



Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet



Communication

Synthesis and orientational assemblies of MgO nanosheets with exposed (111) facets

Min Tang, Yuanhang Ren, Yichen Hu, Lin Ye, Bin Yue*, Heyong He*

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China

ARTICLE INFO

Article history:

Received 29 July 2017

Received in revised form 18 November 2017

Accepted 15 December 2017

Available online xxx

Keyword:

MgO

Oriental assembly

Polar and non-polar solvents

X-ray diffraction

UV-vis spectroscopy

ABSTRACT

MgO nanosheets with exposed (111) facets were obtained through the preparation of $\text{Mg}(\text{OH})_2$ precursor by a hydrothermal method in the presence of oleylamine and subsequent calcination in air. The different preferred orientational assemblies of MgO nanosheets, achieved by adjusting the polarity of dispersing solvents (ethanol and cyclohexane) during the sample preparation, show different structural and spectral features.

© 2018 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

MgO possesses a typical rock salt structure. It is one of the promising metal oxides which may serve as basic catalyst in organic reactions such as Claisen-Schmidt condensation, catalyst support, and adsorbent of reactive dyes [1–3]. Through common methods, for example, thermal decomposition of magnesium salts or direct burning of magnesium ribbons, the non-polar (100) facets of MgO are easier to be obtained than other high-index facets as a result of low surface energy [4,5]. Recently, several attempts have been made to manufacture MgO with (111) exposed facets [6–8]. Unlike the non-polar (100) facets, the (111) facets of MgO are consisted of alternate equidistant atomic layers with either Mg^{2+} cations or O^{2-} anions, thus they are of great interest for their high surface energy and surface polarity [9].

The composition, geometry, and spatial arrangement have a great impact on the properties of assemblies of nanomaterials [10–12]. For instance, the optical or magnetic property of the assembly is usually different from those of the randomly arranged nanomaterials due to their ordered spatial arrangement of the nano-sized building blocks [13,14]. Although the assembly of isotropic spherical or pseudo-spherical nanomaterials has been intensively investigated [15–17], the reports of the controlled assembly of anisotropic nanomaterials are relatively rare and are limited to metal species [14]. Anisotropic nanomaterials such as

nanorods and nanoplates fabricated with special exposed crystal facets may possess shape-dependent catalytic or photocatalytic properties [18,19]. In practice, if a large amount of anisotropic nanomaterials are randomly arranged into disordered architectures, their anisotropic optical, magnetic and crystallographic properties would be weakened or even undetectable. The controlled assembly of anisotropic nanomaterials is thus becoming highly attractive [20]. Han *et al.* found that two kinds of assembly of Ag nanoprisms could be prepared by dropping Ag nanoprisms solution onto the clean substrates with or without using the interfacial entrapment method [21]. By adjusting the interaction between nanoprism faces, assemblies of vertically and parallelly aligned Ag nanoprisms could be fabricated and both assemblies showed different optical, crystallographic, and surface-enhanced Raman scattering features. These results indicate that the shape-dependent properties are also related to the orientational assembly. For the ionic solids, it is anticipated that the different assemblies of anisotropic nanomaterials should have orientation-dependent properties as well. In this work, we report the synthesis of MgO nanosheets with (111) exposed facets by the calcination of $\text{Mg}(\text{OH})_2$ precursor which is obtained by a simple and rapid hydrothermal method using oleylamine as a precipitant as well as a surface directing agent. We also investigate the polarity effect of solvents on dispersing anisotropic MgO nanosheets, uncovering two novel assemblies of anisotropic nanomaterials fabricated by the drop deposition method.

In a typical synthesis of MgO nanosheets, 1.07 g of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (5 mmol, Sinopharm) was dissolved in

* Corresponding authors.

E-mail addresses: yuebin@fudan.edu.cn (B. Yue), heyonghe@fudan.edu.cn (H. He).

20 mL of deionized water under stirring at room temperature. A white gel was produced when a mixture of 2 mL of oleylamine (Aldrich, 70 wt%) and 5 mL of ethanol (Shanghai Zhenxing, ≥ 99.7 wt%) was added dropwise to the above solution (all the chemicals are used as received without further purification). The resulting gel was transferred into a 40 mL autoclave with a Teflon liner and kept at 180°C for 12 h. White powders were collected by centrifugation at 3000 rpm and washed several times with deionized water and ethanol, and then dried in an oven at 80°C overnight. The obtained $\text{Mg}(\text{OH})_2$ precursor was calcined in air at 550°C for 3 h to form the final MgO nanosheets.

The powder X-ray diffraction (XRD) patterns of $\text{Mg}(\text{OH})_2$ and MgO samples were collected on the Bruker AXS D8 Advance X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies were examined by using scanning electron microscopy (SEM) on a Philips XL30 electron microscope. The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 spectrometer. The transmission electron microscopic (TEM) and selected area electron diffraction (SAED) images were taken on a JEOL JEM2010 transmission electron microscope. The high resolution transmission electron microscopic (HRTEM) images were obtained from a JEOL JEM-2100F field emission transmission electron microscope. The UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV-2450 spectrometer with an integrating sphere.

In the preparation of MgO nanosheets, $\text{Mg}(\text{OH})_2$ precursor was prepared by adding oleylamine/ethanol mixture to $\text{Mg}(\text{CH}_3\text{COO})_2$ solution and then hydrothermally treated. The $\text{Mg}(\text{OH})_2$ precursor is sheet-like (Figs. S1a and S1b in Supporting information), and the XRD pattern of the precursor (Fig. S1c in Supporting information) can be indexed to a brucite $\text{Mg}(\text{OH})_2$ (JCPDS No. 44-1482). The $-\text{CH}_2$ symmetric and asymmetric stretching vibrations at $\sim 2850 \text{ cm}^{-1}$ and $\sim 2925 \text{ cm}^{-1}$ of oleylamine are found in the FT-IR spectrum of the $\text{Mg}(\text{OH})_2$ precursor (Fig. S1d in Supporting information). MgO nanosheets were obtained by the calcination of $\text{Mg}(\text{OH})_2$ precursor in air. XRD pattern of the final product (Fig. S2 in Supporting information) can be indexed to a periclase MgO (JCPDS No. 45-0946; space group $\text{Fm}\bar{3}\text{m}$, $a = 4.211 \text{ \AA}$). As observed in SEM images, the sheets are *pseudo*-hexagonal with the width of 500 nm to $1.5 \mu\text{m}$ and the thickness of *ca.* 40 nm (Fig. S3 in Supporting information). Fig. S4 (Supporting information) displays the FT-IR spectra of the commercial MgO and the MgO nanosheets. The $-\text{CH}_2$ symmetric and asymmetric stretching vibrations at $\sim 2850 \text{ cm}^{-1}$ and $\sim 2925 \text{ cm}^{-1}$, respectively, cannot be observed in the spectra, indicating the oleylamine is completely removed by calcination.

HRTEM was also utilized to prove that these MgO nanosheets are exposed with a large amount of (111) facets. The zone axis of the fast Fourier transformation (FFT) patterns is [111], indicating that the sheets with the exposed (111) planes lay on the specimen holder (Fig. 1a). The lattice fringes of 0.15 nm match the (-220) and (-202) lattice spacings in MgO (Figs. 1b and c), which suggests that the nanosheets grow along the direction perpendicular to [111]. The SAED patterns of several random-selected sheets also show that the most exposed facets of the nanosheets are (111) facets (Fig. S5 in Supporting information). The HRTEM images of a MgO nanosheet standing uprightly on the carbon film (Fig. S6 in Supporting information) exhibit lattice fringe with a distance of 0.24 nm, which is in agreement with the (111) lattice spacings in MgO.

In the previous studies, specific ligands such as biological linkers [14] and interfacial entrapment reagents [21] or special treatments of the substrates [20] have been applied to fabricate controlled assembly of anisotropic metal nanomaterials. The specificity of those methods limited their applications in other anisotropic nanomaterials. A rational design based on surface

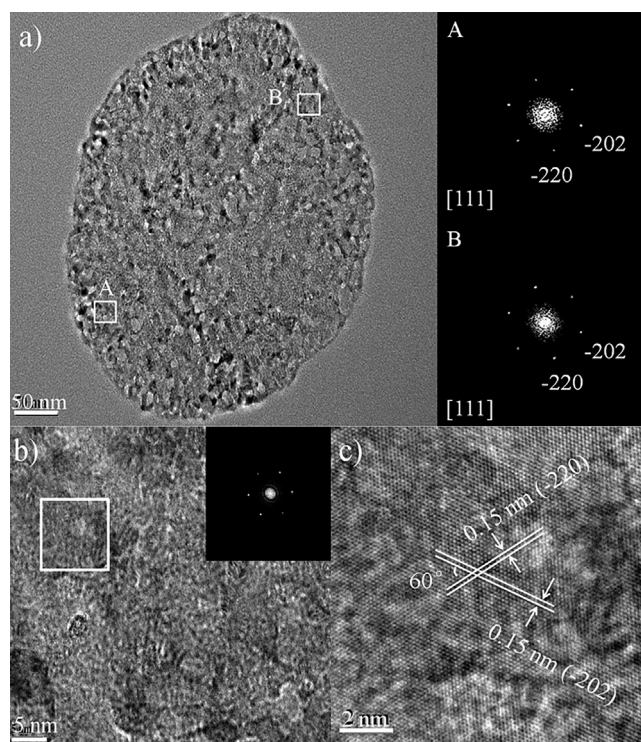


Fig. 1. (a) HRTEM image of a MgO nanosheet and FFT patterns of selected A and B parts. (b) HRTEM image of a MgO nanosheet (inserted is the corresponding FFT pattern) and (c) the lattice fringes of 0.15 nm corresponding to the (-220) and (-202) lattice planes enlarged from the selected white square in (b).

polarity may bring a more general method to fabricate controlled assembly. Owing to the exposed polar facets of MgO, which may have different interactions with polar and non-polar molecules, a new strategy to manufacture controlled assembly of anisotropic metal oxide nanomaterials was developed in this work. Two different assemblies were obtained by dropping MgO nanosheets suspension onto the clean glass substrates and drying slowly at room temperature for one day along with further heating in the muffle furnace at 350°C for 2 h to remove the residual solvents. The only difference is one used the polar solvent ethanol as dispersant (notated as sample PS) and another used the non-polar solvent cyclohexane as dispersant (notated as sample NPS).

For the sample PS, SEM images (Figs. 2a and b) show that these nanosheets retain their original size and shape, and almost every sheet stacks in a face-down manner (on (111) plane) on the sample holder. For the sample NPS (Figs. 2c and d), these nanosheets also retain their size and shape, and most of them tend to stack with each other and stand along their edges on the sample holder. We describe this phenomenon as *like disperses like*, an extension of *like dissolves like* principle [22]. In the ethanol system, the sheets mainly with polar surfaces would be dispersed evenly in the polar solvent (Fig. S7a in Supporting information) because of the strong interaction between polar solvent molecules and polar MgO surfaces. Therefore, when the ethanol suspension was dropped onto the glass substrate, the nanosheets were face-to-face stacked on the substrate by the attracting force of ethanol among the nanosheets. After evaporation of ethanol, the assembly paralleled with the substrate remains (Figs. 2a and b). However, cyclohexane is a non-polar solvent so it would not be able to disperse the nanosheets well (Fig. S7b in Supporting information) due to the repulsion between non-polar solvent molecules and polar MgO surfaces. Thus, when the cyclohexane suspension was dropped onto the glass substrate, the surface tension of the interface between solvent and sheets is very high so that it can even drive

Download English Version:

<https://daneshyari.com/en/article/7693407>

Download Persian Version:

<https://daneshyari.com/article/7693407>

[Daneshyari.com](https://daneshyari.com)