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# Bamboo-Shaped Ag-Doped $TiO_2$ Nanowires with Heterojunctions

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Bamboo-shaped Ag-doped $TiO_2$ nanowires with heterojunctions were synthesized by a simple solvothermal method. The diameter of the nanowires was about 50–100 nm, and they had a length of up to a few millimeters. The detailed structure of the heterojunction in the nanowire was also characterized.

Since the report of carbon nanobamboos in 1993,[1] there has been a growing interest in the synthesis of bamboo-shaped carbon,[2,3] BN,[4] CN,[5] and $MoS_2$[6] nanotubes based on their specific applications as both structural and functional materials. At present, some methods, such as arc discharge, catalytic pyrolysis, etc., have been developed to synthesize bamboo-shaped nanotubes. However, until now, bamboo-shaped nanowires have received little attention.

One-dimensional nanostructures provide a better model system for investigating the dependence of electronic transport, optical, and mechanical properties on size confinement and dimensionality.[7] In particular, nanowires play an important role as both interconnects and active components in fabricating nanoscale electronic and photonic devices. Although controlling the size of the nanowires can bring about changes in some of properties, doping of the nanowires through either in situ or postprocessing techniques provides a far more favorable approach to modulate their properties. $TiO_2$ is one of the most important semiconductor materials and has been studied extensively because of its potential applications in the areas of photocatalysis, photovoltaics, and photochromics.[8−12] Selective doping with various metal ions has proven to be an efficient route to improve the photoactivity and enhance the photocatalytic activity of titania.[13−16] Although many publications have focused on the metal-ion-doped $TiO_2$ nanoparticles,[17,18] little attention has been paid to the metal-ion-doped $TiO_2$ nanowires. Herein, we developed a simple solvothermal method and have successfully synthesized bamboo-shaped Ag-doped $TiO_2$ nanowire heterojunctions. The detailed structure for the heterojunction in the nanowire was characterized. To the best of our knowledge, the synthesis of bamboo-shaped Ag-doped $TiO_2$ nanowire heterojunctions has not yet been reported to date.

In a typical procedure, solutions of titanium butoxide [$Ti(OC_4H_9)_4$] in ethanol and solutions of sodium hydroxide (NaOH) in water were prepared as stock solutions in advance. A total of 10 mL of a 0.2 M titanium butoxide stock solution in ethanol was mixed with 10 mL of a 10 M NaOH aqueous solution, and 25 mg of $AgNO_3$ solid was added to the above mixed solution. The mixed solution was magnetically stirred for 1 h, then transferred into a Teflon-lined stainless steel autoclave, and heated at 200 °C for 24 h. The resulting precipitate was collected, washed with a 0.1 M HCl aqueous solution and deionized water until the pH value of the washing solution was about 7, and dried in air at 100 °C for 6 h.

Transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were obtained on a JEOL JEM-CX200 microscope at an acceleration voltage of 160 kV. The high-resolution TEM (HRTEM) images were carried out on a Philips CM200/FEG microscope at an acceleration

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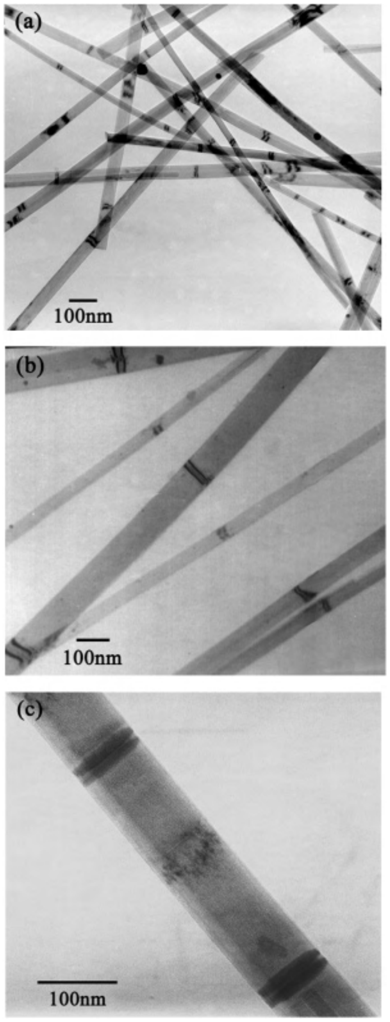


**Figure 1.** TEM images of the synthesized bamboo-shaped Ag-doped $TiO_2$ nanowires: (a) low magnification; (b) higher magnification; (c) a typical individual nanowire with two knots.

voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) was performed using a nanoprobe mode on a JEOL scanning electron microscope.

Parts a and b of Figure 1 show low-magnification TEM images of Ag-doped $TiO_2$ nanowire heterojunctions. The diameter of the nanowires is about 50−100 nm, and they have lengths of up to a few millimeters. The geometry of the nanowire is uniform. One of the important features of Ag-doped $TiO_2$ nanowire heterojunctions synthesized is that they are produced in high yield. The transformation of the reactants is very complete. A typical TEM image of an individual nanowire is shown in Figure 1c. It can be clearly seen that the sample shows knots in the nanowire structures, which makes the nanowires resemble a bamboo shape. The interval between two knots is not equal and ranges from several tens to hundreds of nanometers.

Figure 2a shows a TEM image of a Ag-doped $TiO_2$ nanowire with a heterojunction. The inset is an ED pattern taken from a knot of the nanowire along its [010] zone axis (area A). The diffraction spots can be indexed as diffraction of anatase $TiO_2$, which reveals the crystal nature of the nanowire. The diffraction rings come from polycrystalline Ag diffraction. Figure 2b shows a HRTEM image of a

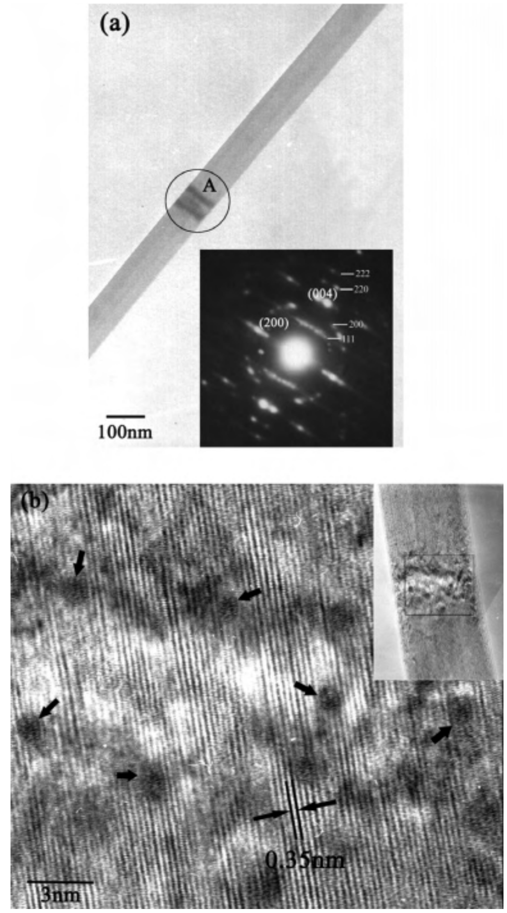


**Figure 2.** (a) TEM image of a nanowire heterojunction. The inset is the ED pattern from area A. (b) High-resolution TEM image of a nanowire heterojunction from the selected area in the knot. The Ag phase is marked by black arrows.

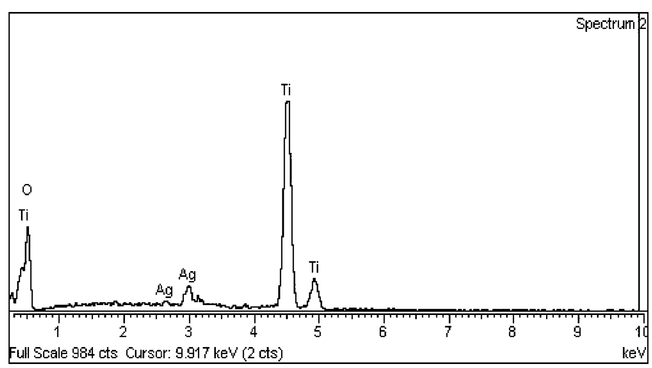


**Figure 3.** EDS spectrum from the knot in area A of the $TiO_2$ nanowire in Figure 2a.

nanowire heterojunction from the knot, on which the Ag phase is marked by a black arrow. Clearly, the presence of the Ag phase has not changed the whole crystal lattice in the knot. The interplanar spacing is about 0.35 nm, which corresponds to the distance between two (101) planes of anatase $TiO_2$. The EDS spectrum from the knot (area A) shown in Figure 3 indicates its composition.

In the absence of Ag ions, we only synthesized uniform and ultralong single-crystal $TiO_2$ nanowires with well-defined structures, on which no knots were observed.[19] Apparently,

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the formation of the specific bamboo-shaped structures seems to be closely connected with the dopant. However, very perfect lattice structures of single-crystasl $TiO_2$ nanowires would force Ag to segregate in heterojunctions, and the Ag phase could only exist in the surface of the single-crystal $TiO_2$ nanowires. The observation of a HRTEM image is consistent with the above explanation. Further studies on the mechanistic details are in progress.

In summary, this report provides a novel method to large-scale synthesize ultralong bamboo-shaped metal Ag-doped $TiO_2$ nanowires with heterojunctions and explores the detailed heterojunction structure of Ag-doped $TiO_2$.

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