

Supporting Information

TiO₂ Nanotube (T_NT) surface treatment revisited: Implications of ZnO, TiCl₄, and H₂O₂ treatment on the photoelectrochemical properties of T_NT and T_NT/CdSe

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1. Supplementary Information 1 (SI_1)

Preparation and Surface treatment of TiO₂ nanotubes

1.1 Preparation of the TiO₂ nanotube arrays(T_NT) on Ti by anodization Titanium (Ti) foils (99% purity, 0.2 mm thick) supplied from ESPI[®] international were slightly polished with abrasive paper to remove any possible oxide layer. Then the foils were degreased by ultrasonication in acetone and isopropanol for 5 minutes each prior to anodization. The cleaned Ti foil was anodized in a two-electrode cell at 40 V (D.C.) for two hours with platinum foil as the cathode. A fluorinated solution (0.5% w/w) of ethylene glycol and water (10% w/w) mixture was used as electrolyte. The anodized T_NT samples were then ultrasonicated for five seconds in deionized water to remove post-anodization surface deposits. The anodized nanotube samples are mostly amorphous and were annealed at 350°C or 450°C for three hours for effecting a phase transformation (crystallization). Further details on the anodization can be found elsewhere.¹

1.2 Surface treatment of T_NT

TiCl₄ treatment 20mM TiCl₄ solution was prepared by dissolving required amount of TiCl₄ in 100 ml of ice cold deionized water followed by stirring overnight. This results in whitish semitransparent solution. T_NT samples were kept in this solution under stirring condition at 60°C for 1 hour and then washed with D.I water, air dried and annealed again at 450°C for 30 mins.

Zn(NH₃)₄²⁺ treatment 20 mM Zn(NH₃)₄²⁺ solution is prepared by taking an appropriate amount of ZnCl₂ in D.I water followed by drop wise addition of 10% NH₃ solution until pH of 9.5 is reached. Final volume of the solution was made to 100 ml maintaining the pH value. T_NT substrates were dipped in Zn(NH₃)₄²⁺ solution for 1 min followed by washing in D.I water for 1 min. This cycle was repeated for 3 times. Finally the sample was air dried and annealed again at 450°C for 30 mins.

1. Y. Sohn, Y. Smith, M. Misra and V. Subramanian, *Applied Catalysis B-Environmental*, 2008, **84**, 372-378.

H₂O₂ treatment: H₂O₂ treatment was performed by placing the T_NT substrate in a solution composed of 0.1M Tetrabutyl ammonium hydroxide(TBAH) in 10% H₂O₂ for 30 minutes followed by air drying. At the end of 30 minute treatment sample turned from bluish to off white.

1.3 CdSe deposition

CdSe deposition was performed by SILAR (successive ion layer absorption and reaction) method. 0.02 M Cd(NO₃)₂ and 0.02 M selenide (2 mmol Se powder dissolved in 100 ml of 0.2M NaBH₄ solution resulting in colorless Na₂Se solution) solutions were used as Cd and Se sources. Treated T_NT samples were dipped in Cd and Se-based salt solution for 1 minute each. After each dipping samples were washed with D.I water by keeping the sample in D.I water for 3 minutes. This cycle was repeated for 7 times. A dark brown coating was formed at the end of 7 cycles.

2. Supplementary Information 2 (SI_2)

Characterization of nanotube samples

2.1 Structural and Optical characterization X-Ray powder diffraction data were collected using a Philips12045 B/3 diffractometer at a scan rate of 1.6°/min using Cu K α radiation.

UV-visible absorbance measurements were performed using a Shimadzu UV-2501PC spectrophotometer equipped with a diffuse reflectance measurement unit (Integrating sphere). The light from the grating was incident normally to the sample surface. The associated software directly converts the reflectance data to an absorbance Vs time plots using the Kubelka-Munk function. The scan range for the measurements was 300 nm-800 nm.

Scanning electron micrographs were taken using a Hitachi FESEM (S4700) equipped with an Oxford EDS analyzer. The SEM samples were platinum coated prior to inspection.

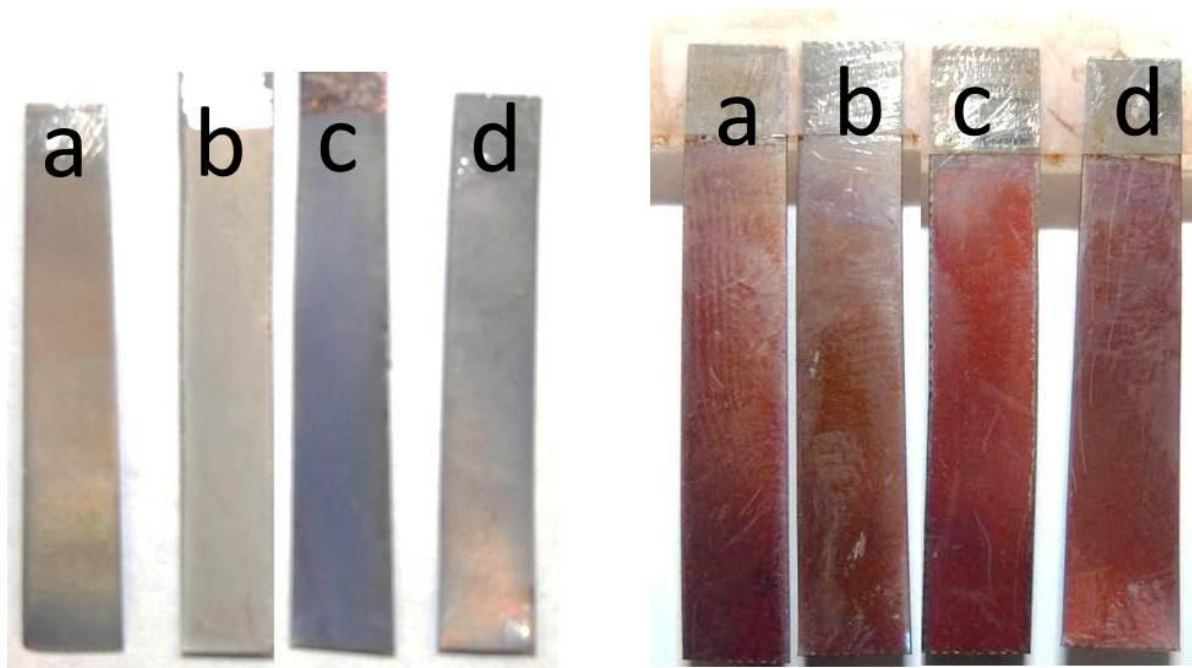
2.2 Photoelectrochemical characterization Photoelectrochemical studies were carried out in a three-electrode quartz cell with Pt wire as the counter electrode, and a leak-free Ag/AgCl (in 3M KCl) as the reference electrode. A 0.1M tetrabutylammonium sulfide and 0.1 M Na₂S solutions in water were used as the electrolyte. TBAS was synthesized with modification of an earlier reported method (ref. 29) where the electrolyte used was composed of 0.01 M tetramethyl ammonium sulfide ((CH₃)₄N)₂S, 0.002 M S, 0.02 M LiClO₄, 0.02 M 4-tert-butylpyridine(TBP) and 3-Methoxypropionitrile (C₄H₇NO) as a solvent for the electrolyte. In the method used here tetramethyl ammonium hydroxide and ammonium sulfide were used instead. The ((CH₃)₄N)₂S was prepared by heating tetramethyl ammonium hydroxide ((CH₃)₄NOH) and ammonium sulfide (NH₄)₂S at 100°C.

It is to be noted that a larger cation is required instead of Na^+ to avoid any complications due to cationic intercalation. Therefore aqueous 0.1 M tetrabutylammonium sulfide was prepared by heating aqueous (25% w/V) tetrabutylammonium hydroxide and aqueous ammonium sulfide (3M) in 2:1 molar ratio at 100°C and finally diluted to 0.1M concentration. I-V responses were collected using an Autolab PGSTAT 30 electrochemical analyzer. The working electrode was irradiated with a 500 W Newport Xenon lamp equipped with 0.5 M CuSO_4 solution as a far UV cut-off filter.

Mott-Schottky analysis was performed on a Gamry P4 potentiostat in dark using the same three-electrode setup described above but with 0.1M tetrabutylammonium hydroxide (TBAH) as electrolyte. C-V scans were run at 100Hz. This frequency was chosen because in the Bode representation of "Z' vs Frequency" plot, resistance increases steeply below 100Hz and remains almost constant at frequencies higher than 100 Hz. This is true for all nanotube samples. Therefore all the samples are compared at the same 100 Hz frequency.

Replication of data Wherever possible, T_NT was prepared from the same Ti substrate and the CdSe deposition was performed in one single solvothermal reactor to produce a batch of samples for a certain test. 3 such sets were prepared. Multiple measurements on single sample does not vary >5%. Absolute values between different sets vary up to 10%. Always, samples that belong to the same set are therefore, reported

3. Supplementary Information 3 (SI_3)



Photographs of **(left)** surface treated T_NT samples a) T_NT, b) T_NT-H₂O₂, T_NT-TiCl₄, d) T_NT-Zn(NH₃)₄²⁺ **(right)** a) T_NT/CdSe, b) T_NT-H₂O₂/CdSe, T_NT-TiCl₄/CdSe, d) T_NT-Zn(NH₃)₄²⁺/CdSe

4. Supplementary Information 4 (SI_4)

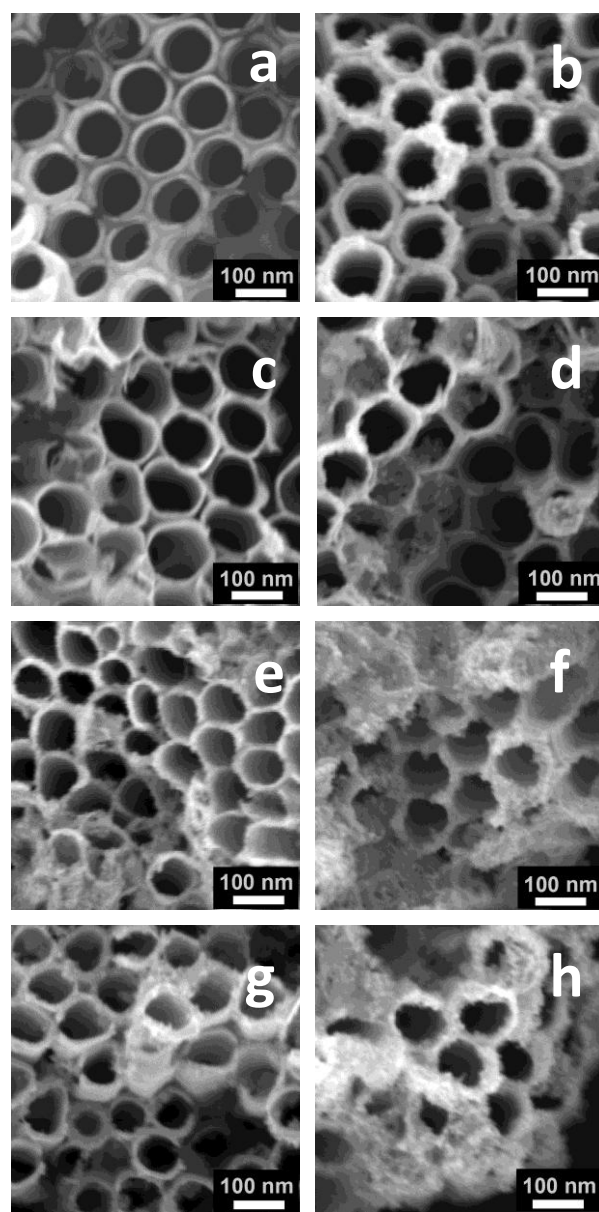


Figure 2 Scanning electron micrographs of a) Untreated T_NT b) T_NT/CdSe c) T_NT/H₂O₂ d) T_NT/H₂O₂/CdSe e) T_NT/T_NP/ f) T_NT/T_NP/CdSe g) T_NT/ZnO h) T_NT/ZnO/CdSe

5. Supplementary Information 5 (SI_5)

