CU solvent and manganese chloride are needed in the reaction system, in which the CU acts as reaction medium as well as control agent for particle growth. A shape transformation of $MnCO_3$ particles from well-defined rhombohedral mesocrystals to ellipsoidal polycrystal ensembles, and to nanoparticulate aggregates is observed when heating the reaction system for 4 h at 120, 150, and 180 °C, respectively. With a longer aging time at 120 °C, etching and disassembly of $MnCO_3$ mesocrystals happened. The correlation between the microstructure and the underlying formation mechanism is highlighted. Porous and nanowire-like MnO_x nanostructures are obtained through a facile thermal conversion process from the diverse $MnCO_3$ precursors, which are demonstrated as effective and efficient adsorbents to remove organic waste (e.g. Congo red) from water. Significantly, the nanowire-like MnO_x nanostructures obtained by annealing the $MnCO_3$ mesocrystals at 300 °C for 4 h can remove about 95% Congo red in waste water at room temperature in only one minute, which is superior to the reported hierarchical hollow nanostructured MnO_2.

1. Introduction

Nanostructured manganese oxides have attracted considerable attentions due to their low cost, environmental friendliness, and potential applications including molecular adsorption, catalysis, and electrochemical storage [1–4]. Adsorption has been considered as one of the most practical technique in water treatment [5]. The adsorption process is a surface phenomenon. The adsorption performance is strongly determined by the structure of adsorbens. Some previous researches demonstrated that MnO_2 with defined nanostructure showed a good ability to adsorb organic pollutant [1,6–8]. In these reports, manganese oxides with different structures including core/shell, porous or hierarchical hollow were prepared. These manganese oxides showed reusability and good capacity as adsorbents. But generally the adsorption took more than 30 min to reach equilibrium. In fact, such gradual adsorption processes are not only widely observed for various adsorbents based on microscale porous metal oxides [5,9,10], but also traditional activated carbon [11,12]. These time consuming adsorption processes should be due to diffusion kinetic limitation at the interface of the adsorbents and the liquid phases. Some attempts have been devoted to fabricate graphene composites adsorbents with fast removal ability for heavy metal ions [13,14]. However, few manganese compounds have been fabricated with fast adsorption ability. Metal carbonates have been intensively investigated due to their abundance in nature and interesting topotactic transformation to their respective nanostructured metal oxides through chemical/thermal conversion [15–19]. In a thermal transformal process to prepare MnO_x, the structure of the MnO_x product is strongly determined by the structure of the $MnCO_3$ precursors. Calcite type metal carbonate phase has been found to form unusual morphologies under suitable conditions [20–23]. Controlling the morphology of $MnCO_3$ can be a powerful way to obtain MnO_x with unique morphology. Thus, developing a way to manipulate the structure of MnO_x by controlling the structure of the $MnCO_3$ precursors should be meaningful.

Inorganic mesocrystals and superstructures via a self-assembly (SA) process of nanoparticles (NPs) are of both theoretical and technological interest due to their size/shape-dependent applications and properties on a nanometer scale [24–27]. Ionic liquids (ILs) are perceived as solvents of the future due to their ubiquitous

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properties derived from their ionic nature. Recently, a review paper summarized the usage of ILs as an amphiphile self-assembly solvent and their fundamental character [28]. However, the adoption of ILs for creating mesocrystals and superstructure ensembles with well-defined morphologies and tunable sizes remains a research focus and a challenging issue. Unlike conventional ILs, deep eutectic solvents (DESs) can be easily prepared at low cost and with high purity [29,30]. DESs have been demonstrated to not only allow the design of eco-efficient processes but also to open a straightforward access to new chemicals and materials [31–34]. Recently, Kotov and co-workers proposed the possible formation pathways underlying the SA of PbS nanocrystals into hyperbranched star-like superstructures in a choline chloride/urea (CU) type DES [35]. Based on the partial decomposition of urea at high temperature, we have fabricated nanostructured nickel and cobalt hydroxides with metastable phases and desired morphologies for electrochemical energy storage applications in the CU system [36,37].

In this work, we propose a facile ionothermal method to fabricate $MnCO_3$ mesocrystals with different geometries in a CU solution dissolved with $MnCl_2{\cdot}4H_2O$. To the best of our knowledge, it is the first time to report the formation of $MnCO_3$ mesocrystals in such an “all in one” ionothermal route, in which no other reactant is needed. The formation mechanism and driving force underlying the SA process of $MnCO_3$ mesocrystals are discussed. The transformation from $MnCO_3$ to MnO_x can be achieved through simple thermal conversion. It is found the structure of $MnCO_3$ can strongly influence the structure of MnO_x products, thus further influencing the adsorbability of MnO_x. Significantly, the MnO_x products with suitable structure can achieve fast adsorption toward Congo red, a common organic pollutant, in one minutes.

2. Experimental section

All experiments concerning the morphology of $MnCO_3$ were repeated at least twice. While some variations occurred sometimes, representative data are given throughout.

2.1. Preparation of ionic liquid and its Mn^{2+} solution

ChCl (AR, Aladdin) was dried at 70 °C for 24 h before used. Urea (AR, Aladdin) was used as received. The ChCl/urea mixture-based DES was formed by stirring the two components in a molar ratio of 1 ChCl:2 urea at 80 °C, until a homogeneous colorless liquid was formed. During heating and storage, the container was covered by an air proof plastic film. The ChCl/urea mixture-based ionic liquid will be hereafter denoted as CU for convenience. The water content of as-prepared CU is about 5000 ppm. For preparing $MnCl_2$:CU ($MnCl_2$:CU) solution, an appropriate amount of $MnCl_2{\cdot}4H_2O$ was dissolved in CU at 60 °C under magnetic stirring to form a 0.5 M Mn^{2+} solution. The colorless liquid turned light pink, which is a typical color of concentrated Mn^{2+} ion. The water content of 0.5 M $MnCl_2$:CU increased to about 35,000 ppm mainly due to crystal water of $MnCl_2{\cdot}4H_2O$.

2.2. Preparation of $MnCO_3$ for discussing the influence of temperature

50 ml 0.5 M $MnCl_2$:CU solution was put to a Telfon-lined autoclave and sealed in a steel container. The container was then transferred to an oven which had been pre-heated at different temperatures (120 °C, 150 °C and 180 °C). After 4 h, the container was taken out quickly and cooled to room temperature by flowing water. The obtained precipitates were washed with methanol, distilled water and ethanol alternatively for several times, centrifuged and dried. It is worth noticing that only after washed with ethanol for three times can water be used. Otherwise amorphous impurities will precipitate. The obtained products are denoted as 120–4 h-$MnCO_3$, 150–4 h-$MnCO_3$, and 180–4 h-$MnCO_3$, respectively.

2.3. Preparation of MnO_x by annealing

The manganese oxides were obtained by simply annealing the as-prepared $MnCO_3$ at 300 °C for 4 h in a furnace under air with heating rate of 10 °C min^{-1}. The samples were then cooled gradually with the muffle to 100 °C, then taken out and cooled to room temperature in the air.

2.4. Material characterization

Structure and morphology of the obtained materials were characterized by X-ray diffraction (XRD, RigakuD/Max-3B), X-ray photoelectron spectroscopy (XPS, AXIS UTL-TRADLD), scanning electron microscope (SEM, Hitachi S-4800), and transmission electron microscope (TEM, JEM 200CX at 160 kV, Tecnai G2 F20 at 200 kV). The surface area was characterized by BET (Brunauer–Emmett–Teller) measurements using a AUTOSORB-1-C (QUANTACHROME, USA). UV–Vis spectra were recorded using UV-3600 (SHIMADZU, Japan). The thermo-gravimetric (TG) analysis of $MnCO_3$ during annealing was obtained using a TA Q600 instrument in a temperature range from 25 to 600 °C with a heating rate of 10 °C min^{-1} in air.

2.5. Characterization of the CU solution during thermal decomposition

TG-DSC data were obtained using NETZSCH STA 449F3. The conductivity of CU solution was characterized with a conductivity meter (DDBJ-350, Shanghai, China). For measuring conductivity and characterizing the crystallization habit, the CU solutions were put in a 150 °C oven for a given time and then cooled in water bath. The containers were then transferred to a 45 °C oven and kept for 6 h before measuring the conductivities. In order to guarantee the conductivity of the CU solution did not change in the 45 °C oven, the conductivities were measured again after 36 h. Then, the solutions were kept at room temperature (5–20 °C from night to daytime) for three days before recording their digital pictures.

2.6. Water treatment experiment

Congo red solutions with different concentrations were prepared to obtain a calibration curve. Then, required amount of manganese oxides were dispersed in Congo red ($C_{32}H_{22}N_6O_6S_2Na_2$, Aldrich) solution (100 mg L^{-1}). After a given time, the solution was centrifuged (14,000 r/min, 10 min) and the supernatant solution was sampled for UV–Vis analysis. The concentration of the unadsorbed Congo red was calculated using the absorbance at 500 nm.

3. Results and discussion

3.1. Temperature-dependent self-assembly of $MnCO_3$ mesocrystals

The physiochemical property of CU changes dramatically within the range from 100 to 200 °C. Unlike previous reports which commonly used DES as an inert media, we aim to develop a general ionothermal protocol based on reactive DESs without any surfactants. In this case, CU acts as the reactant as well as the control agent for particle growth, thereby allowing the synthesis of high purity nanoparticles. The ionothermal experiments were performed for 4 h at 120, 150, and 180 °C, respectively. For the following discussion, the samples are denoted according to the