

THERMAL GROWTH AND VISIBLE-LIGHT PHOTOCATALYSIS OF TiO₂ NANOWIRES

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Introduction

TiO₂ nanowires have been extensively studied for various promising photocatalysis applications such as elimination of pollutants and splitting of water for hydrogen fuel [1-4]. TiO₂ nanowires have been reported to enhance the photocatalytic reactivity and to avoid several problems of commercial TiO₂ powder catalysts [3,4]. The powder catalysts have difficulties in the separation of the catalyst from suspension after reaction. Besides, the suspended particles tend to aggregate in highly concentrated suspensions diminishing the photocatalytic reactivity. The TiO₂ nanowires grown on substrate can be an excellent alternative satisfying for a high specific surface area and an easy catalyst recovery process.

Recently, many methods have been developed for the synthesis of TiO₂ nanowires, including vapor phase deposition [5], oxidation of Ti metal [6], solution chemistry synthesis [3], and template-assisted approach [4]. Nevertheless, it is interesting and important to explore more controllable and cheaper synthesis method on large-scale substrates. Another important aspect is the modification of TiO₂ by doping to realize photocatalytic reactivity under visible light. The wide bandgap energy (~3.0-3.2 eV) of TiO₂ limits its photocatalytic reactivity to ultraviolet light. In order to extend the photocatalytic reactivity to visible light regime, transition metals or nonmetals such as carbon and nitrogen should be doped into TiO₂. In this study, we synthesized TiO₂ nanowires via a simple thermal treatment of Ti metal thin film under methanol vapor. The method not only is adequate for low-cost mass production, but also provides self-doped carbon to be utilized for the efficient visible-light photocatalysis. We will discuss the growth results including the growth mechanism and the photocatalytic characteristics.

Experimental

The Ti metal film was deposited onto Si (100) WAFERS by dc magnetron sputtering. The thickness of Ti film was varied from 0.4 to 1.2 μm. The Ti/Si substrates were subsequently loaded into a quartz-tube furnace. Then, the

nanowires were grown with supplying methanol vapor at a desired temperature (600-850 °C). The methanol was bubbled at 10 °C with the argon gas flow rate at 150 SCCM. The furnace pressure was varied between the ranges of 4 and 100 Torr.

The morphology and size of the TiO₂ nanowires were characterized by using a field-emission scanning electron microscopy (FESEM, Jeol JSM 7000F). The crystal structure of the TiO₂ nanowires was analyzed by using transmission electron microcopies (TEM, Philips CM200 at 200 kV, FEI Tecnai F20 UT at 200 kV). The chemical states of the TiO₂ nanowires were studied by using x-ray photoelectron spectroscopy (XPS, Escalab 200R) using Al K_α anode. The photocatalytic activity was studied by measuring the decomposition of methylene blue (MB) in aqueous solution by using UV-VIS spectroscopy. The initial concentration of MB solution was about 10⁻⁵ mol·l⁻¹. The white light (100 mW·cm⁻²) of a common room lighting bulb was used as visible light.

Results and Discussion

Figure 1 shows a typical SEM image of the TiO₂ nanowires grown under methanol vapor at 750 °C for 60 min. The Ti metal film thickness was 0.8 μm. It is clearly seen that the TiO₂ nanowires are formed at a high density. The nanowires appear to be grown homogeneously with a length of ~7-9 μm and ~40-50 nm of diameter. We note that the TiO₂ film was formed when the water vapor was used instead of methanol vapor, indicating that the carbon, supplied by the decomposition of methanol, plays a critical role in the nanowire growth.

The crystal structure of the nanowires was investigated by TEM (not shown here). The TEM diffraction patterns revealed that the nanowires grown at 700 °C were single-crystalline rutile and were grown along the rutile [110] zone-axis. The high-resolution TEM lattice image showed a lattice spacing of 0.32 nm along the [110] direction, which is consistent with the (110) plane spacing of the TiO₂ rutile structure. The TiO₂ nanowires seems to be grown preferentially along the [110] direction because the (110) plane is the most thermodynamically stable in the TiO₂ rutile structure.

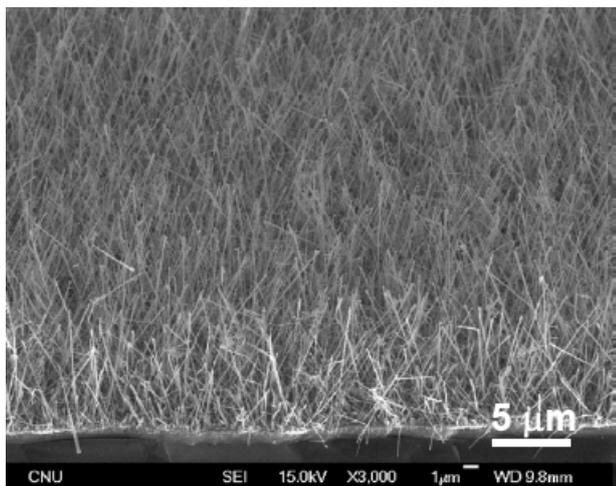


Fig. 1 SEM image of the TiO₂ nanowires grown on a Ti/Si(100) wafer at 750 °C.

The XPS study showed the binding energies of Ti 2p and O 1s corresponding to a typical TiO₂ bond. Importantly, the XPS revealed a C 1s at 284.5 eV along with a shoulder peaks at ~287.5 eV. The peak at 284.5 eV corresponds to non-functionalized C-C bond. The shoulder peak around 287.5 eV can be attributed to the adventitious elemental carbon and carbonate species for visible-light photocatalysis.

The effects of the self-doped carbon on the photocatalysis were evaluated by measuring the decomposition of methylene blue (MB) in an aqueous solution. As seen in Fig. 2, the nanowires decompose MB effectively under visible light irradiation. The activity can be attributed to the self-doped carbons incorporated during the nanowire growth. Carbon doping has been reported to narrow the bandgap energy of TiO₂, resulting in the visible-light photocatalysis [7]. The visible-light photocatalytic activity was further enhanced by thermal annealing and plasma treatment.

Conclusion

We demonstrated TiO₂ nanowire growth via a simple thermal treatment (600-850 °C) of Ti metal film under methanol vapor. The carbon, supplied by the decomposition of methanol, seemed to play an important role in the nanowire growth. Moreover, the carbon was self-doped in the TiO₂ nanowires so that efficient visible-light photocatalysis could be realized. The photocatalytic activity was more enhanced by thermal annealing and plasma treatment. In this presentation, we will further discuss the growth mechanism and the photocatalytic characteristics.

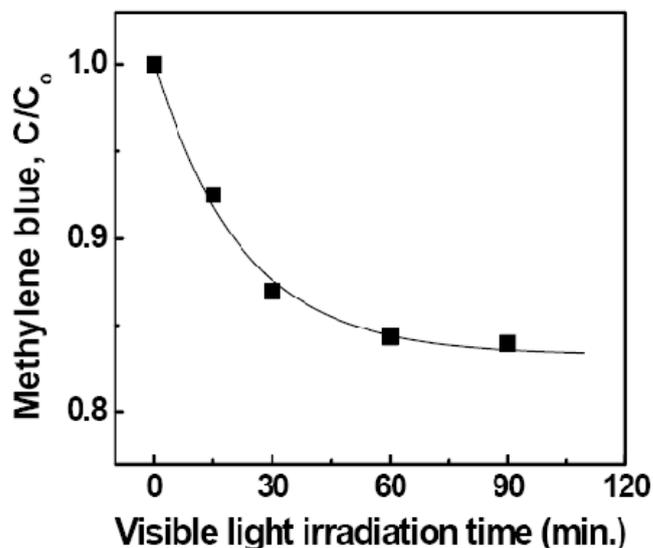


Fig. 2 Decomposition of MB by the TiO₂ nanowires as a function of visible-light irradiation time. The ratio (C/C₀) represents the remained concentration to the initial concentration of methylene blue in aqueous solution.

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