Experimental Supplementary Information

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

Pengfei Zeng, Zhaoyue Liu*, Ziying Hu, Jin Zhai* and Lei Jiang
Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, P. R. China.
E-mail: liuzy@buaa.edu.cn; zhaijin@buaa.edu.cn
Fax: +86-10-82317801; Tel: +86-10-82317801

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 TiO$_2$ nanotubular film was then transferred onto transparent conductive glass (FTO). A TiO$_2$ nanoparticle viscous paste was prepared by mixing TiO$_2$ nanoparticles (P25, Degussa) with 3 vol % acetic acid solution at a weight ratio of 3:10 and stirred for 1 h. The P25 paste was coated onto FTO glass by doctor blade coating and the self-standing TiO$_2$ nanotubular film was immediately transferred onto the P25 layer. After being dried in air, the TiO$_2$ 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 TiO$_2$ nanotubular arrays. 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 (NO$_3$)$_2$ aqueous solution at a constant current density of 1 mA/cm$^2$. The morphology of TiO$_2$ 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 Kα X-ray source. Cyclic voltammetry (CV) measurements were performed in NaHCO$_3$/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 TiO$_2$ nanotubular arrays was obtained by irradiating the heterostructure with ultraviolet (UV) light with a wavelength of 365 nm (2 mW/cm$^2$) in a NaHCO$_3$/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.

Scheme S1 Flow chart for the fabrication of heterostructure based on Ni(OH)$_2$ and TiO$_2$ 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 TiO$_2$ nanotubular arrays in NaHCO$_3$/NaOH buffer without (a) and with (b) N$_2$ purging. (A) Before UV irradiation. (B) After UV irradiation.

**Figure S5.** Photographs of Ni(OH)$_2$ loaded TiO$_2$ nanotubular arrays. (a) before light irradiation. (b, c) after irradiation by 486 nm (b) and 426 nm (c) light for 2 h.