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Synthesis and Photocatalytic Properties of BiOCl Nanowire Arrays

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Abstract

Bismuth oxychloride (BiOCl) nanowire arrays have been successfully prepared employing the Anodic Aluminum Oxide (AAO) template assisted sol-gel method. Nanowires of 100 nm diameter and length 2- 6 μm, assembled in the porous of AAO templates, were formed. XRD and HRTEM results show that the nanowires are pure BiOCl polycrystal phase without Bi_2O_3 or $BiCl_3$. The photocatalytic activity of BiOCl nanowire arrays was investigated by the degradation of Rhodamine B dye solution under UV irradiation.

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1. Introduction

During the last few decades low dimensional nanostructured materials have attracted special interest due to their novel properties and potential applications in electronics, photonic devices, and photocatalytic media [1- 3]. As these novel properties are highly dependent on shape and size, the size and morphological control of nanostructured materials becomes increasingly important in nanoscience and nanotechnology [4]. In particular, ordered nanostructures are extremely desirable in photocatalytic actions, because their enhance surface-to-volume and substrate-support ratio [5,6].

There has been considerable effort towards the synthesis of ordered structures, the most common being via the nanoporous anodized aluminum oxide (AAO) assisted route. Using easily controlled AAO membranes as a template and combined with electrodepositon deposition, sol–gel deposition, or polymerization, the size and shape of the products can be adjusted [7]. Normally, the pore size of AAO templates can be adjusted from 25 to 300 nm by changing the anodizing conditions, and the aspect ratio of the AAO membrane can be changed by controlling the anodizing time [8]. Until now, nanotubes, nanowires and nanowire arrays of a variety of inorganic materials have been successfully prepared using this method [9-11].

Bismuth oxychloride (BiOCl), with a bandgap of 3.5 eV, has industrial applications as a pigment in cosmetic industry, has been used as a catalyst for the oxidative cracking of hydrocarbons and also as photoluminescent material [12]. Recently, Zhang et al. reported that BiOCl nanoparticles can be an efficient photocatalyst in decomposing methyl orange under UV light [13]. This indicates that BiOCl is a potential photocatalyst under UV light irradiation and can compete with TiO_2. In 2009, Lee et al. also reported that a

$BiOCl/Bi_2O_3$ heterojunction is a new visible light photocatalyst [14]. This harmless and green material has already been synthesized as spherical nanofibers, nanobelts and hierarchical nanoplate microspheres [15-17]. However, to our knowledge, no attempt has been made to fabricate nanowire arrays which will be helpful in photocatalysis reactions [5]. Herein, we exploit the AAO template combined with sol-gel method to prepare BiOCl nanowire arrays. We characterize the nanostructure and analyze their photocatalytic properties.

2. Experimental

BiOCl powders were first prepared by dissolving Bi_2O_3 (AR, Shanghai) in an excessive concentrated HCl [16]. The resulting pure BiOCl (2 g) was then dissolved in 20 ml of ethanol (95% v/v) by adding 5 M HCl to adjust the pH value to 1 under constant stirring. Thereafter the resultant solution was stirred at 60 °C for 3h to form sol solution. Subsequently, AAO templates prepared by a two step anodization process were placed in a vessel containing an appropriate amount of BiOCl sol. The sol was allowed to permeate through the membrane for 30 min under vacuum conditions, and the sol was crystallized in this process. Finally, the templates assembled with precursor were dried at 100 °C for 10 h. To remove the templates, the samples were dissolved using 5% NaOH and rinsed with distilled water.

The Field Emission Scanning Electron Microscope (FESEM) images and energy-dispersive x-ray spectroscopies (EDS) were recorded on a FEI-SIRION Field Emission Gun-Scanning Electron Microscope. High Resolution Transmission Electron Microscopy (HRTEM) images and Selected-area Electron Diffraction (SAED) patterns

were obtained on a JEOL 2010 FEG. The phase structure characterization of BiOCl nanowire arrays was carried out by X-ray Diffraction (XRD) on a Bruker D8 diffractometer with Cu Kα radiation. The UV-Vis absorption spectra were examined using a Hitachi U-3010 spectrometer.

The photocatalytic activity of the samples was evaluated by the degradation of a Rhodamine B (Rh B) dye solution. Prior to the photocatalytic test, part of the template assembled by BiOCl nanowires was dissolved. 3 cm^2 BiOCl nanowire arrays were placed in 20 ml 0.01mmol Rh B solution. This solution was immersed in darkness for 24 h to reach the adsorption-desorption equilibrium. Then it was irradiated by a 35 W Hg lamp with a main emission wavelength of 313 nm. At given intervals of illumination, the samples of the reaction solution were taken out and analyzed using a UV-vis spectrometer (Hitachi U-3010), without centrifugation and filtratation.

3. Results and discussion

The morphology and composition of the synthesized products were characterized by FESEM and EDS, respectively. The top view image of the bare AAO template is displayed in Fig.1 (a). The pore size is about 100 nm and the hexagonal structure is well ordered. From Fig.1 (b), it is observed that BiOCl nanowire arrays are immersed in the AAO template. The diameter of the nanowires is about 100 nm, which is equal to the pore size of the template used. The pore filling of the AAO template is almost complete. After part of the AAO templates was dissolved, bundles of nanowires were isolated from the templates (Fig.1(c)). The nanowires are nearly parallel to each other and vertically oriented to form an array. The composition of the nanowires was examined using EDS. Fig.1 (d) is one of EDS spectra taken from the cross-section of the nanowires. It indicates

the presence of Bi, Cl, and O, and that the Bi : Cl atomic ratio is nearly equal to 1:1. The Na peaks in the spectrum come from the NaOH solution used for dissolving AAO template.

XRD was employed to identify the crystal structure and phase purity of these nanowire arrays. Fig. 2 shows the XRD pattern of the BiOCl nanowire arrays in the AAO template. A tetragonal lattice was obtained with a = 3.89 Å, c = 7.369 Å and the three strongest peaks are indexed as (101), (110) and (211). Although the background diffraction peaks of Al_2O_3 template are present, almost all of the diffraction peaks in the XRD pattern coincide with the standard JCPDS file (No. 85-0861) of BiOCl. There is no other peak corresponding to the peaks of Bi_2O_3 or $BiCl_3$. Thus, the synthesized nanowires are crystallized in BiOCl with high purity. Moreover, the XRD pattern did not change after the photocatalytic reaction, indicating that the synthesized photocatalysts are stable.

HRTEM images were taken in order to observe microstructural details of the BiOCl nanowires. The AAO template was dissolved completely and Fig. 3 (a) shows a TEM image of the isolated nanowires. The average diameter of the nanowires is about 100 nm. The length is only 2 μm, because it was fractured during the preparation of the TEM samples. We also observed one separated nanowires with the length of 6μm after the template was completely dissolved. The selected area electron diffraction pattern (SAED) (Fig. 3b) shows that the nanowires are polycrystalline, which further confirms the XRD result. The HRTEM (Fig. 3c) also displays a single nanowire that is composed by some small nanocrystals with different orientations.

According to the UV-Visible diffuse reflectance spectra, the band gap of BiOCl is about 3.4 eV. Thus it could be a good candidate as photoelectrode and photocatalytic materials.

Therefore, the photocatalytic activity of BiOCl nanowire arrays was evaluated by degradation of Rh B dye under UV light irradiation. Fig. 4(a) shows the absorption spectra of the Rh B solution with BiOCl nanowire arrays in the processes of adsorption in darkness and UV light irradiation for different times. The strong absorption peak of Rh B solution located at 554 nm steadily decreased as the UV irradiation time increased, indicating gradual degradation of the Rh B [18]. The initial concentration decreased by 32% after the dark adsorption and the surface of BiOCl nanowire arrays turned red. Irradiated under UV light, the red color on both surfaces of BiOCl nanowire arrays and dye solutions are decreased gradually and could be degraded almost completely after 130 min. Fig. 4(b) shows photodegradation efficiency of Rhodamine B as a function of irradiation time. C_0 and C are the initial and reaction concentrations of aqueous Rhodamine B, respectively. It can be seen that, there is not any degradation of Rh B after adsorption and irriadiation with only bare AAO templates. This indicates that the degradation of Rh B is caused by the appearance of BiOCl nanowires. The photocatalytic reaction can simply be described by $-d[C]/dt = k[C]$, where k is the degradation rate constant, t is the irradiation time, and [c] is the concentration of Rh B. In this work, k was found to be 0.017 min^{-1}. Since the BiOCl nanowire arrays embed in AAO templates, they can be collected easily without losing any nanowires in the solution. Therefore, they can be recycled for photocatalytic reaction and the efficiency is almost the same. In addition, the large surface-to-volume (S/V) ratio of nanowire arrays results in an enhanced photocatalytic efficiency [5,6]. Both the fixity and the large surface areas in contact with the dye are favorable to the photocatalytic reactions.

4. Conclusions

Highly ordered BiOCl nanowire arrays with high photocatalytic efficiency have been successfully prepared via the sol-gel template method. It was found that the nanowires in the arrays were polycrystal, with 100 nm diameter and 6 μm length. BiOCl nanowire arrays with the band gap of 3.4 eV can efficiently degrade Rh B under UV irridation.

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Figure captions:

Fig.1 FESEM images: (a) bare AAO template; (b) top view of BiOCl nanowire arrays; (c) cross-section of BiOCl nanowires after part of the template was dissolved; (d) EDS spectrum of the nanowires.

Fig. 2 XRD pattern of BiOCl nanowire arrays.

Fig. 3 (a) TEM image of BiOCl nanowires; (b) SEAD pattern of the BiOCl nanowires; (c) HRTEM image of BiOCl nanowire.

Fig. 4 Absorption spectra of the RhB solutions with BiOCl nanowire arrays at different stages.

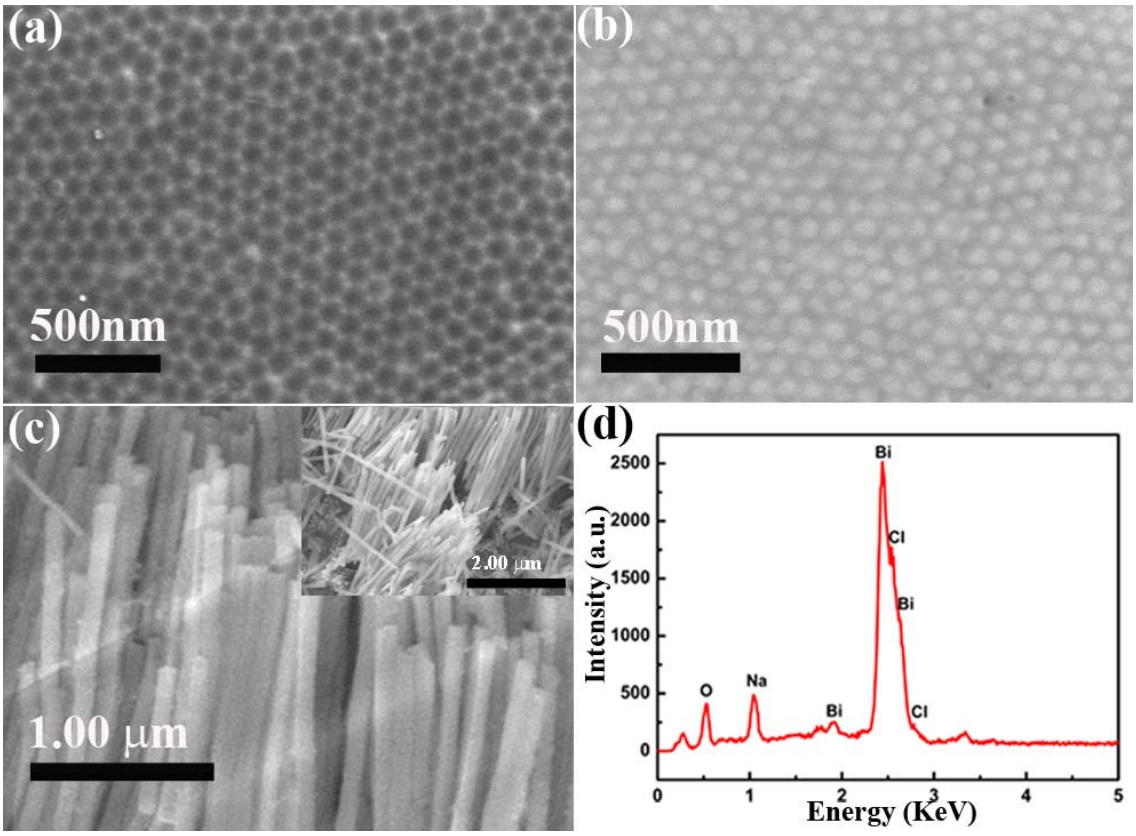
(a)
500nm
(b)
500nm
(c)
2.00 μm
1.00 μm
(d)
Intensity (a.u.)
Energy (KeV)
O
Na
Bi
Cl
Bi
Bi
Cl

Fig.1

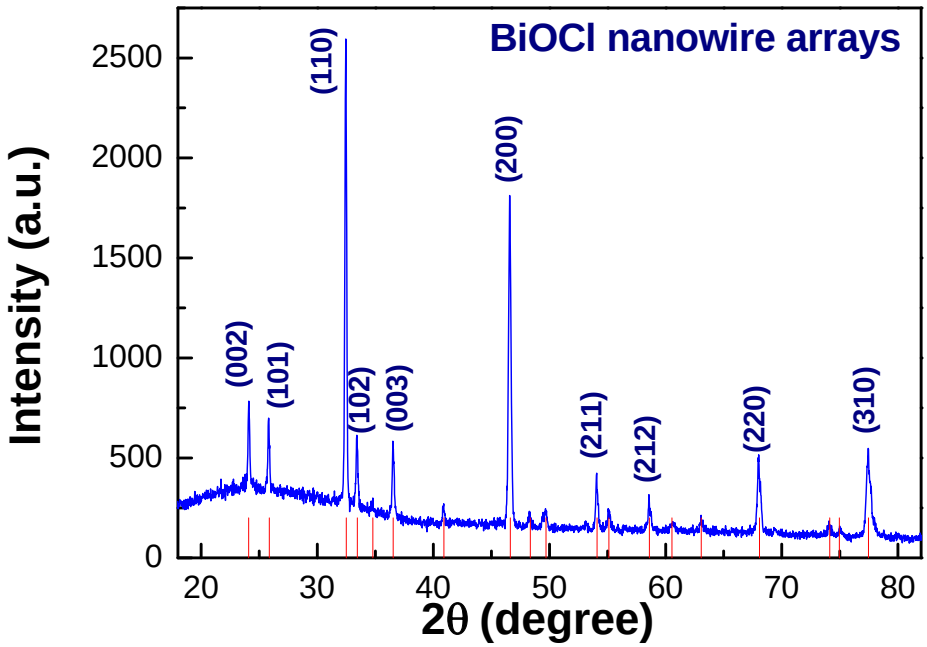
BiOCl nanowire arrays
Intensity (a.u.)
2θ (degree)
(002)
(101)
(110)
(102)
(003)
(200)
(211)
(212)
(220)
(310)
0
500
1000
1500
2000
2500
20
30
40
50
60
70
80

Fig.2

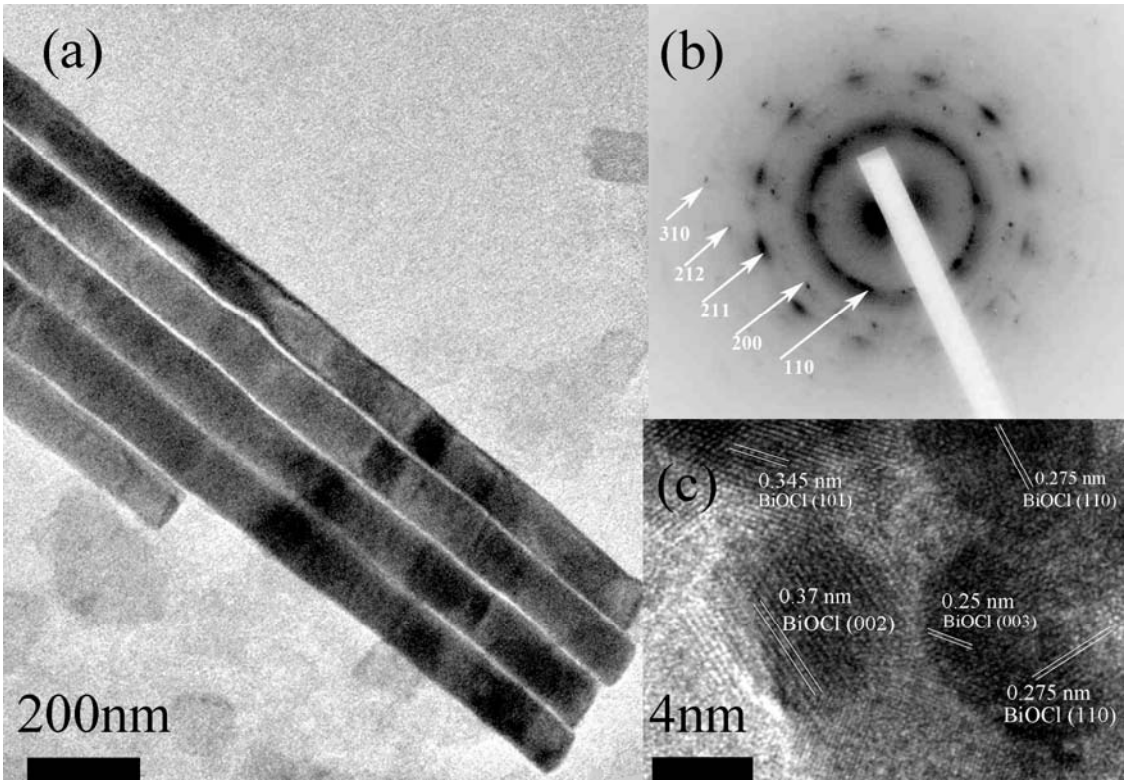
(a)
200nm
(b)
310
212
211
200
110
(c)
0.345 nm
BiOCl (101)
0.275 nm
BiOCl (110)
0.37 nm
BiOCl (002)
0.25 nm
BiOCl (003)
0.275 nm
BiOCl (110)
4nm

Fig.3

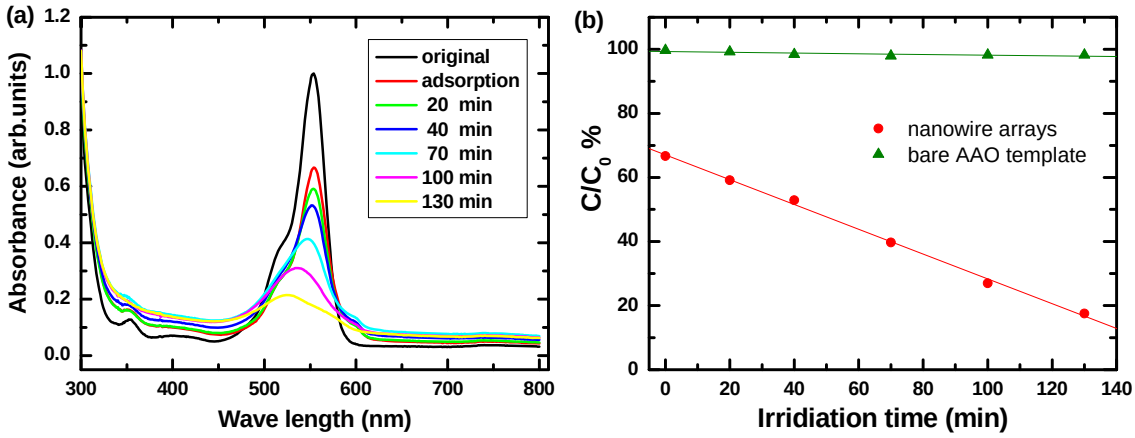
(a)
Absorbance (arb.units)
Wave length (nm)
original
adsorption
20 min
40 min
70 min
100 min
130 min
(b)
C/C0 %
Irridiation time (min)
nanowire arrays
bare AAO template

Fig.4