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Free-standing carbon nanotube–titania photoactive sheets

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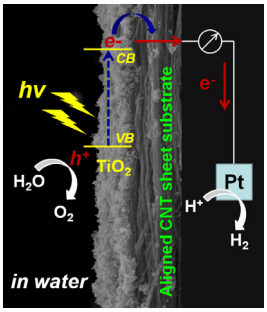
GRAPHICAL ABSTRACT



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ABSTRACT

We report on the development of a new photoactive material via titania (TiO_2) nanoparticle deposition on free-standing aligned carbon nanotube (CNT) sheets. Controlling homogeneous dispersion of negatively charged TiO_2 nanoparticles, achieved by adjusting pH higher than the point of zero charge (PZC), influenced electrochemical deposition of TiO_2 on CNT sheets substrate. Varying deposition time with constant voltage, 5 V allowed different thickness of TiO_2 to be deposited layer on the CNT sheets. The thickness and morphology of CNT–TiO_2 sheets was verified by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Electrochemical experiments show that diffusion coefficient of $Fe(CN)_6^{3-}$ was 5.56×10^{-6} $cm^2 s^{-1}$ at pristine CNT sheets and 2.19×10^{-6} $cm^2 s^{-1}$ at the CNT–TiO_2 sheets. Photocatalytic activity for CNT–TiO_2 sheets exhibits high photocurrent density (when deposition time = 30 min, 4.3 μA cm^{-2} in N_2, 13.4 μA cm^{-2} in CO_2). This paper proved a possibility to use CNT–TiO_2 sheets based on highly-aligned CNT sheets substrate as new photoactive material.

1. Introduction

Many photocatalytic materials have been used for environmental remediation, dye-sensitized solar cell (DSSC), and generating hydrogen gas from water splitting [1–7]. Titania (TiO_2), a photocatalytic material, has been extensively studied because of its chemical stability, possible non-toxicity, photocatalytic activity, environmental sustainability, and low cost [8–14]. Further conjugation with carbon nanotubes (CNTs) to provide TiO_2–CNT nanoparticles enhances charge separation of the photogenerated electron–hole from TiO_2 [15,16].

Individual CNTs, based on their composition and geometry, high specific conductivity [17], chemically inertness [18], high surface area [19], excellent charge carrier mobility [20], and high

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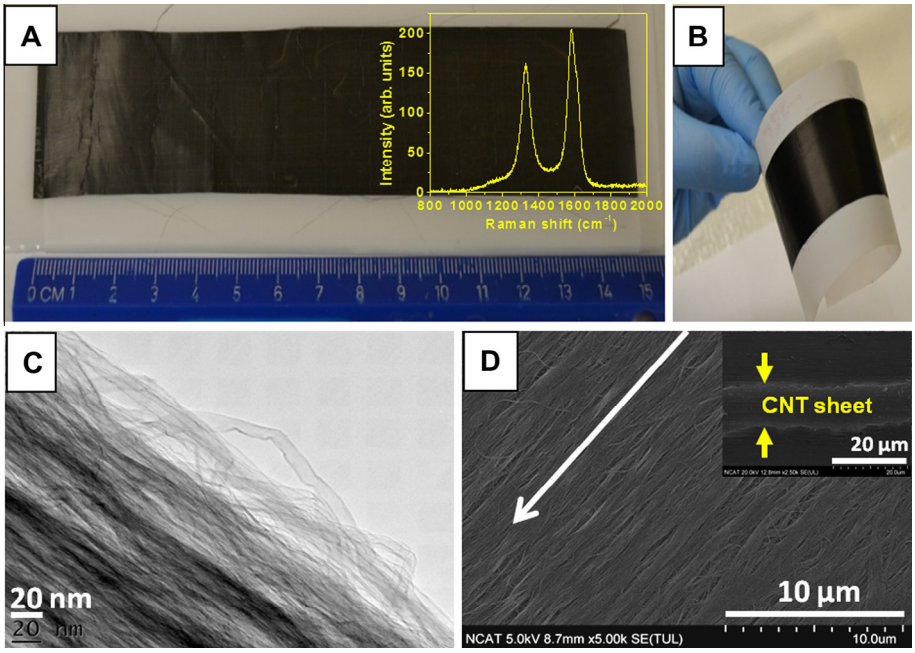

Fig. 1. Pristine CNT sheets (A) 200 layer CNT sheets on Teflon™ belt and Raman spectrum of the CNT sheets substrate (inset), (B) bent CNT sheets, (C) TEM image of individual aligned CNT sheets, and (D) SEM image of top and cross-section (inset).

mechanical strength [21]. In electrochemical point, CNT particles can promote fast electron-transfer and improve reversibility of electrochemical reaction [22]. However, for these particles to be used as an electrode, additional supporting electrodes such as fluorine-doped SnO_2 (FTO, 15 Ω/square), indium tin oxide (ITO, 8 Ω/square) conductive glass slides, graphite, and metal electrode [23–26] are needed.

Extrapolating properties to macro scale is still challenging. One of the promising scale-up methods was recently established by deposition of multiple layers of dry-spun CNT sheets [27]. Spinnable CNT arrays grown by chemical vapor deposition (CVD) allow for the formation of a continuous web from one edge of the array, comprising of highly aligned multi-walled CNTs [21,28,29]. This free-standing web is laid on top of itself multiple times to produce an aligned CNT sheets without the need of any polymer binder. The CNT sheets are flexible, capable of forming multi-layer stacks, reusable, much lighter than metals, and conductive [30]. Recently, Di et al. have reported a flexible and conductive CNT/TiO_2 core/shell heterostructure film without using additional transparent conducting oxide (TCO) substrates [31]. However, free-standing substrate, which does not require any binder, is challenging for light weight and flexible devices.

Herein, we report, the development of free-standing photoactive CNT–TiO_2 sheets using the durable CNT sheets. Adjusting pH in solution allows control over surface charge of TiO_2 nanoparticles, leading to electrochemical deposition of TiO_2 on CNT sheets. The influence of the different deposition time on photocurrent response was investigated in this paper. This report demonstrates that the conjugation of TiO_2 on CNT sheets is relatively simple and scalable for structural and functional application in environment and energy applications.

2. Experimental

2.1. Materials

Nanosized bicrystalline TiO_2 (P25, 50 m^2/g, 80% anatase, 20% rutile) was supplied from Degussa. Titanium(IV) isopropoxide, absolute ethanol (CH_3CH_2OH, 99.5%), hydrogen peroxide (H_2O_2, 30 wt% in H_2O) were from Fisher Scientific, ammonium hydroxide (NH_4OH, 30% v/v aqueous solution) from Sigma Aldrich. It was used without any further purification. All solutions were prepared with high purity. Millipore Milli-Q deionized water used as a solvent.

2.2. Fabrication of CNT sheets and electrochemical deposition

Highly-aligned CNT sheets was pre-synthesized using our previously reported method [30]. The 200 layered CNT sheets were drawn from 0.5 mm-tall multi-walled carbon nanotubes (MWCNT) arrays synthesized by a water-assisted chemical vapor deposition (CVD). A electrolyte solution was prepared by combining two solutions, (1) solution A was prepared by mixing with 0.2 mmol H_2O_2 and 0.2 mmol titanium (IV) isopropoxide (TTIP) with absolute ethanol for 15 min, (2) solution B was prepared by stirring to a solution of 1.2 mmol TiO_2 (P25) in deionized water for 15 min. Solution B was slowly added into solution A and 0.2 mmol NH_4OH were added to adjust pH between 10 and 11. Final solution was homogeneously dispersed at room temperature. Electrochemical deposition of TiO_2 on CNT sheets was conducted using a potentiostat (Reference 600, Gamry Instrument, USA). Oxygen in the electrolyte was removed by bubbling purified N_2 (99.9%. Airgas, USA) for 1 h with 5 mL/min flow rate. The CNT sheets (2 cm × 2 cm) served as substrate of the working electrode. The platinum plate of 2 cm × 2 cm and Ag/AgCl electrodes were used as a counter electrode and reference electrode respectively. The deposition of TiO_2 on CNT sheets was carried out at a constant voltage of 5.0 V. Finally, the CNT sheets deposited with TiO_2 were rinsed with deionized water until we eliminate the residual components of the suspension. Final CNT–TiO_2 sheets were dried at 25 °C under vacuum for 3 h.

2.3. Characterization

Raman analysis was performed to reveal the structure of the as-prepared CNT sheets substrate using a LabRAM ARAMIS (HORIBA Scientific) with excitation laser beam (wavelength, 633 nm).The surface morphologies as well as the thicknesses of the prepared