

Characterization of TiO₂ Nanorods: The Phase Transformation from Anatase to Rutile

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Titania (TiO₂) has been found as an important functional material and applied to various fields, such as photochemical water-splitting under UV illumination [1] and dye-sensitized photovoltaic cells [2]. Nanostructured TiO₂ with different morphologies has attracted great interest since unique shape and structure dependent properties might be originated from titania nanomaterials. Crystalline TiO₂ has three polymorphs and they are anatase, rutile and brookite. Among them, rutile is the most stable phase and is normally prepared by calcinations of anatase at high temperatures. As a photocatalyst, anatase TiO₂ is usually considered to be more active than the crystalline rutile. Rutile has a lower bandgap (3.02 eV) than anatase (3.23 eV) and therefore absorbs more strongly than anatase in the near-ultraviolet-light region (360–400 nm). In some cases rutile had higher photocatalytic property than anatase. Obviously, photocatalytic activity is related to the crystallinity and the specific surface area. Indeed, the enhanced photocatalytic property has been observed in the rutile and anatase mixed phase. Here, we report a two-step fabrication procedure to grow rutile TiO₂ nanorods above anatase TiO₂ films on an arbitrary substrate. In present work, a thin layer (about 20–50 nm) anatase TiO₂ was firstly fabricated on an arbitrary substrate followed by growth of rutile TiO₂. The morphology and interface structure were characterized by x-ray powder diffraction and electron microscopy.

The SEM images of the nanorods synthesized at 175 °C for 3 hour were shown in fig.1 (a) and (b). The nanorods had an average length about 700 nm and diameter of about 80 nm. A cross-section STEM image of the nanorods and interface was shown in fig.1 (c), where the Z-contrast image was collected by a high-angle annular dark-field detector. The interface between large rod-like rutile particle and small rounded anatase particles was found in an area closed to the substrate, as shown in fig.2(a). The structures of the nanoparticles were identified by doing Fourier transform of the HREM image and calculating the *d*-spacing of the crystalline lattice, which could be measured with the peaks shown in diffractogram. As shown in fig. 2(b), the [211] direction of the rutile TiO₂ particle is almost along the incident beam direction. The anatase nanoparticle cannot be indexed as any low-order zone (the center-symmetry in intensity shown in the diffractogram was imposed by the Fourier transform). However, the lattice plane of 0.35 nm (as shown by an arrowhead in fig.2c) is a typical spacing of the (110) plane of anatase. Along the interface there is a distorted and defects concentrated area, as shown by the black arrows. Without the polycrystalline anatase TiO₂ layer, rutile TiO₂ nanorods could not grow directly on Si substrate by hydrothermal method with the same growth parameters. This implies that the anatase TiO₂ layer can efficiently act as a nucleation layer for the growth of rutile TiO₂.

References

1. Fujishima, A. and Honda, K. *Nature*. 238 (1972) 37.
2. Kongkanand, A. *et al. J. Am. Chem. Soc.* 130 (2008) 4007.
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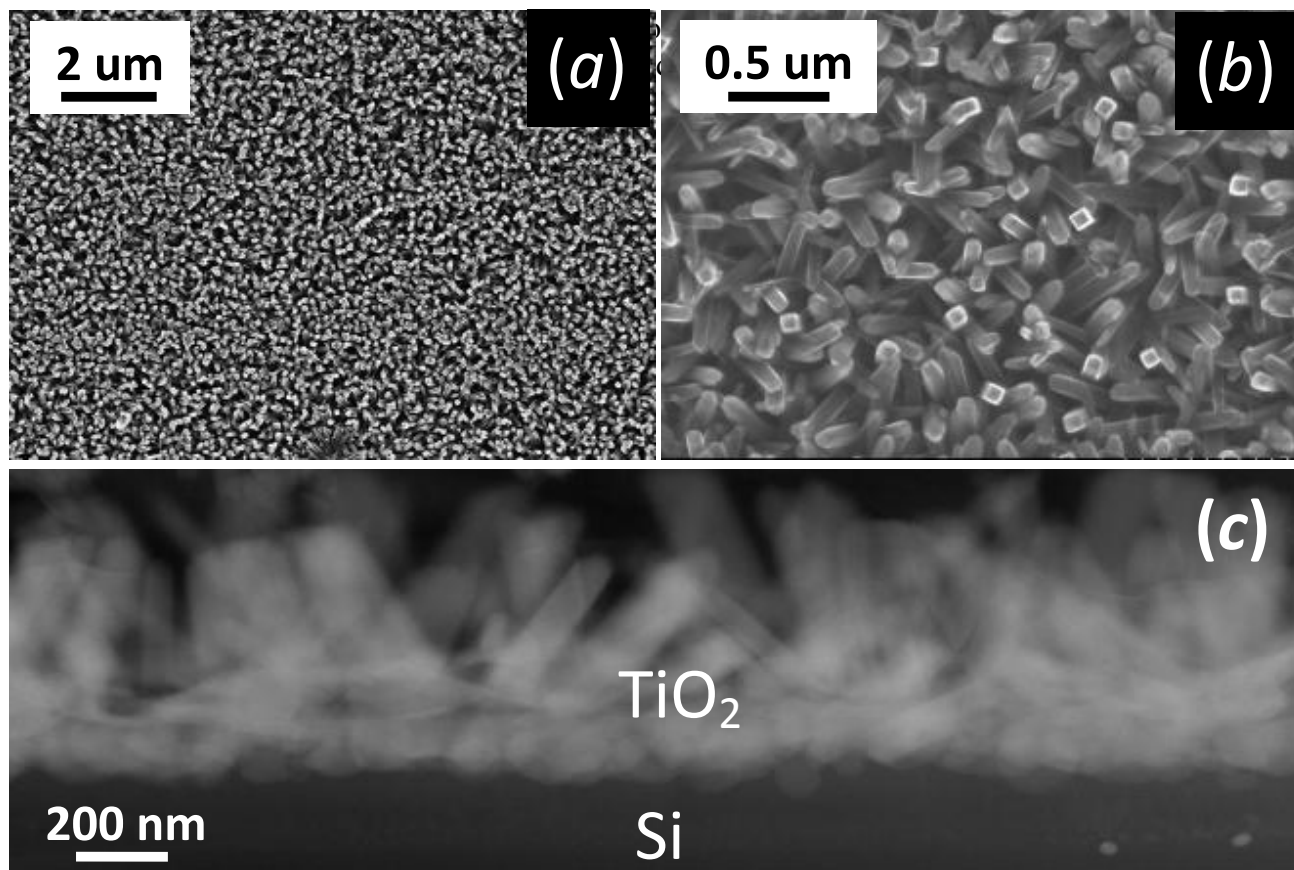


Figure.1 (a) Low-magnification and (b) medium magnification SEM images of TiO_2 rods grown on anatase film at 175 degree for 3 hours. (c) STEM image of cross-section of the TiO_2 nanorods/anatase TiO_2/Si interface, collected by annular-dark field detector.

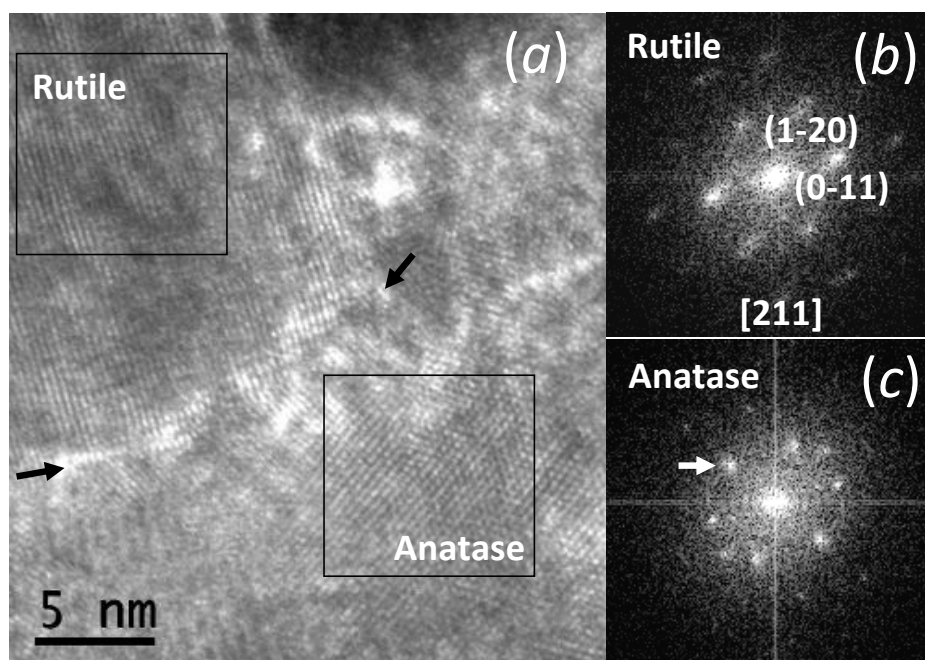


Figure.2 (a) a HREM image of the interface of Rutile TiO_2 nanorod and Anatase TiO_2 nanoparticle. The interface is tilted and incoherent. (b) and (c) are corresponding Fourier transform of the area shown by rectangles in (a), which can be indexed by using either Rutile or Anatase structure.