

Supporting Information

Development of a Highly Efficient 1D/0D TiO₂ Nanotube/n-CdTe Photoanode: Single-step Attachment, Coverage, and Size Control by Solvothermal Approach

Swagotom Sarker, Bratindranath Mukherjee, Eric Crone,
and Vaidyanathan (Ravi) Subramanian*

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¹Chemical and Materials Engineering, University of Nevada, Reno

*Author to whom correspondence should be addressed.

Department of Chemical and Materials Engineering

University of Nevada, Reno – 89557

Tel: (775) 784 4686, Fax: (775) 327 5059

ravisv@unr.edu

Supporting Information 1

Synthesis Protocol

Formation of the TiO₂ Nanotube Substrate by Anodization- Titanium (Ti) foil (99% purity, 0.2 mm thickness) was purchased from ESPI International. Prior to anodization, titanium foil was polished and, later, ultrasonicated in 2-propanol and acetone separately for 10 minutes each to remove organic residues. The cleaned foil was anodized at 40 V (DC) for 2 hours in a two-electrode cell where platinum (Pt) functions as cathode. For anodization, a fluorinated (ammonium fluoride at 0.5% w/w of EG) solution of ethylene glycol (EG) & water (10% w/w) was used as electrolyte. The anodized samples were ultrasonicated in DI water for 3-5 seconds for the removal of loosely attached post-anodization surface deposits. Since the anodized samples were mostly amorphous structure, annealing of those samples was conducted in the presence of N₂ gas for 2 hours at 450 °C to achieve the desired crystalline structure.

Deposition of Cadmium Telluride (CdTe) Nanocrystals on T_NT- Solvothermal coating method was followed to deposit controlled size CdTe nanocrystals on T_NT surface. It has been reported that the bonding strength along with the steric effects of the ligands plays a crucial role to determine not only the reactivity of the precursors but also stability of the nanocrystals.¹ It can also be mentioned here that, in case of non-coordinating solvents, ligand concentration sourced from fatty acids and chain length is very important to obtain fine-tuned nanocrystals.^{2,3} For the beneficial role of the ligand, oleic acid was chosen in case of this organometallic approach.^{4,5} To simplify the CdTe nanocrystal deposition procedure, cadmium oleate was synthesized from cadmium acetate dihydrate (reagent grade, 98%) and oleic acid, (90%). 1 mmol of Te (99.8%, powder, 200 mesh) was added to 0.8 mL of tri-n-butylphosphine (95%) and ultrasonicated for an hour. Later, it was loaded into the teflon-lined container. An equivalent 1 mmol of cadmium oleate was also added. A T_NT/Ti substrate (40 mm × 8 mm × 0.2 mm) was placed vertically in a 125 mL teflon-lined stainless steel autoclave (model 4748, Parr Instrument Company). Finally, toluene, as non-coordinating solvent, was added to fill up to 80% of 125 mL reaction chamber.

The reactor, along with its contents, was closed shut and maintained at a constant elevated temperature (say 140 °C) for 24 hours. After this period of reaction time, the Parr reactor was allowed to cool to room temperature conditions and the T_NT substrate with coated

deposits was collected from the vessel. The T_NT substrate with the deposits was cleaned in warm toluene to remove loosely attached nanocrystals and organic materials from the substrate surface (if any). This cleaned sample, is referred to as T_NT/CdTe_u [Subscript “U” stands for untreated T_NT/CdTe]. The solution from the reactor was collected for UV-vis. absorbance study. Separate temperature studies were performed by synthesizing the hetero-composite at 160 °C, 180 °C, 200 °C and 220 °C, besides 140 °C.

T_NT/CdTe Surface Treatment- Each T_NT/CdTe_u substrate of which CdTe nanocrystal surface is surrounded by bound ligand anions sourced from fatty acids had to undergo surface treatment.¹ Thiol group (-SH) can play an efficient role to modify such ligand capped surface.^{6,7} Each T_NT/CdTe_u sample was kept in mercaptoacetic acid (MAA) solution (200 μL in 20 mL of 2-propanol) for 12 hours.⁸ CdTe surface treatment helps to facilitate annealing at lower temperature. The MAA-treated sample is referred to as T_NT/CdTe_MAA. Annealing of each T_NT/CdTe_MAA was performed at 350 °C in presence of N₂ gas for 3 hours to obtain the final form of photoelectrode which is T_NT/CdTe.

Supporting Information 2

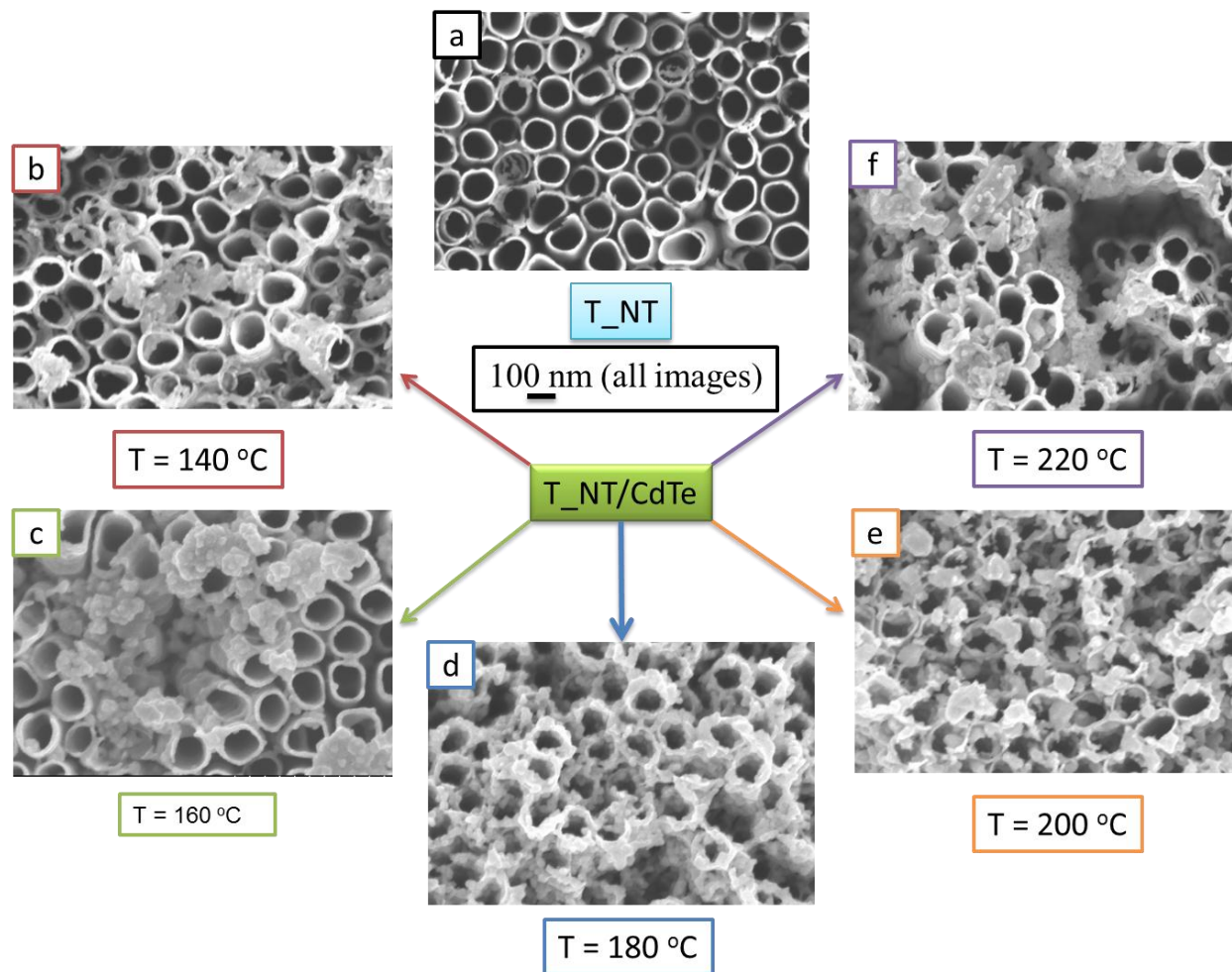
Characterization

Surface and Optical Characterization

The physical features of the deposits were characterized using a Hitachi S-4700 scanning electron microscope under high resolution in the UHR mode (working distance = 4 mm and accelerating voltage = 3 KV). A Shimadzu UV-2501PC spectrophotometer equipped with diffuse reflectance accessories was used to perform optical studies. HRTEM analysis was performed using a JEOL[®] 2100F instrument.

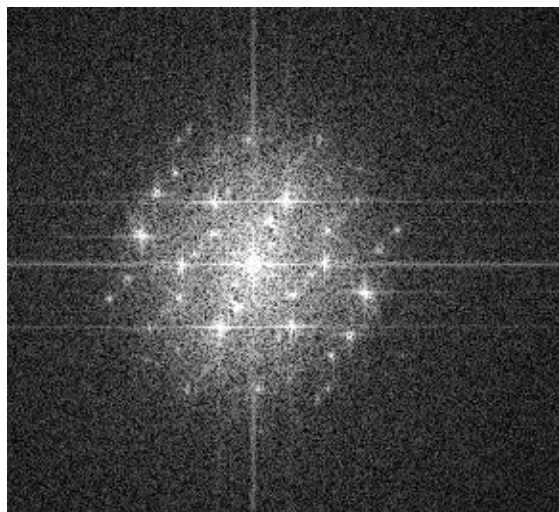
X-Ray diffraction measurements were performed with the Philips12045 B/3 diffractometer. The samples were scanned at a rate of 1 °/min using with the aid of CuK α radiation.

Supporting Information 3



SI 3. Top view SEM images of (a) T_NT, and (b-f) T_NT/CdTe synthesized using the solvothermal process at (b) 140 °C, (c) 160 °C, (d) 180 °C, (e) 200 °C, and (f) 220 °C.

Supporting Information 4



SI 4. Selected area electron diffraction (SAED) pattern of T_{NT}/CdTe heterostructure.

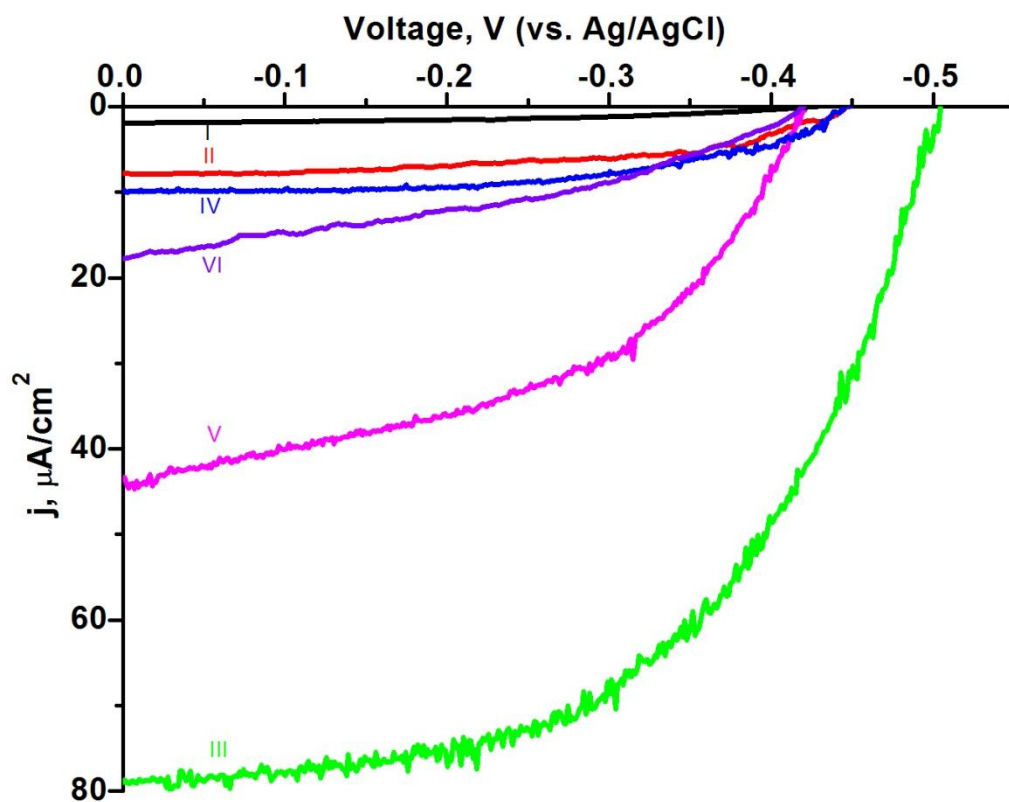
Supporting Information 5

Photoelectrochemical characterization

An Autolab PGSTAT 30 electrochemical analyzer was used as the primary instrument to perform photoelectrochemical studies. All experiments were carried out in a three-electrode cell. T_NT and T_NT/CdTe films were used as the working electrode. Pt was used as the counter electrode along with Ag/AgCl/3.4 M KCl as the reference electrode. The photoelectrochemical responses were obtained using 0.1 M Na₂S solution as the electrolyte. Specifically, a 500 W Newport Xenon lamp was used to illuminate the samples with appropriate filters to reduce intensity 90 mW/cm².

Supporting Information 6

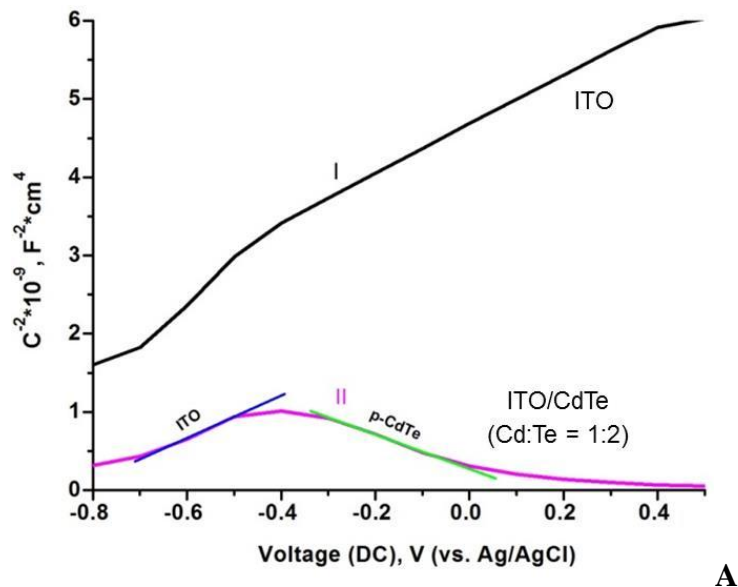
j/V characteristics of T_{NT} and T_{NT}/CdTe in the absence of illumination



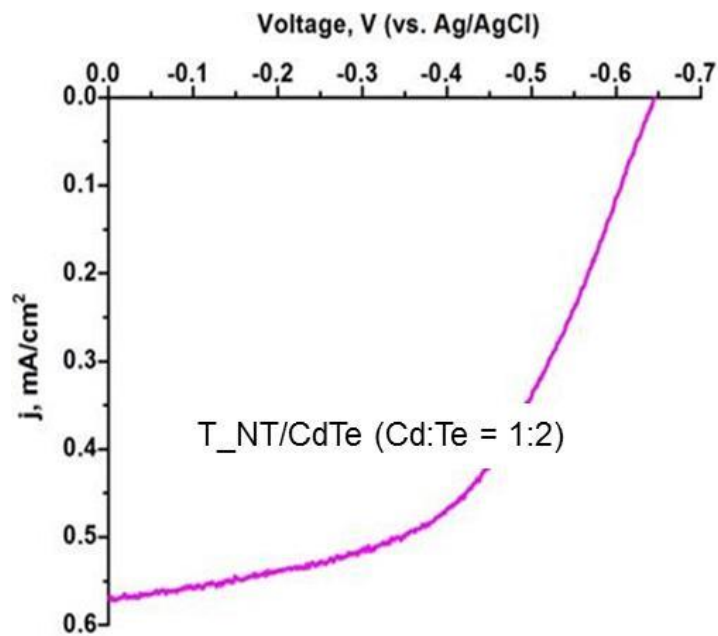
SI 6. j/V characteristics of the I) TNT, II) T_{NT}/CdTe [140 °C], III) T_{NT}/CdTe [160 °C], IV) T_{NT}/CdTe [180 °C], V) T_{NT}/CdTe [200 °C], and VI) T_{NT}/CdTe [220 °C] in the absence of illumination.

Supporting Information 7

(Photo)electrochemical characterization of p-CdTe



A



B

SI 7. (A) Mott-Schottky analysis of the ITO/CdTe [200 °C] indicating the formation of the p-type CdTe and (B) j/V response of the T_NT/p-CdTe [200 °C].

Discussions on SI 7

p-type CdTe was synthesized by increasing the Te ratio in CdTe. As an example, the Te-rich CdTe was prepared with Cd:Te precursor (in mmol) molar ratio at 1:2.

MS analysis [SI 7 (A)] was performed to confirm p-type characteristics in the Te-rich CdTe, (ITO was used as the substrate to prevent TiO₂ interference during MS analysis). Note that the Te-rich CdTe was synthesized at 200 °C since the best result with n-type was noted at this temperature. In the MS graph, plot I is for plain ITO and plot II is for ITO/CdTe. The MS confirms the formation of p-type CdTe.

j/V analysis [SI 7 (B)] was performed with the T_{NT}/p-CdTe [200 °C]. The low current with p-type CdTe confirms that, as expected, p-type CdTe leads to a decrease in the current density.

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