Electronic Supplementary Information

Electropolymerization as a new route to g-C_3N_4 coatings on TiO_2 nanotubes for solar applications

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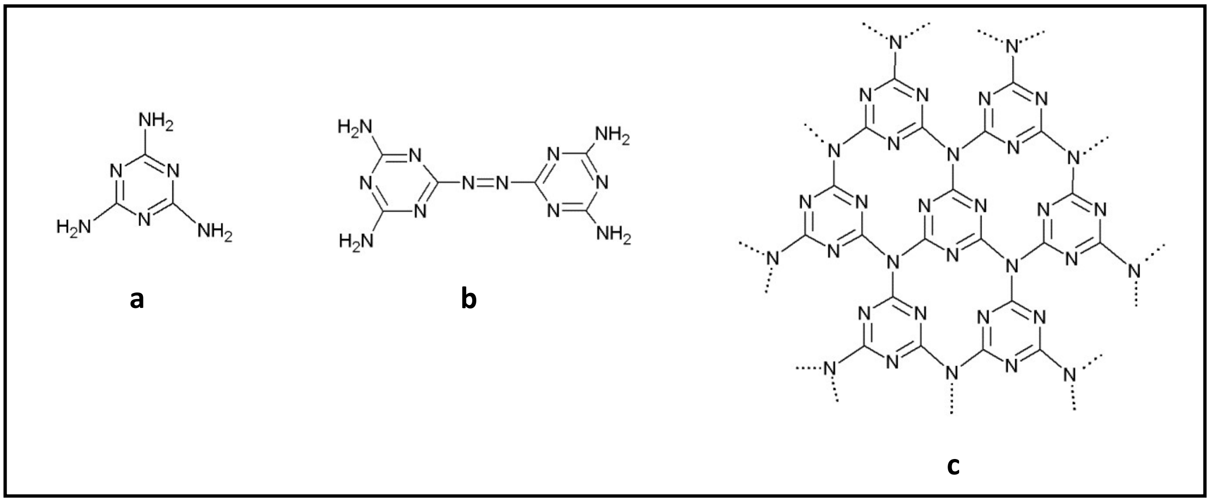
Experimental details

1. Preparation of Ti/TiO_2NTs and coatings

Aqueous solutions were prepared with deionized water (18.2 MOcm, Millipore) and all compounds and reagents were of analytical grade. TiO_2NTs electrodes were fabricated on a Ti foil (Sigma-Aldrich 0.25 mm thick, 99.7% purity) by electrochemical anodization. In a typical process, Ti foils were first ultrasonically cleaned with acetone for 15 min. The anodic oxidation was performed using Ti foil as anode and platinum mesh as cathode with an applied voltage of 30 V for 90 min under the assistance of magnetic stirring. The electrolyte was a mixture of ethylene glycol and water (92:8 vol.) containing 0.3 wt % NH_4F. The obtained amorphous nanotube arrays were then annealed at 500°C for 1 hour in air. Cyclic voltammetric (CV) and chronoamperometric (CA) experiments were carried out with a Gamry potentiostat (series G™300). The electrochemical system for electropolymwrization (EP) consisted of Ti/TiO_2NTs (geometric area, 2 cm^2), Pt, and Ag/AgCl/KCl (satd.) as working, counter and reference electrodes, respectively. After the EP process, TiO_2NTs samples were heat treated in air at 550˚C (heating rate: 5˚C /min) for a period of 4 hours. Samples with adsorbed melamine (adsM) were prepared by dipping Ti/TiO_2NTs in 1 mM melamine in water for 1 hour and annealed as described above.

2. Characterization

Morphology of the TiO_2NTs was examined using high resolution scanning electron microscopy (HR-SEM, JEOL JSM-7400F). Transmission electron microscopy (TEM) imaging was carried out using Tecnai 12 G2 TWIN. High resolution transmission electron microscopy (HRTEM) imaging was carried out using a JEOL JEM-2100F analytical TEM operating at 200 keV equipped with GATAN 894 US1000 camera. Electron energy-loss spectroscopy (EELS) studies were conducted in the scanning transmission electron microscopy (STEM) mode with a GATAN 806 HAADF STEM detector and Gatan quantum energy filter. TEM samples were prepared by directly scratching off a portion of TiO_2NTs onto a Cu grid coated with lacey carbon. The nature of the coatings was examined by X-ray diffraction (XRD, Philips PW 1050/70), X-ray photoelectron spectroscopy with an Al X-ray source and monochromator (XPS, ESCALAB 250), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra using a Bruker Tensor 27 FTIR with a Bruker Platinum ATR accessory equipped with a single reflection diamond crystal. The spectra of the coated samples were recorded after subtraction those of the uncoated Ti/TiO_2 ones. Raman spectra were obtained with excitation sources of a Melles-Griot Argon laser (514.5 nm, LabRam HR). Diffuse reflectance spectroscopy (DRS) was used to analyze the optical properties of the samples. The diffuse reflectance spectra were recorded by a UV-vis spectrophotometer (USB4000, Ocean Optics), equipped with QR400-7 reflection probe. The equipment was calibrated with a Spectralon standard (Labsphere USRS-99-010, 99% reflectance).



Scheme S1 Chemical structure of melamine (a), dimer obtained during anodic polymerization of melamine (b), and g-C_3N_4 (c).

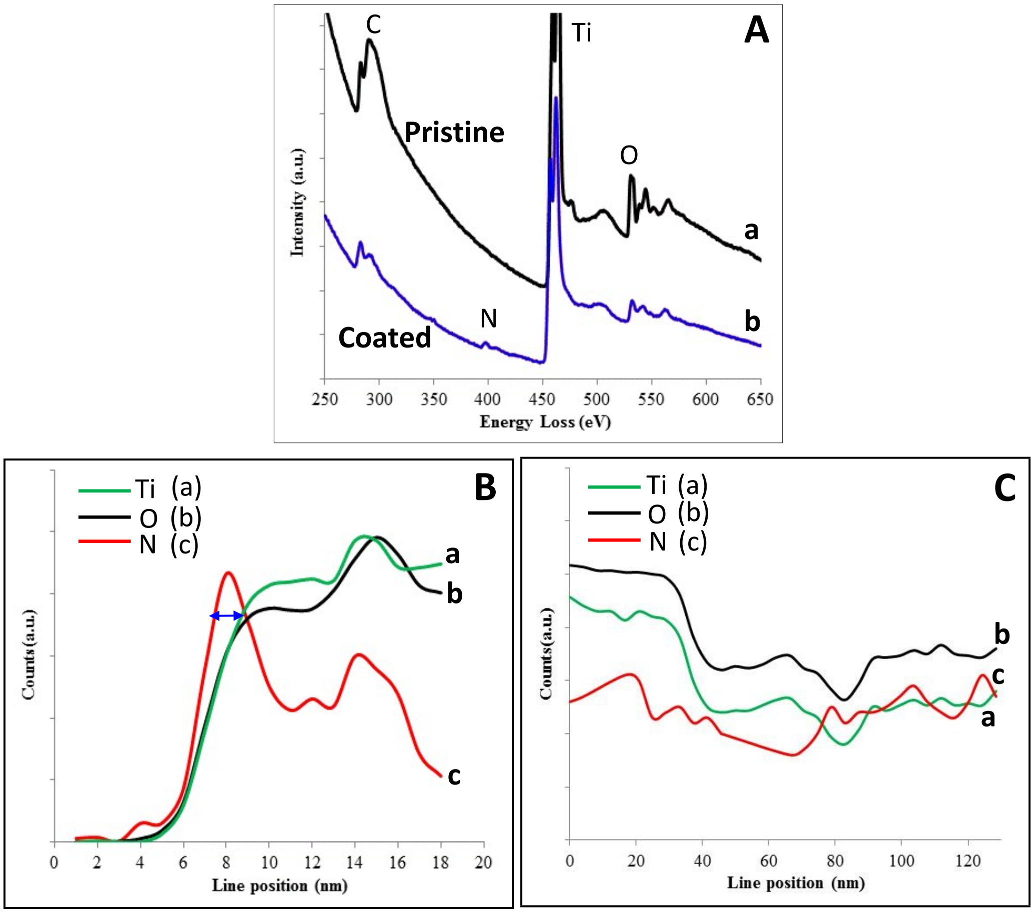


Figure S2 (A) EELS spectrum of the pristine (a) and coated (b) TiO_2NTs; (B) and (C) are EELS concentration profiles for Ti (a), O (b) and N (c) along directions y and x (arrows marked in Fig 1D), respectively.

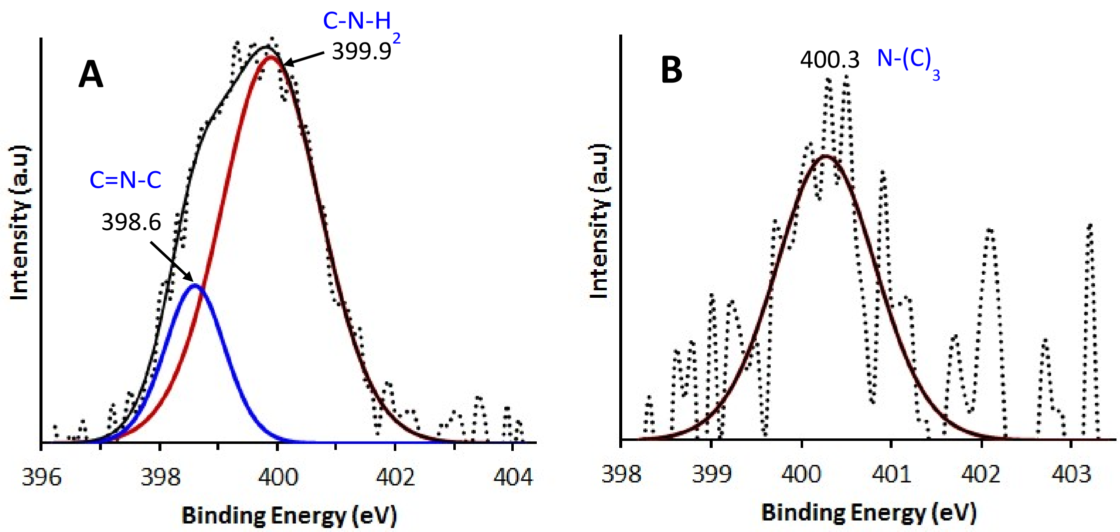


Figure S3 XPS N1s spectrum of TiO_2 NTs/adsM before (A), and after heat treatment (B).