Nanoparticle and Nanorod TiO_2 Composite Photoelectrodes with Improved Performance

Supporting Information

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Fabrication of TiO_2 NR array, NP, NP-NR and NP+NR mixed photoelectrodes: The TiO_2 NR arrays are fabricated directly onto the FTO substrate by hydrothermal method, similarly to that described by Liu et al. [1]The FTO is ultrasonic cleaned with acetone, ethanol and deionized (DI) water for ten minutes each and dried in nitrogen. They are put in a sealed Teflon reactor (60 mL) with well mixed solution which contains 15 mL of DI water, 15 mL of hydrochloride acid (36-38 wt %) and 0.5mL of tetrabutyl titanate. The reactor is heated to 160 °C for 12 hours. The resulting TiO_2 NRs are put into an acid Ti^{4+} precursor solution to fabricate NP-NR electrode. Typically, the Ti^{4+} concentration is 0.3-0.7M, and it was heated at about 70°C for 2-4h. The as-prepared film was pull out of the solution and dry in air, and the resulting solution is then dried and well dispersed in alcohol to make the TiO_2 NP film by spin coating method. The TiO_2 NP+NR mixed photoanodes were fabricated by mixed NP and NR with 1:1 in weight and following the same procedure as the NP film.

DSSC Cell configuration: TiO_2 NR, NP, NP-NR and NP+NR mixed photoanodes are annealed for one hour at 450 °C in air to improve the crystal structure. Then they are dipped in N719 solution for a whole day. The dye sensitized photoanodes and platinum coated glass are sandwiched using 25μm surlyn-film. The electrolyte is composed of 0.1 M of LiI, 0.6 M of 1, 2-dimethyl-3-n-propylimidazolium iodide (DMPII), 0.05 M of I_2, 1 M of 4-tert-butylpyridine (TBP) in methoxyacetonitrile. The cell area is about 0.12 cm^2. The dye desorption of each TiO_2 sample is carried out by treatment in a certain volume of 0.1M NaOH (aq). A UV-vis spectrophotometer (UV 5000 spectrometer, Cary) was employed to measure the dye absorption of different concentration of the desorbed-dye solution at 500nm.

Characterization of TiO_2 NR arrays, NP, NP-NR and NP+NR mixed photoelectrodes: The morphology characterizations of the TiO_2 NP-NR photoanode are carried out using a field-emission gun FEI Quanta 600F scanning electron microscope and a Tecnai G20 transmission electron microscope. A Rigaku D/max-rA12kW X-ray diffraction system is used to test the structure of the samples. The device performance of the TiO_2 NP-NR structure based DSSC is recorded by an electrochemical analyzer (CHI660C Instruments), under AM 1.5 simulated sunlight, produced by a 300-W Oriel Solar Simulator (Model, 91160) with the illumination intensity being 100mW/cm^2. The efficiency is calculated by the following formula, $\eta = \frac{P_{max}}{I_0} = \frac{I_{max} V_{max}}{I_0}$, where P_{max} is the maximum output power; I_{max} and V_{max} is the corresponding current density and photo-voltage, respectively; I_0 is the

incident light intensity. The IPCE are tested using power meter model 2931-c with motorized 1/4 monochromator models 74125 as the light source.

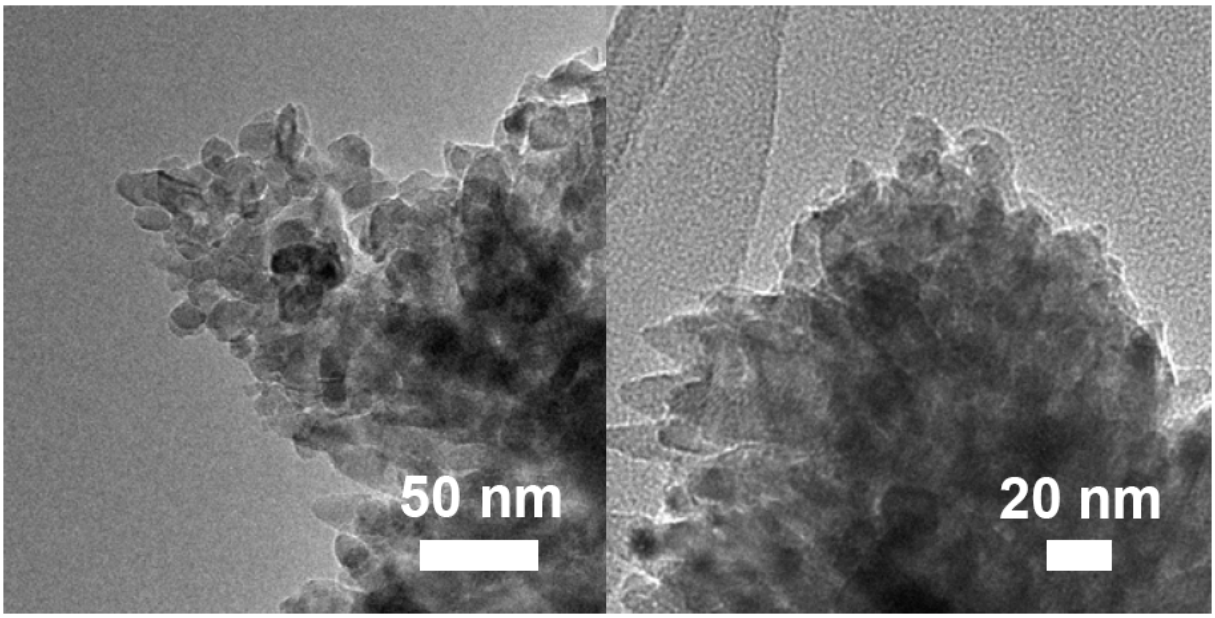

Fig S1 TEM images of the NPs in NP-NR composite electrode (high magnitude)

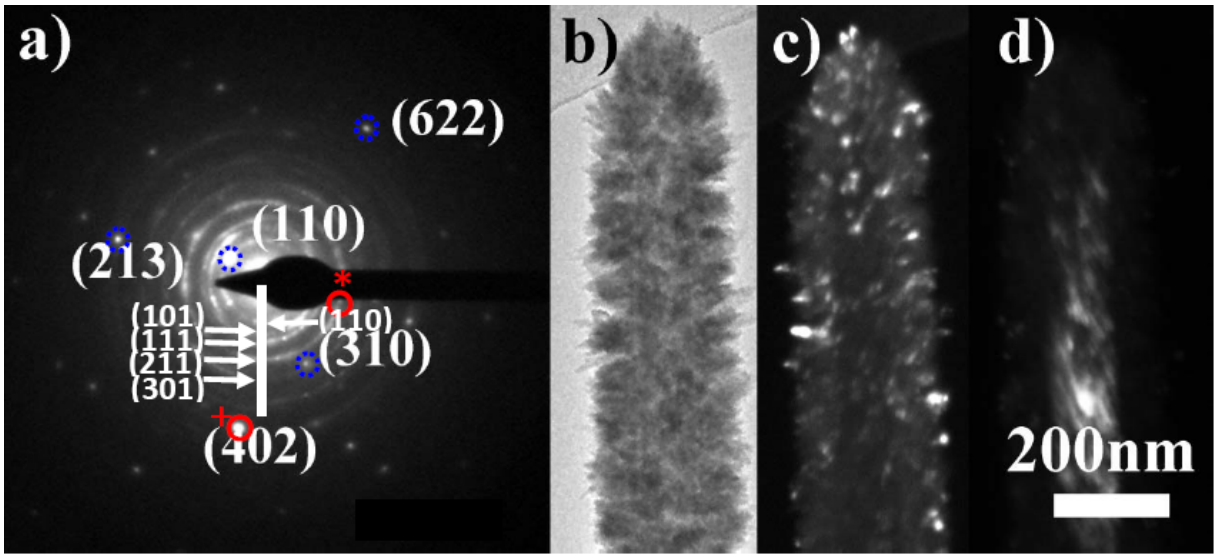

Fig S2 (a) Selected-area electron-diffraction (SAED) of TiO_2 NP-NR composite (b)TEM image of the NP-NR composite and dark field images(c), (d) from the diffraction spots marked by red star and plus in Figure S2 (a) respectively.

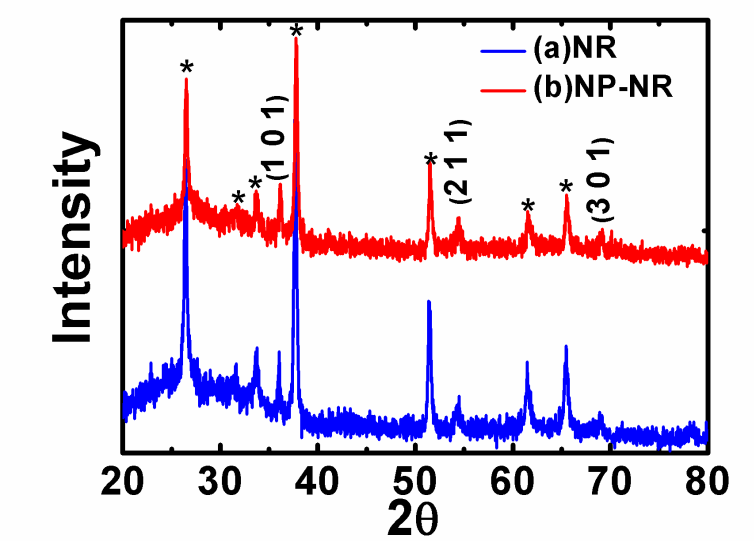

Fig S3 XRD patterns of TiO_2 NRs (blue) and NP-NRs (red) (asterisks stands for FTO substrate).

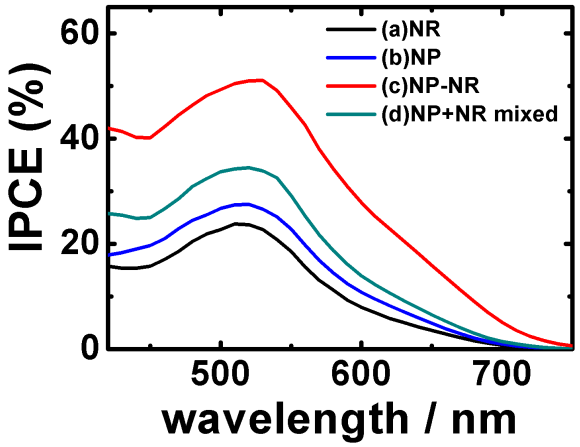

Fig S4 Incident photon-current conversion efficiency of NR, NP, NP-NR and NP+NR mixed solar cells.

Reference

1 B. Liu, E. S. Aydil, *J. Am. Chem. Soc.*, 2009, **131**, 3985.