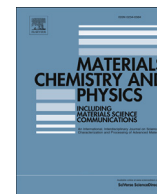




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## Silver nanoparticles embedded titania nanotube with tunable blue light band gap

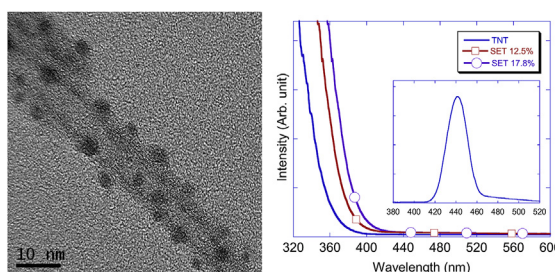
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## HIGHLIGHTS

- The self-assembly silver nanoparticles are embedded on titania nanotube.
- The charge of silver atoms is neutral in the formation of silver nanoparticles.
- The quantitative microanalysis data confirm that ratio of Ag/Ti is  $15.2 \pm 2.7\%$ .
- The band gap of SET locates in the desirable blue light region.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Silver nanoparticles embedded titania nanotube (SET) have been successfully prepared by titania nanotubes and silver nanoparticles via a template-free reaction. Powder X-ray diffraction (P-XRD) spectra and Fourier transform infrared (FT-IR) spectra show that the charge of silver atoms maintains neutral in the formation of silver nanoparticles. The Ag atom of Ag nanoparticles and the oxygen atom of  $\text{TiO}_2$  possess a chemical bonding with an ionic character rather than a covalent character. The quantitative microanalysis data collected from X-ray photo-emission (XPS) spectra indicate that the ratio of Ag/Ti in SET is  $15.2 \pm 2.7\%$ . The cut-off band gap of SET is adjustable from 420 nm (Ag/Ti = 12.5%) to 430 nm (Ag/Ti = 17.8%).

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## 1. Introduction

In the past decade, low-dimensional titania nanostructural materials have attracted much scientific and technological attentions due to their strong photo-oxidizing ability, high chemical stability, and potential applications in solar cell system [1]. Flexible control of size and shape of titania nanotube is of great importance because the tubes or wires in the nanoscale region possess more

novel properties than those of nanoparticles [2]. In contrast to the size control, control of the shape of titania nanomaterials is more difficult and challenging. Additionally, the wide band-gap (3.2 eV for anatase phase) of titania requires ultraviolet (UV) irradiation for photocatalytic activation [3–6]. Unfortunately, UV spectrum accounts for a very small fraction (8%) of the solar spectrum, in comparison with visible light (45%) [6]. Thus, any shift in the light absorbance of titania from the UV towards visible spectrum region will improve the photocatalytic and photoelectron chemical utility of the material. Accordingly, titania band gap can be narrowed by doping metal material, such as Fe, Mo, Ru, Os and V on the surface

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of titania nanomaterials [7–9]. In this study, we employ a solution method to prepare silver nanoparticles embedded titania nanotube (SET). The titania nanotubes are synthesized from the as-prepared titania nanoparticles via an aqueous solution. Silver nanoparticles are self-assembled from silver atoms, reduced from silver ions by vitamin C. The as-synthesized Ag nanoparticles are allowed to self-embed on the surface of titania nanotube by either electron affinity or chemical force. The aqueous solution method is environmentally friendly and economically affordable route in the preparation of one dimensional titania nano-tube with desirable blue-light band gap.

## 2. Experimental section

A typical synthesis of titania nanotube was prepared as follows. Potassium chloride (0.1 M) 0.4 mL was added in ethanol (>99%, Aldrich) 100 mL as a starting solvent. Tetrabutyl orthotitate (>97%, Fluka) 2.2 mL was slowly introduced into the starting solvent with a stirring speed at 250 rpm for 10 min. The color of solution turned to milky white gradually. The mixture was left in a hood for precipitation. After 24 h of precipitation, the upper clear layer was discarded and the white precipitation was transferred to an oven. The temperature of oven was set at 60 °C for 1 h, and then changed to 550 °C with a rate of 10 °C/min for another 4 h. After calcinations, a white product was collected, denoted as TNP, for next step of the experiment.

The as-prepared TNP (0.1 g) was mixed with 20 mL NaOH (99%, J-T Backer) in a 30 mL Teflon-lined stainless steel autoclave. The mixture was sealed and well stirred for 1 h before the sealed vessel was heated at 160 °C for 1 d. A white-flake product was obtained after the solvothermal reaction. Hydrogen chloride (0.05 M) was added to the white-flake product by drops until the pH value of solution decreased to pH = 2. De-ionized water 100 mL was added into the solution to raise the pH value of solution to neutral. The neutral solution was transferred to an oven again. The temperature of oven was set at 60 °C for 24 h. The obtained white powder is denoted as TNT (titania nano-tube) for future characterization.

In the preparation of the final product, TNT (0.03 g) was mixed with 0.01 g AgNO<sub>3</sub> (99.8%, Riedel) 200 mL in a vessel. HNO<sub>3</sub> (0.1 M)

30 mL was added by drops into the mixture until the pH value reached pH = 2. The mixture was stirring for 24 h. Ascorbic acid, i.e. vitamin C, (0.08 M) was slowly introduced to the mixture. The addition of ascorbic acid kept going, until the color of solution was changed from milk-white to tangerine. The color-change of solution is an indicator to confirm that silver ions are reduced to silver atoms completely. The mixture was set at hood for several h to wait the formation of precipitation. The precipitation was then washed by DI water and ethanol several times. The final product was dried as small crystals or suspended in ethanol for further study. These small crystals are stable in atmosphere for several months.

## 3. Results

### 3.1. TEM and EDX of TEM

The typical transmission electron microscopy (TEM) images for TNT are given in Fig. 1. The tube-shaped crystal shown in Fig. 1(a) is the dominate morphology for TNT. The diameter of the tube-shaped architecture is generally <20 nm. The length ranges from several tens to several hundred nm. The selected area electron diffraction (SAED), Fig. 1(b), shows a ring pattern, suggesting that the TNT tube is crystalline in nanometer scale [5,6].

The TEM images of the final products, obtained from the reaction of TNT and AgNO<sub>3</sub> in an acidic solvent, is provided in Fig. 2. In Fig. 2(a), the surface of tube-shaped crystal is hierarchically embedded with nanoparticles. In a blow-up micrograph, Fig. 2(b), the diameters of the self-embedded nanoparticles are clearly discernible. The size of the nanoparticle ranges from 3 nm to 5 nm. The energy dispersive X-ray spectrum (EDX) for the tube-shaped crystal with self-embedded nanoparticles is given in Fig. 2(c). Two peaks assigned for titania,  $K\alpha = 4.51$ ;  $K\beta = 4.93$ , and one peak attributed for silver,  $L\beta = 3.15$ , are identified [10]. The data of EDX suggest that the tube-shaped product is titania, and the nanoparticle is composed by silver atoms.

### 3.2. Powder X-ray diffraction (P-XRD)

For further confirmation the gradual changes in the crystallinity

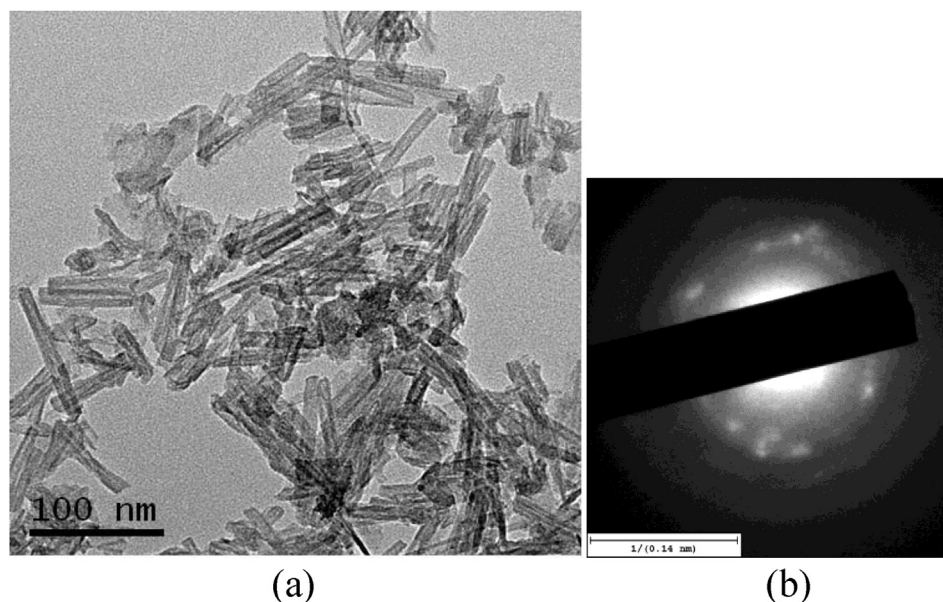


Fig. 1. (a) The diameter of tube-shaped crystals is generally < 20 nm, with length ranging from several tens to several hundred nm. (b) Selected area electron diffraction (SAED) shows ring pattern.

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