

Electronic Supplementary Information

TiO₂ Nanotubular Arrays Loaded with Ni(OH)₂: Naked-eye Visible Photoswitchable Color Change Induced by Oxidative Energy Storage

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Experimental Section

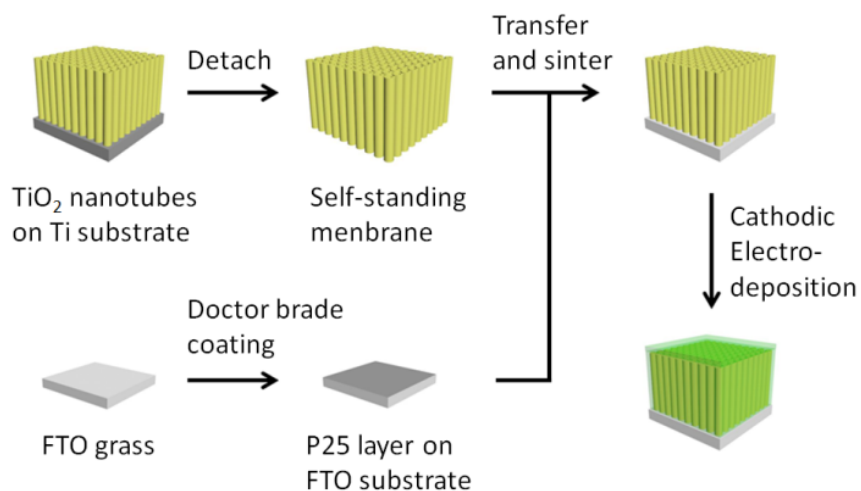
To form TiO₂ nanotubular arrays on Ti substrate, a two-electrode electrochemical cell was applied with Ti foil (thickness=0.25 mm, 99.7%, Aldrich) as a working electrode and platinum foil as a counter electrode.^{1, 2} A two-step electrochemical anodization was carried out in an ethylene glycol (Beijing Chemical Works) electrolyte containing 0.25 wt% NH₄F (Xilong Chemical Factory) and 2 vol% Milli-Q water under a temperature of 20 °C and a constant voltage of 60 V. The voltage was provided by a DC power supply (DH1724A-1, Beijing Dahua Electronic). In the first step, Ti foil was anodized at 60 V for 0.5 h to obtain TiO₂ nanotubes, which was subjected to ultrasonication in 1 M HCl (Beijing Chemical Factory) to remove the anodized layer completely. The textured Ti surface was then anodized in the same electrolyte at 60 V for another 1.5 h, followed by calcined at 450 °C under ambient air for 3 h to induce TiO₂ crystallization. Afterwards, the crystallized TiO₂ nanotubes were completely detached from the metallic Ti substrate by the third-step anodization in a different electrolyte consisting of 0.56wt % NH₄F and 0.5vol % Milli-Q water in ethylene glycol at 100 V. A self-standing TiO₂ nanotubular film that could be easily handled with tweezers was obtained.

The self-standing TiO₂ nanotubular film was then transferred onto transparent conductive glass (FTO). A TiO₂ nanoparticle viscous paste was prepared by mixing TiO₂ nanoparticles (P25, Degussa) with 3 vol % acetic acid solution at a weight ratio of 3:10 and stirred for 1 h.³ The P25 paste was coated onto FTO glass by doctor blade coating and the self-standing TiO₂ nanotubular film was immediately transferred onto the P25 layer. After being dried in air, the TiO₂ nanotubular film on the FTO glass substrate was sintered at 450 °C for 3 h in air.

A Ni(OH)₂ layer was prepared by cathodic electrodeposition onto the TiO₂ nanotubular arrays.⁴ A three-electrode electrochemical cell was used with an Ag/AgCl wire and a Pt wire as reference and counter electrode respectively. The deposition was carried out in 0.02 M Ni (NO₃)₂ aqueous solution at a constant current density of 1 mA/cm². The morphology of TiO₂ nanotubular arrays before and after loaded with Ni(OH)₂ were characterized by environmental scanning electron microscopy (SEM, FEI, Quanta FEG 250). The crystal structure was characterized by using an X-ray diffraction spectrometer (XRD-6000, Shimadzu) with a Cu K α X-ray source. Cyclic voltammetry (CV) measurements were performed in NaHCO₃/NaOH buffer solution (pH=10) at a scanning rate of 20 mV/s with an electrochemical analyzer (CHI 660D, Shanghai Chenhua).

The naked-eye visible photochromism of Ni(OH)₂-loaded TiO₂ nanotubular arrays was obtained by irradiating the heterostructure with ultraviolet (UV) light with a wavelength of 365 nm (2 mW/cm²) in a NaHCO₃/NaOH buffer (pH=10). The absorbance changes of the film were measured by a UV-Vis spectrophotometer (UV-3600, Hitachi). The reversible photochromic behavior was realized by taking out the stored oxidative energy (photogenerated holes) using reducing agent.

- [1] Q. Zhang, Z. Liu, X. Hou, X. Fan, J. Zhai and L. Jiang, *Chem. Commun.*, 2012, **48**, 5901.
- [2] Q. Chen and D. Xu, *J. Phys. Chem. C*, 2009, **113**, 6310.
- [3] J. Lin, J. Chen and X. Chen, *Nanoscale Res. Lett.*, 2011, **6**, 475.
- [4] Y. Takahashi and T. Tatsuma, *Langmuir*, 2005, **21**, 12357.



Scheme S1 Flow chart for the fabrication of heterostructure based on Ni(OH)₂ and TiO₂ nanotubular arrays on a transparent conductive substrate (FTO).

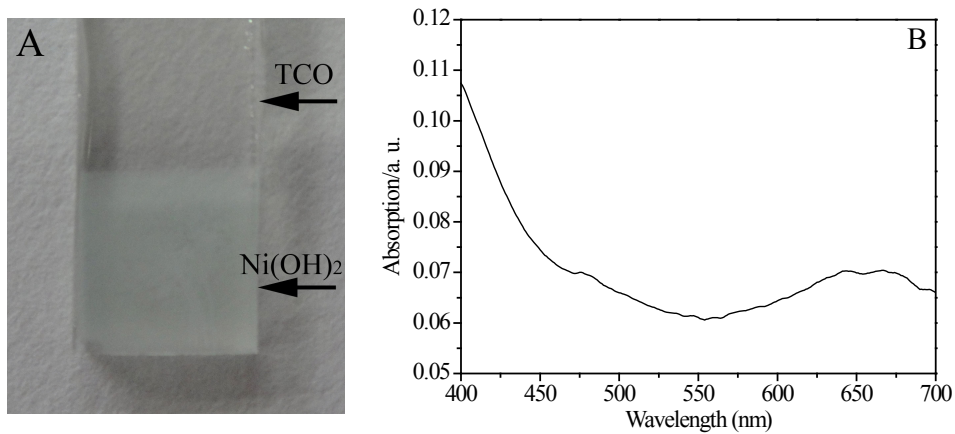


Figure S1. (A) Photograph and (B) UV-visible absorption spectra of Ni(OH)₂ coating on transparent conductive glass (TCO).

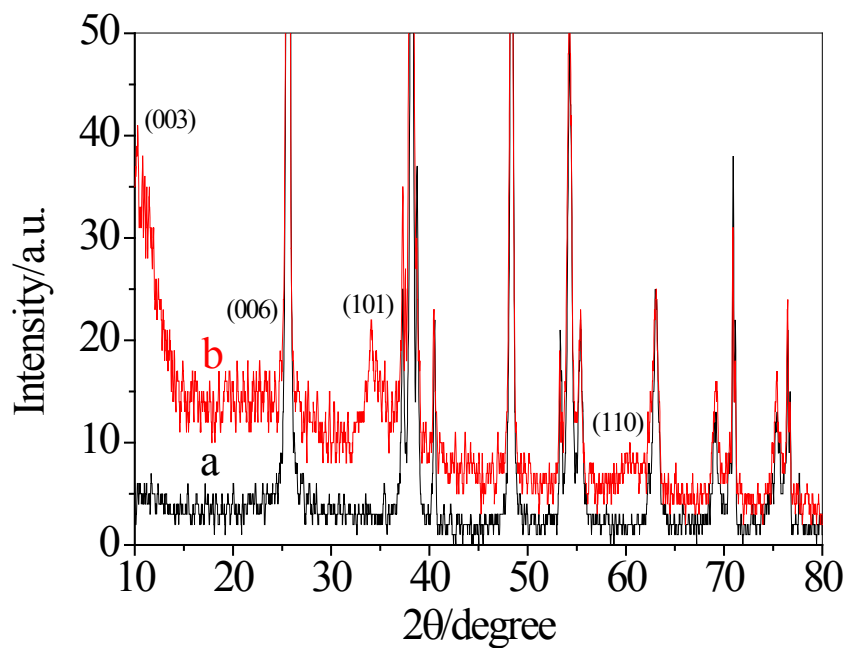


Figure S2. XRD patterns of TiO₂ nanotubular arrays before (a) and after (b) loaded with Ni(OH)₂.

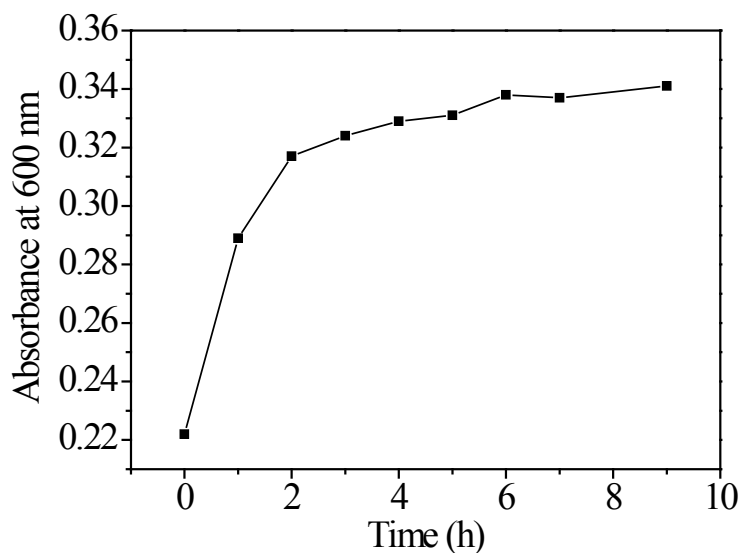


Figure S3. The variation of absorption at 600 nm of Ni(OH)₂-loaded TiO₂ nanotubular arrays following the time of UV irradiation (365 nm).

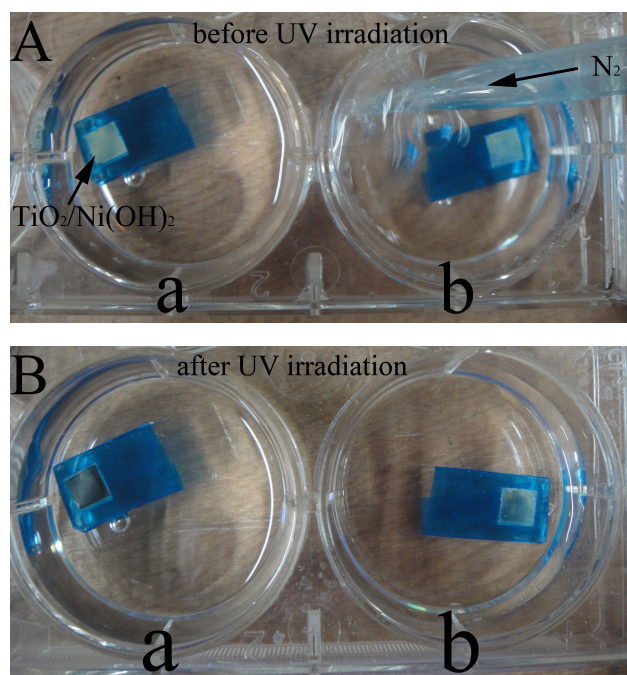


Figure S4. Photoswitched color change of Ni(OH)₂ loaded TiO₂ nanotubular arrays in NaHCO₃/NaOH buffer without (a) and with (b) N₂ purging. (A) Before UV irradiation. (B) After UV irradiation.

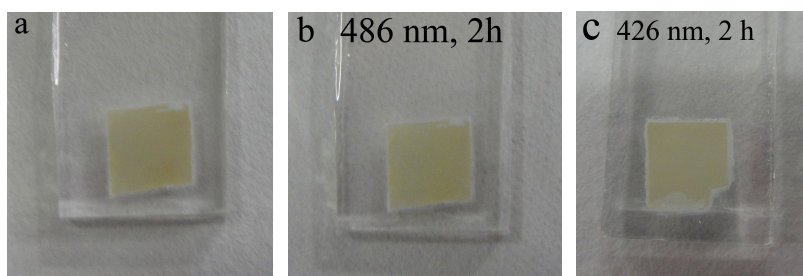


Figure S5. Photographs of Ni(OH)₂ loaded TiO₂ nanotubular arrays. (a) before light irradiation. (b, c) after irradiation by 486 nm (b) and 426 nm (c) light for 2 h.