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The visible light absorption property of Cu-doped hydrogen titanate nanotube thin films: An experimental and theoretical study

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ABSTRACT

Hydrogen titanate nanotube thin films were synthesized by alkaline hydrothermal method using titanium plates as starting material and then doped with Cu through ion-exchange method. The experimental results show that Cu ions incorporate into the walls of nanotubes and exist as Cu^{2+}. Cu doping leads to a red shift of the optical absorption edge from the ultraviolet region to the visible light region. First-principles calculation results reveal that Cu doping substantially reduces the band gap of hydrogen titanate nanotubes due to the presence of the impurity energy band of Cu 3d in intrinsic band gap. The valence and conduction band positions of Cu-doped hydrogen titanate nanotubes were determined by valence band spectra. The valence band is shifted to lower potential while the conduction band is shifted to higher potential after Cu doping, explaining the origin of the band gap narrowing and red shift.

1. Introduction

Since Kasuga et al. [1] first reported the TiO_2-based nanotubes synthesized by the hydrothermal treatment of TiO_2 particles in NaOH aqueous solution, one-dimensional titanate nanotubes (TNTs) have been intensively investigated over the past decade and utilized in a wide range of potential applications, including catalysts [2,3], ion-exchangers [4], secondary batteries electrodes [5], lithium storage [6], and dye-sensitizing solar cells [7,8]. TNTs have attracted much attention because of their lower dimensionality, larger surface area, and better adsorption capacity compared with TiO_2 particles. However, the band gap of TNTs is larger than that of TiO_2 (3.0 and 3.2 eV for rutile and anatase, respectively) [9]. TNTs can only be excited by UV light (5% sunlight spectrum), which limits utilization efficiency of natural sunlight [10]. Therefore, it is desirable to extend absorption of the solar spectrum into visible light region (43% sunlight spectrum) [11].

Many attempts such as transition metal doping, nonmetal ions doping, and deposition of noble metals on the surface of TNTs [12–14] have been made to improve the performance of TNTs under visible light irradiation. Due to the open end and multiwall structure of nanotubes, TNTs exhibit excellent structural stability and ion-exchange properties at room temperature [15]. Doping by ion-exchange method is a simple and effective way to modify the optical properties of TNTs. It was reported that sodium or hydrogen ions in the interlayer of TNTs can be easily exchanged with various ions [16–23] in aqueous solution. The intercalation of these ions can improve the optical performance and other chemicophysical properties. However, the TNTs prepared using TiO_2 particles as starting material are usually in the form of powder. The TNT powders could not be desirable for wider applications relative to TNT thin films due to difficulty of recovery of the powders. The reports of TNT thin films were scarce [24–29]. However, the synthesis of Cu doped TNT thin films as well as the effect of Cu doping on the optical properties of titanate nanotubes have not been studied.

We prepared Cu-doped TNT thin films using titanium plates as starting material. The effect of Cu doping on the optical properties and electronic structures of TNTs were studied by both experiments and first-principles calculations.

2. Materials and methods

2.1. Experimental

As described previously [26,27], sodium and hydrogen titanate nanotubes (NaTNTs and HTNTs) were prepared using alkaline hydrothermal method. Titanium plate (20 mm × 30 mm × 0.5 mm) was placed in 20 mL of 10 M NaOH aqueous solution and then heated in a sealed Teflon-lined autoclave at 140 °C for 12 h. White film was formed and adhered to the titanium plate. Then the products were

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washed with de-ionized water until pH reached about 7, dried in air and then NaTNTs samples were obtained. The NaTNTs samples were subsequently soaked in 0.1 M HCl solution for 24 h and then washing with de-ionized water was repeated. The acid treatment converts NaTNTs into hydrogen titanate nanotubes (HTNTs). For Cu-doped hydrogen titanate nanotubes (Cu-HTNTs), the samples were prepared by immersing the HTNTs products into 50 mL of 0.2 M $CuSO_4\cdot 5\,H_2O$ for 24 h at room temperature. The final products were washed with de-ionized water several times and dried at 60 °C.

The morphology of the synthesized materials was investigated with scanning electron microscopy (SEM, FEI Quanta 200FEG) and transmission electron microscopy (TEM, TECNAI G2 F30), while the atomic composition was determined using an EDX spectrometer attached to the SEM. The XRD patterns of samples were recorded using an X-ray diffractometer (XRD, Rigaku D/MAX-RB, Japan) with Cu Kα radiation (40 kV, 30 mA). The samples were dispersed in ethanol by sonication and then supported onto a copper grid coated with a carbon support film for TEM, high resolution transmission electron microscopy (HRTEM), and high angle annular dark field transmission electron microscopy (HADDF-STEM) observation. The X-ray photoelectron spectroscopy (XPS) measurement was performed using an ESCALAB 250 instrument (Thermo scientific) equipped with a monochromatized Al Kα X-ray source ($h\nu = 1486.6$ eV). The total-energy resolution was ~0.6 eV. The binding energy was calibrated against the C (1 s) binding energy (284.6 eV). The XPS data were fitted with an asymmetric Lorentzian–Gaussian sum function and Shirley background subtraction. Ultraviolet–visible (UV–vis) diffused reflectance spectra were performed on a UV–vis spectrophotometer (U4100, Hitachi, Japan) attached with an integral sphere using the reflectance of $BaSO_4$ as a reference. The absorption spectra of the samples were extracted from the equivalent diffuse reflectance spectra using the Kubelka–Munk function.

2.2. Computational methods and models

Similar to our previous study [27], the first-principles calculations for gaining the effect of Cu doping on the electronic structures of TNTs were performed using Cambridge Serial Total Energy Package (CASTEP) with a plane-wave-based method within DFT [30]. The exchange-correlation energy was calculated using the generalized gradient approximation with the Perdew–Bueke–Ernzerh scheme (GGA-PBE) approximation [31]. The interactions between the electrons and ion cores were described by the Vanderbilt-type ultrasoft pseudopotentials [32]. The plane-wave cutoff energy was taken as 340 eV. The valence electron configurations for Ti, O, Cu, H, and Na were $3s^23p^63d^24s^2$, $2s^22p^4$, $3d^{10}4s^1$, $1s^1$, and $2s^22p^63s^1$, respectively. The reciprocal-space integration over the Brillouin zone was carried out by using the Monkhorst–Pack scheme with $3\times 7\times 3$ k-sampling in the irreducible wedge. The atomic positions of all models were relaxed during the structural optimization. All models were relaxed through the conjugate gradient minimization of the total energy to a tolerance of 2.0×10^{-5} eV/atom, the forces to a tolerance of 0.05 eV/Å, and the atomic positions to a tolerance of 2×10^{-3} Å. The 24-atom $Na_2Ti_3O_7$ and $H_2Ti_3O_7$ unit cell was used [33]. The model of $Na_xH_{2-x}Ti_3O_7$ ($0<x<2$) was assumed to be $NaHTi_3O_7$ ($x=1$). $H_2Ti_3O_7$ in which two H atoms were substituted by one Cu bivalent cation was constructed to simulate the Cu-doped model of $H_2CuTi_6O_{14}$. The Cu/Ti atomic ratio (1: 6) and the chemical state of Cu^{2+} were dependent on the EDX and XPS results (discussed below). The models of $NaHTi_3O_7$, $H_2Ti_3O_7$, and $H_2CuTi_6O_{14}$ corresponded to the NaTNTs, HTNTs, and Cu-HTNTs, respectively.

3. Results and discussion

3.1. Morphology and composition of titanate nanotubes

The SEM images in Fig. 1 show that these samples are all uniform and dense fibrous substances with the length up to 2 μm. The EDX spectra show that Cu-HTNTs contained Cu (Fig. 1d), implying Cu ions are intercalated into the nanotubes successfully. Fig. 2 shows the TEM images of nanotubes with an average diameter of about 6 nm. The detailed structure of these nanotubes

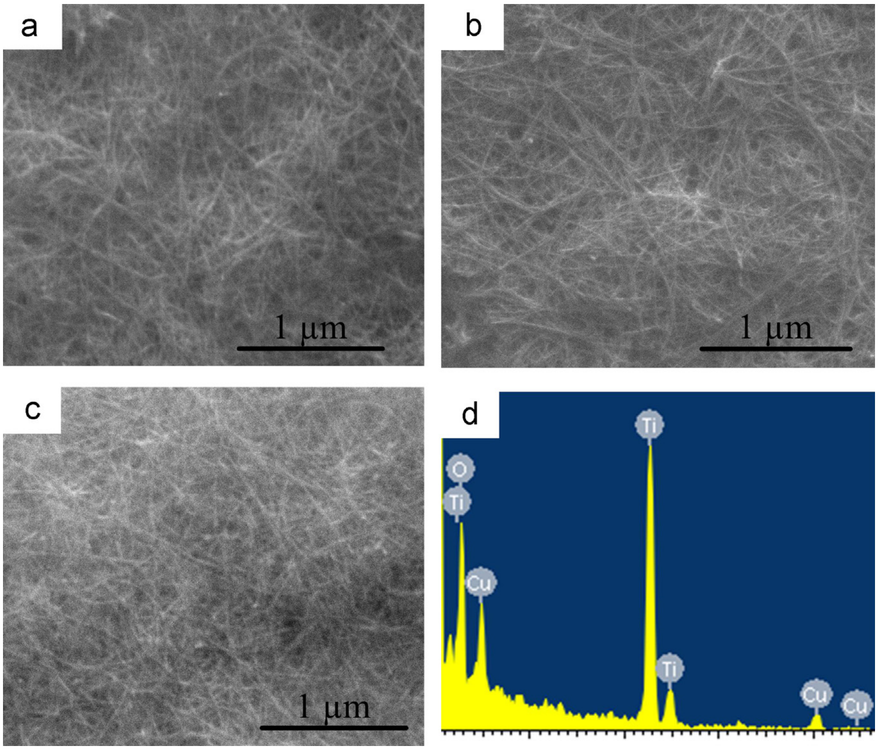

Fig. 1. SEM images of (a) NaTNTs, (b) HTNTs, and (c) Cu-HTNTs. EDX spectra of Cu-HTNTs (d).