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Synthesis, surface group modification of 3D MnV_2O_6 nanostructures and adsorption effect on Rhodamine B

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ABSTRACT

Highly uniform 3D MnV_2O_6 nanostructures modified by oxygen functional groups (–COO–) were successfully prepared in large quantities by an approach involving preparation of vanadyl ethylene glycolate as the precursor. The growth and self-assembly of MnV_2O_6 nanobelts and nanorods could be readily tuned by additive species and quantities, which brought different morphologies and sizes to the final products. With a focus on the regulation of structure, the formation process of 3D architectures of MnV_2O_6 by self-assembly of nanobelts was followed by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The consecutive processes of vanadyl ethylene glycolate and benzoyl peroxide assisted formation of layered structure $Mn_{0.5}V_2O_5{\cdot}nH_2O$, growth of aligned MnV_2O_6 nanobelts, and oriented assembly were proposed for the growth mechanism. The band gap vs. different morphology was also studied. Optical characterization of these MnV_2O_6 with different morphologies showed direct bandgap energies at 1.8–1.95 eV. The adsorption properties of 3D MnV_2O_6 nanostructures synthesized under different conditions were investigated through the removal test of Rhodamine B in aqueous water, and the 3D nanostructures synthesized with 30 g L^{-1} benzoyl peroxide showed good adsorption capability of Rhodamine B.

1. Introduction

The one-dimensional (1D) nanostructured materials, such as nanowires, nanorods, nanobelts, and nanotubes, have attracted considerable interest in the past decades due to their unique fundamental properties and potential applications in nanodevices [1–4]. However, the integration of one-dimensional (1D) nanoscale building blocks into two- and three-dimensional (2D/3D) ordered superstructures or complex functional architectures is a crucial step toward the realization of functional nanosystems [5–7]. Recently, hierarchical nanoarchitectures with extremely high surface-to-volume ratios assembled from nanoscale units have stimulated tremendous interest. The hierarchical nanoarchitectures have been explored for a new generation of advanced devices such as catalysis [8], water treatments [9] and sensors [10] owing to some improved properties originating from their nanobuilding blocks and the manners in which they are organized. A wide variety of inorganic materials with complex 3D shapes, including metal [11], metal oxide [12,13], hydrate [14], borate [15], molybdate [16,17], and tungstate [18], have been successfully prepared. However, oriented assembly of building blocks is generally difficult and usually requires templates or substrates. Thus, development of facile, mild, and easily-controlled methods for hierarchically self-assembled architectures with ideal and controllable morphologies, sizes, and structures is of great significance.

Vanadates have attracted a new interest as an electrode material [19,20]. Manganese vanadium oxides (MnV_2O_6) with brannerite structure are typical promising battery material, because of their structural relationship to γ-MnO_2 and non-stoichiometric form of manganese dioxide used in the battery industry [20–22]. Up to now, several synthesis methods of MnV_2O_6, such as polymer gellation method [22], solid state reaction [23], microwave-assisted solution-based metathesis synthesis [24], and hydrothermal synthesis [21,25,26] have been reported. However, there are few reports on the preparation of pompon-like MnV_2O_6 spheres, nanobundles and hierarchical urchin-like MnV_2O_6 spheres modified by oxygen surface groups, which are expected to exhibit novel properties.

In this paper, we report the synthesis of 3D architectures of MnV_2O_6 with oxygen-containing surface groups (–COO–) using a simple two-step procedure, involving the preparation of vanadyl ethylene glycolate (VEG) as the precursor. A process mechanism has been revealed for the self-assembly of the 3D architectures of MnV_2O_6. In addition, the capability of the as-prepared 3D architectures of MnV_2O_6 synthesized under different conditions

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to adsorb Rhodamine B (RhB) was investigated in aqueous water.

2. Experimental

2.1. Materials

All the reagents, such as NH_4VO_3, ethylene glycol, $Mn(NO_3)_2$, benzoyl peroxide (BPO), HNO_3, NaOH and RhB were of analytical grade and purchased from Shanghai Chemical, which were used as received without further purification.

2.2. Fabrication of VEG

NH_4VO_3 (1.2 g) and ethylene glycol (50 mL) were taken in a Schlenk flask and refluxed at 190 °C for 5 h with N_2 gas. Initially, the colour of the reaction mixture was yellow. After attaining ~140 °C, the solution turned to dark. Upon centrifugation, a purple VEG was obtained, which was then washed with methanol and dried in vacuum at 40 °C for 10 h.

2.3. Fabrication of 3D architectures of MnV_2O_6 with oxygen-containing surface groups

VEG (2 mmol), $Mn(NO_3)_2$ (1 mmol) and BPO (0.315 g) were added into a 65 mL Teflon-lined stainless-steel autoclave, which was then filled with deionized water (45 mL), and the mixture was vigorously stirred. After stirring for 0.5 h, the autoclave was maintained at 180 °C for 24 h and cooled down to room temperature naturally. The brown products were collected and washed with distilled water, rinsed with ethanol and acetone, and then vacuum dried before characterization.

2.4. Adsorption experiments

Sorption experiments were carried out RhB as adsorbate. The pH values of the solutions (pH = 7.25) were adjusted using HNO_3 or NaOH. Solutions containing different concentrations of RhB were prepared and adjusted to pH 7 for the RhB solution. For each sample, 60 mg of the adsorbent sample was added to 20 mL of RhB solution under stirring. The mixture was kept for 6 h to establish adsorption equilibrium at room temperature. The adsorbent was then separated from the mixture by centrifugation. For the adsorption of RhB, UV–vis adsorption spectra were recorded at different intervals to monitor the process. A calibration curve was developed for a range of RhB solutions with defined concentrations. The amount of RhB was estimated spectrophotometrically at λ_{max} 553 nm. The residual dye concentration of the samples was determined using the calibration curve.

2.5. Sample characterization

The products were characterized by X-ray powder diffraction (XRD) by using a Philips X-pert X-ray diffractometer with Cu-K_α radiation (λ = 1.54187 Å). Field emission scanning electron microscopy (FE-SEM) image was taken with a Hitachi S-4800 scanning electron microanalyzer. Structure characterizations were done by transmission electron microscopy (TEM, HITACHI 800) and high-resolution TEM (HRTEM, JEOL 2010 using an accelerating voltage of 200 kV). The nitrogen adsorption and desorption isotherms were measured with a Micrometrics ASAP 2000 system after the sample was degassed in vacuum overnight. X-ray photoelectron spectra (XPS) were obtained by a VG Smart IQ$^+$ Thermo Electron Co. ESCALAB 250 XPS spectrometer with monochromated Mg-$K\alpha$ irradiation. UV–vis absorption spectra were recorded on a SolidSpec-3700 spectrophotometer at room temperature. FTIR spectra were measured on a Bruker Vector-22 FT-IR spectrometer from 4000 to 400 cm^{-1} at room temperature. Thermogravimetric analysis (TGA) was carried out on a TGA-50 thermal analyzer (Shimadzu Corporation) at a heating rate of 10 deg min^{-1} in flowing air.

3. Results and discussion

It is well known that the VEG structure is composed of one dimensional chains. The chain contains edge sharing VO_5 square pyramids, whose oxygens come from a vanadyl group (V═O), a chelating ($-OCH_2CH_2O-$) ligand and one end of two other ($-OCH_2CH_2O-$) ligands. Fig. 1a shows the XRD pattern of VEG. It could be indexed to the monoclinic VEG, which is in good agreement with the reported value (JCPDS 49-2497). Fig. 1b shows XRD pattern of the as-prepared MnV_2O_6 with oxygen-containing surface groups. The calculated cell constants of the product are a = 9.290 Å, b = 3.534 Å, c = 6.763 Å and β = 112.60°, which agree well with those of the literature (JCPDS 72-1837). It is noticed that the related intensity of the (1 1 0) reflection is much stronger than that of the standard powder diffraction pattern, which may suggest the existence of preferential orientation due to the special shape of the microcrystals.

The morphology of the product was determined by FR-SEM and TEM. Fig. 2a–c shows the urchin-like MnV_2O_6 synthesized with the addition of BPO (7 g L^{-1}) at 180 °C for 24 h. It is found that the obtained products consist of a large number of urchin-like architectures (Fig. 2a). After careful observation (Fig. 2b), it is confirmed that the urchin-like architectures are a highly regular sphere-like morphology with an average diameter of about 30–40 μm, and every urchin-like architecture is composed of large numbers of nanobelts, which grow radially from a central core and have a length of 15–20 μm. From Fig. 2c, it can be seen that the nanobelts have a smooth surface and a similar quadrangular cross-section, with thickness and width of 40–50 nm and 600–700 nm, respectively. The products were further characterized by HRTEM, accompanied by the selected-area electron diffraction (SAED) and the energy-dispersive X-ray spectroscopy (EDS). As shown in Fig. 2e, the SAED pattern taken from the individual nanobelt exhibits diffraction characteristic of single crystalline MnV_2O_6 with sharp spots, which is in agreement with the above-mentioned XRD results. The typical HRTEM image (Fig. 2e), recorded from the same nanobelt, reveals a clean and structurally perfect surface, and unambiguously resolves the (2 0 0) and (1 1 0) atomic planes of monoclinic MnV_2O_6 with an interplanar spacings of ca. 4.29 and 3.27 Å, respectively, which

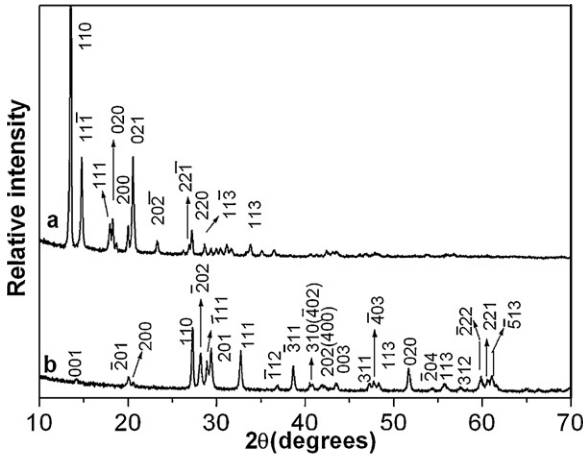

Fig. 1. XRD patterns of precursor VEG (a) and the products synthesized with BPO (7 g L^{-1}) at 180 °C for 24 h (b).