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# Free-standing $TiO_2$ nanotube array films sensitized with CdS as highly active solar light-driven photocatalysts

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ABSTRACT

Self-organized, large-scale, free-standing $TiO_2$ nanotube (TiNT)-array films were fabricated via anodization of titanium (Ti) foil in fluorine-containing ethylene glycol, followed by a facile detachment method to flake the TiNT arrays off the Ti substrate. After annealing, the resulting film consisted of well-ordered, vertically oriented, nanocrystalline TiNT arrays of ~130 nm pore diameter, ~25 nm wall thickness, and ~46 μm length, corresponding to a high aspect ratio (the length/diameter) of ~250. The surface modification of the TiNT-array film using a simple solution-based method was carried out to fabricate a CdS nanoparticle-sensitized TiNT heterostructure-array (CdS/TiNT) film. Except for the significant shift in spectral photoresponse to a lower energy, the induced electron–hole pairs were extracted efficiently by their type-II band alignments in the CdS/TiNT arrays. This was confirmed by the incident photon-to-electron efficiency measurements and the kinetics of photocurrent decay in response to on-off irradiation. As a result of the strong absorption within the solar spectrum and the effective suppression of electron–hole pair recombination, a significant increase of ~10 times in the apparent first-order rate constant ($k_{obs}$) of methylene blue (MB) photo-degradation under simulated sunlight (AM 1.5G) illumination was obtained as compared with the commercial Degussa P25 film. This free-standing film provides the advantage of the use of back-side illumination where light directly strikes the CdS/TiNT arrays, largely reducing incident light loss through the solution. In this case, the $k_{obs}$ value was further increased by ~30% compared with that in front-side illumination. The ease of free-standing $TiO_2$ nanotube array film fabrication and CdS sensitization in this process will facilitate the development of environmental contaminants' solar light-driven decomposition.



## 1. Introduction

The use of metal-oxide semiconductors (e.g., $TiO_2$, ZnO, $WO_3$ and $Fe_2O_3$) is considered to be environment friendly because these semiconductors can decompose the harmful organic and inorganic pollutants present in air and in an aqueous system under sunlight or indoor fluorescent light [1–3]. Of the materials being developed as photocatalysts, $TiO_2$ is currently the most promising because of its special features, such as its low cost and photochemical stability [4]. However, the poor utilization of solar energy and the short diffusion length of a photogenerated electron–hole pair are the two major factors limiting the further improvement of photocatalytic efficiency. Therefore, an indispensable and challenging issue in this field is the development of new and efficient sunlight-sensitive photocatalysts.

Efforts to shift the band gap of $TiO_2$ via, for example, substitutional doping with N, C, and S [4–6], and coupling photosensitizers (e.g., CdS, PdS, and polymer) [2,7–9] have successfully extended its photoresponse to visible light. In addition to narrowing the band gap, a thick $TiO_2$ film to enhance the total absorption of solar light and a high contact area with the solution to allow the efficient decomposition of contaminants are also critical in maximizing photocatalytic efficiency. The ordered arrays of one-dimensional (1-D) $TiO_2$ architectures allow a direct path for charge collection and access to the solution, thus improving light harvesting as a thicker film to enhance the absorption of light without adversely affecting charge recombination [10,11]. The tubular structure facilitating the availability of both internal and external areas of the nanotubes for reaction [11] has been recognized to be preferable because these applications are mostly surface area controlled.

The growth of highly ordered $TiO_2$ nanotube (TiNT) arrays with a length of a few hundred nanometers has been first reported using the electrochemical anodization of a Ti foil in aqueous hydrofluoric acid solution [12,13]. Later, the length of the TiNT arrays increased

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up to a few micrometers via tailing the electrochemical conditions [14,15]. Recently, TiNT arrays with a high aspect ratio of tens or hundreds of micrometer length have been produced through the anodization of Ti foil in non-aqueous organic electrolytes [16,17]. Early works [18–22] had shown that a highly ordered TiNT-array architecture as immobilized photocatalysts is environmental promising. However, the nature of the abovementioned TiNT arrays attached to the opaque Ti foil has restricted their feasibility for extensive applications. Very recently, the detachment of the TiNT film from the underlying Ti substrate has been reported to involve the use of ultrasonic agitation [23]. In addition, Albu et al. [24] used a selective dissolution of the Ti substrate in a corrosive $CH_3OH/Br_2$ solution to obtain a free-standing TiNT film. Wang and Lin [25] described the delamination of the barrier layer between $TiO_2$ nanotube arrays and Ti substrate via a methanol evaporation method.

In the present work, a free-standing TiNT film was prepared through a simple and environment-friendly process. Subsequently, the TiNT film was sensitized using CdS nanoparticles through the solution-based method. Such heterostructure film of CdS/TiNT showed superior light-harvesting and electron-transport property efficiency, which were confirmed by the incident photon-to-electron efficiency (IPCE) measurements and the kinetics of photocurrent decay in response to on-off irradiation. A remarkably

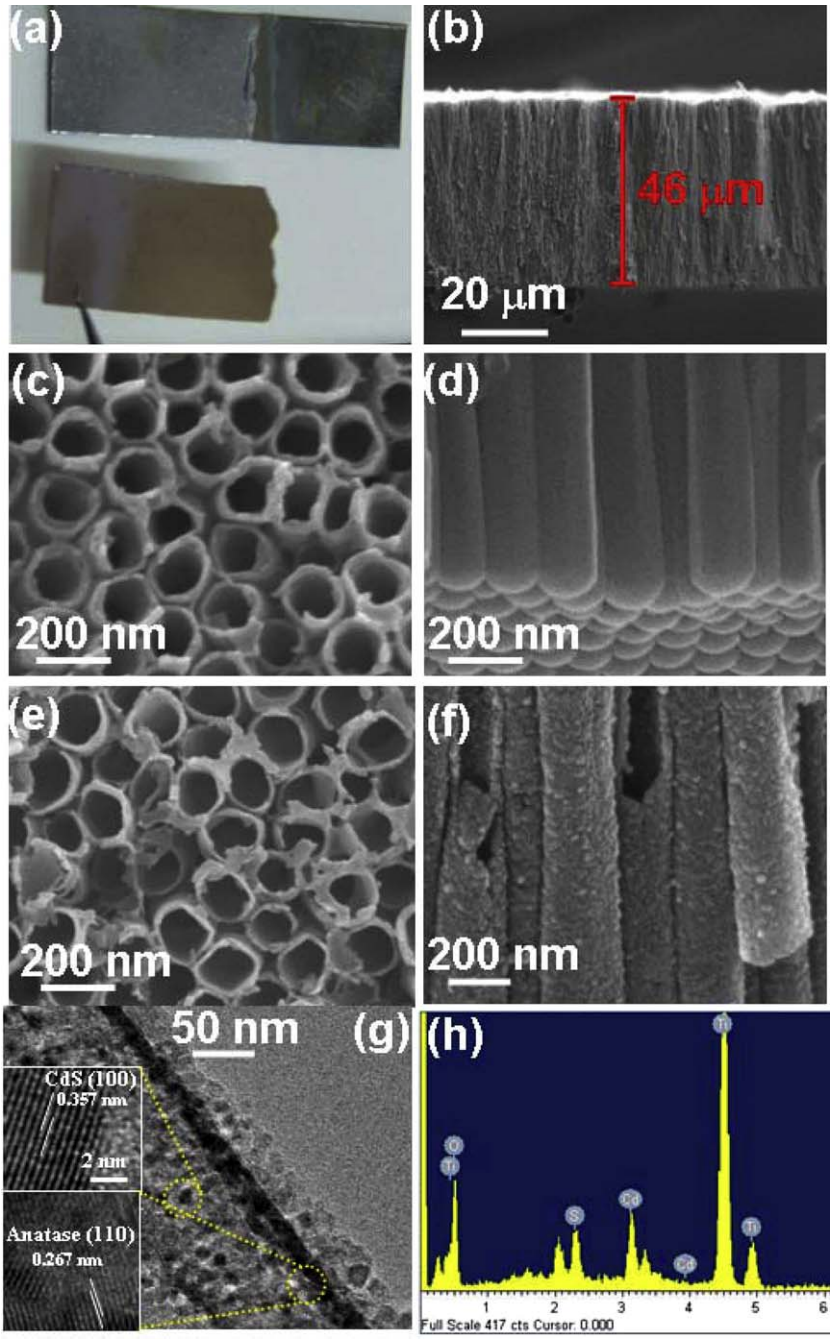


**Fig. 1.** (a) Photographic image of the detached TiNT-array film, and morphologies of TiNT-array films. (b) Side-view FE-SEM image of the TiNT array. (c) Top-view FE-SEM image of the TiNT array. (d) Bottom-view FE-SEM image of the TiNT array. (e) Top-view FE-SEM image of the 10-CdS/TiNT arrays. (f) Side-view FE-SEM image of the 10-CdS/TiNT arrays. (g) Low-magnification HR-TEM image of the 10-CdS/TiNT. The insets are high-magnification HR-TEM image of the 10-CdS/TiNT. (h) The EDX spectrum of the 10-CdS/TiNT arrays.