# Solution-phase synthesis of single-crystalline $Bi_{12}TiO_{20}$ nanowires with photocatalytic properties†

**Jungang Hou,[ab] Yuanfang Qu,[b] Dalibor Krsmanovic,[a] Caterina Ducati,[a] Dominik Eder*[a] and R. V. Kumar*[a]**

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**Single-crystalline sillenite-type bismuth titanate nanowires with photocatalytic properties have been synthesized *via* a simple solution-phase synthesis route.**

Nanoscale structures, such as nanoparticles, nanorods, nanowires, nanocubes, and nanotubes, have attracted extensive attention as a result of their unique physical properties and their wide range of potential applications in nanodevices.[1] There are a variety of methods for synthesizing or fabricating one-dimensional (1D) nanostructures for different materials. The physical properties greatly depend upon the material, which can be metals, alloys, semiconductors, carbon, polymers, or molecular, but may also depend on shape, morphology, and structure (*i.e.*, crystalline or amorphous).[1] Developing approaches to prepare new sillenite oxides in controlled nano-morphology still remains a challenge.

Bismuth titanates, a large family that includes several phases in the Bi–Ti–O system, have recently drawn much interest due to their physical properties and technological applications.[2–4] The sillenites, with the general formula $Bi_{12}TiO_{20}$, exhibit good photocatalytic properties with potential applications.[3,4] Solid-state-reaction methods are the most common synthesis route for this material.[4] Due to its high temperatures, this route typically results in large agglomerated particles with low specific surface areas. Chemical methods such as co-precipitation and chemical solution decomposition routes have also been reported, these also require elevated calcination temperatures to develop full crystallinity which is accompanied by loss in BET surface area.[3,5] To the best of our knowledge, there have been no reports on the successful synthesis of one-dimensional $Bi_{12}TiO_{20}$ nanowires (NWs).

In this communication, we report a solution-phase synthesis route to single-crystalline $Bi_{12}TiO_{20}$ NWs. Bismuth nitrate and titanium isopropoxide were used as starting materials with the molar ratio of bismuth : titanium = 12 : 1. 1.03 g $Bi(NO_3)_3{\cdot}5H_2O$, and 0.05 g $Ti(OC_3H_7)_4$ were dissolved in 10 mL of deionized water under vigorous stirring. The pH value of the solution was adjusted to 14 using potassium hydroxide, which also served as a mineraliser, followed by adding 0.5 g poly(vinyl alcohol) (PVA) as a surfactant. Before being transferred to a 23 mL Teflon-lined autoclave, the solution mixture was prepared under an ultrasonic water bath for 30 min and kept at a filling ratio of 80% (v/v). The hydrothermal synthesis was conducted at 180 °C for 20 h in an electric oven. After the reaction, crystalline $Bi_{12}TiO_{20}$ was harvested by centrifugation followed by thorough washings with deionized water. The obtained nanowires were characterized with field emission scanning electron microscopy (FESEM, JEOL, JSM-6340F), X-ray diffraction (XRD) with Cu Kα radiation ($\lambda$ = 1.5406 Å) operated at a current of 40 kV and a voltage of 40 mA, and transmission electron microscopy, selected area electron diffraction (TEM/SAED, CM30) operated at an accelerating voltage of 200 kV. The high resolution TEM image was acquired using a JEOL 4000EX microscope, operated at 400 kV.

The morphology of the as-synthesized nanowires is shown in Fig. 1 and reveals that the material consists of nanowires with uniform diameters throughout their axial direction, and their lengths ranging between 1 μm and 10 μm. The NWs are flexible enough to bend while maintaining their uniform diameter.

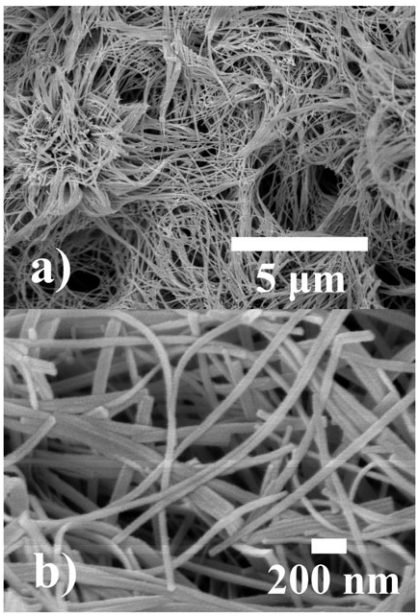


**Fig. 1** SEM images of as-prepared $Bi_{12}TiO_{20}$ NWs at different magnifications (a and b).

[a] *Department of Materials Science and Metallurgy, University of Cambridge, New Museums Site, Pembroke Street, Cambridge, United Kingdom CB2 3QZ. E-mail: rvk10@cam.ac.uk, de235@cam.ac.uk; Fax: +44 1223 334467; Tel: +44 1223 334327*
[b] *Key Laboratory for Advanced Ceramic and Machining Technology of Ministry of Education, Tianjin University, Tianjin, 300072, China*

† Electronic supplementary information (ESI) available: Experimental details; characterisation; SAED pattern; morphology at pH 14 in the absence of PVA; ball and stick model of $Bi_{12}TiO_{20}$. See DOI: 10.1039/b906290d

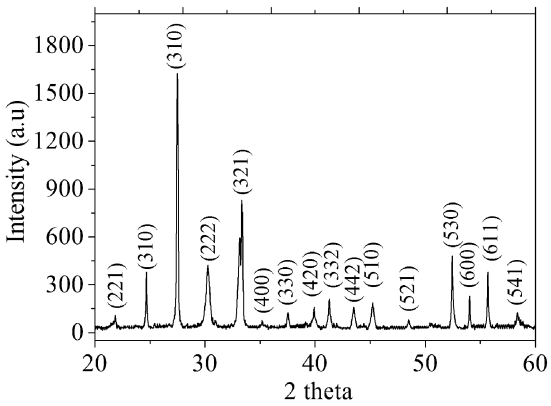


**Fig. 2** XRD pattern of as-prepared $Bi_{12}TiO_{20}$ nanowires.

The crystallinity of the as-prepared products was examined using XRD (Fig. 2). The crystallographic phase of these nanowires belongs to the cubic phase (space group: *Pm3m*), and the measured lattice parameters of the cubic $Bi_{12}TiO_{20}$ phase are $a = b = c = 10.18$ Å, in good agreement with that given in the JCPDS data file (No. 34-0097) for crystalline $Bi_{12}TiO_{20}$. This is of great importance as it has been proven difficult to produce single phase $Bi_{12}TiO_{20}$, due to phase transformations at higher temperature.[16] Thus, the solution-phase route is a facile and efficient process to synthesize single-phase $Bi_{12}TiO_{20}$ NWs with high crystallinity at the relatively low temperature of 180 °C.

Representative TEM images of the nanowires are shown in Fig. 3. The mean diameter of the NWs are ~50 nm with a standard deviation of ~10 nm. Each nanowire has a uniform diameter along its entire length and can achieve large aspect ratios approaching 200. In particular, no branching was observed, which implies that the nanowires were grown from spontaneous nucleation with high crystal perfection. Fig. 3c shows a SAED pattern of an individual $Bi_{12}TiO_{20}$ NW, which confirms the single-crystallinity of the nanowires. The diffraction pattern of the nanowire in Fig. 3c can be indexed as the growth direction along the [100] zone axis, and excellent single crystallinity is thus elucidated, corresponding to the schematic representation of the crystal structure of $Bi_{12}TiO_{20}$. The inner spots sit at the corners of a square. The ball-and-stick computer model for the $Bi_{12}TiO_{20}$ might help visualizing the structure. Ti atoms are in light grey, Bi atoms in medium grey, O atoms in black (small spheres).[5] As shown in Fig. 3b, two nanowires are joined together, indicating growth *via* a "cementing mechanism" (also called "oriented attachment").[6,7] The "chopstick" arrangement shows that the nanowires have inherent flexibility to attach themselves by bending without breaking. Furthermore, a high resolution TEM image of a $Bi_{12}TiO_{20}$ NW is shown in Fig. 4, seen close to the [001] zone axis. The largest plane spacing observed along the length of the nanowire corresponds to the {100}. Since this is a cubic system, we can argue that the growth direction, orthogonal to the [100], is [010].

Regarding the growth process in the hydrothermal synthesis, the concentration of hydroxyl ions and the presence of PVA play an important role in affecting the morphology. It has been reported that the aspect ratio of low-dimensional

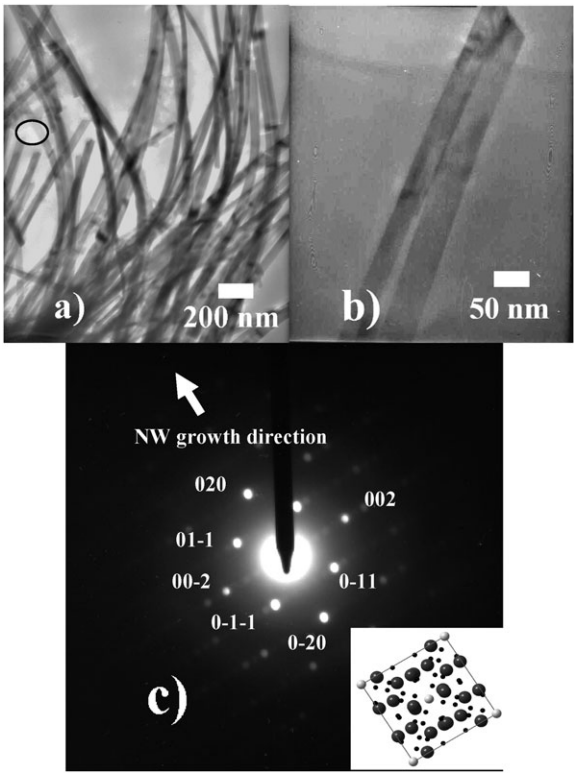


**Fig. 3** (a) TEM images of the as-prepared $Bi_{12}TiO_{20}$ NWs; (b) two NWs *via* a bending attachment process; (c) SAED pattern of the nanowire in (a), corresponding to the schematic representation of the crystal structure of $Bi_{12}TiO_{20}$ along the growth direction (Ti atoms are in light grey, Bi atoms in medium grey, O atoms in black).

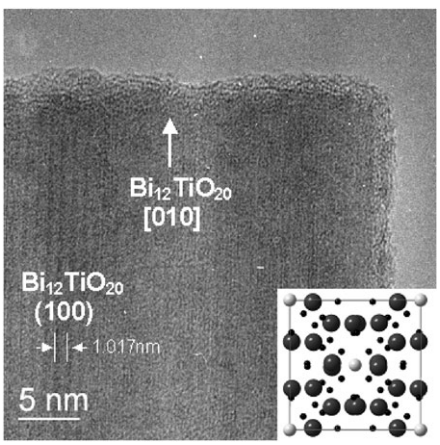


**Fig. 4** HRTEM image of the as-prepared $Bi_{12}TiO_{20}$ nanowires, indicating clear faceting parallel to the (010) facet and corresponding to the schematic representation of the crystal structure of $Bi_{12}TiO_{20}$.

oxide nanocrystals can be controlled by adjusting the $OH^-$ concentration, suggesting that $OH^-$ ions can behave as a surfactant in the hydrothermal process.[8,9] At lower pH (with or without PVA), the morphology were closer to 3D nanocubes and 2D nanoplates (not shown here). At the higher pH of 14, in the absence of PVA, the morphology can be described as non-uniform nanorods and some nanoplates (see ESI†). Addition of PVA at this pH was crucial for forming the nanowire structure. As a polymer surfactant,

 

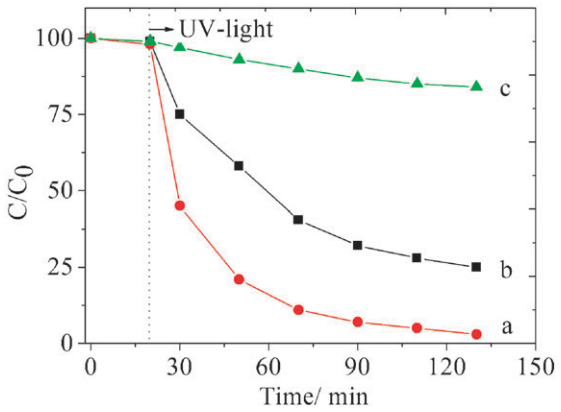


**Fig. 5** Photodegradation of methyl orange under UV-light irradiation with 150 mg of $Bi_{12}TiO_{20}$ NWs (a), bulk $Bi_{12}TiO_{20}$ particles (b), and without any NWs or bulk particles (c).

PVA exhibits strong hydrogen bonding, and has been often used in the hydrothermal synthesis of nanowires and nanocables.[10–12] Thus, the concentrations of $OH^-$ and the surfactant are the key parameters in ensuring the formation of Bi–O–Ti networks and a controlled release of this species from the solution phase to the $Bi_{12}TiO_{20}$ nanostructures.

Photocatalytic properties of $Bi_{12}TiO_{20}$ micro- and nanocrystals and films have been demonstrated through the degradation of methyl orange (MO) in aqueous solutions under UV-light irradiation.[3,13,14] MO is a useful model for the evaluation of the photocatalytic properties of materials. The photocatalytic performance of the synthesized $Bi_{12}TiO_{20}$ NWs was tested for the degradation of MO under UV-light irradiation and compared with a bulk sample of $Bi_{12}TiO_{20}$, which was calcined at 600 °C for two hours and the morphology consisted of large agglomerations of sub-micron particles. Without any catalyst, there was a negligible decrease in the MO arising only from the slow evaporation of the solvent during the irradiation (Fig. 5). 150 mg of the $Bi_{12}TiO_{20}$ was put in a quartz beaker and, with the aid of ultrasonication, dispersed in 100 ml of deionized water containing MO (0.005 M). After 20 min of stirring, the suspension was illuminated with UV light (254 nm, 6 W). At 10 min intervals, 0.5 ml of the suspension was taken, centrifuged and analysed by UV-Vis spectroscopy (Perkin Elmer Lambda 850). The absorbance of MO (maximum at 464 nm) is related to its concentration and was followed as a function of time. Fig. 5 shows the results for photodegradation of methyl orange under UV-light irradiation with both the NWs and the bulk material. It is clear that the concentration of methyl orange decreased faster for the nanowires than for the micron-sized crystals, indicating a higher photocatalytic activity for the $Bi_{12}TiO_{20}$ NWs. The improved photocatalytic performance of the $Bi_{12}TiO_{20}$ nanowires is attributed to a considerably higher specific surface area (25 $m^2\ g^{-1}$) compared with the $Bi_{12}TiO_{20}$ particles calcined at 600 °C (~1.4 $m^2\ g^{-1}$), providing more active sites for the photocatalytic reaction and promoting the efficiency of the electron–hole separation due to high crystallinity.[15]

In summary, we present a simple and effective process for the synthesis of single-crystalline $Bi_{12}TiO_{20}$ nanowires with diameters of 50 nm and large aspect ratios. The nanowires were highly crystalline while maintaining high BET surface area arising from the low synthesis temperature. The nanowires exhibited significantly improved photocatalytic activity for the degradation of methyl orange under UV-light irradiation compared with the bulk material. Control of morphology is considered critical in determining properties of nanocrystals. The method suggested in this communication offers a controlled technique for producing highly crystalline high aspect ratio nanowires of cubic $Bi_{12}TiO_{20}$.

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## Notes and references

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