

Supporting Information

A novel visible-light-driven photochromic material with high-reversibility: tungsten oxide-based organic-inorganic hybrid microflowers

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[1] Experimental details:

Preparation of tungsten oxide-based organic-inorganic (TOI) hybrid microflowers: WCl_6 (0.397 g, 1 mmol) and hexamethylenetetramine (HMT) (1.4 g, 10 mmol) were added to 40 mL of absolute ethanol. The mixture was loaded into a Teflon-lined autoclave, which was sealed, maintained at 180 °C for 12 h, and cooled to room temperature naturally. The bronze precipitate was collected, and rinsed several times with distilled water and then with absolute ethanol.

Preparation of WO_3 microflowers: Solid products were heated from room temperature to 450 °C for 6 h, and annealed at 450 °C for another 3 h to obtain the final yellow product.

Characterization: A Hitachi S-4800 field emission scanning electron microscope (FE-SEM, Hitachi Co. Ltd. S-4800) was used to investigate the morphology. X-ray powder diffraction (XRD, Rigaku Co. Ltd. Ultima-X) measurements were carried out using filtered $\text{CuK}\alpha$ radiation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were carried out on a Seiko Instruments SPS1700HVR spectrometer. Fourier transform infrared spectroscopy (FTIR) spectra were collected within a range of 400-4000 cm^{-1} using KBr pellets on a varian 7000e FTIR spectrophotometer equipped with a liquid nitrogen cooled MCT detector. Thermogravimetric analysis (TGA) was carried out using a Rigaku TGA-8120 instrument in the temperature range of 25-1000 °C at a heating rate of 1 °C min^{-1} under an air flow.

Photochromic Measurement: Experiments were performed in a cylindrical glass air-filled static reactor (500 mL total volume) with a quartz window. An acetaldehyde (500 ppmv)- N_2 gas mixture was used to fill the reaction vessel. The sample was illuminated with a 300 W Xe lamp (Hayashi Watch-works Co. Ltd.). All UV-vis spectra were measured by spectrophotometer (Shimadzu UV-2100) by using the diffuse reflectance method. Barium sulfate powder was used as a reference standard.

[2] CHN elemental analysis, ICP-AES, FTIR, XRD and TG analysis of TOI microflowers

The elemental composition of the TOI microflowers, that is the W, C, H, N content, was measured by CHN elemental analysis and ICP-AES. According to these results, the elemental composition of the hybrid microflowers can be expressed by the formula $\text{WO}_{5.05}\text{H}_{11.65}\text{C}_{5.70}\text{N}_{2.08}$ (oxygen providing by the remaining mass of the sample). It is assumed that the nitrogen may stem from HMT or the decomposed NH_4^+ groups in the hybrid structure. FTIR spectroscopy clearly proves that the strong characteristic infrared bands of NH_4^+ groups are missing (1400 cm^{-1} , 3200 cm^{-1}), while the adsorption bands for the $-\text{CH}_2-$ (centered at 2965 cm^{-1}) and C–N ($1020\text{--}1220\text{ cm}^{-1}$) functional groups can be seen (Figure S1). This indicates that a part of HMT but not NH_4^+ groups has been intercalated into the hybrid structure. A comparative experiment was carried out to investigate the solvothermal transformation of HMT in absolute ethanol without WCl_6 at $180\text{ }^\circ\text{C}$. It was found that only HMT was present in the final powder product, which also gives evidence that HMT is stable in the solvothermal reaction and the intercalated organic molecules are indeed HMT.

However, the C/N ratio of the TOI microflowers is 2.74, much higher than that of pure HMT (1.29). Thus pure HMT intercalation can be excluded. The presence of a strong band at 1695 cm^{-1} in FTIR spectrum, assignable to C=O stretching, strongly point to the possibility that ethanol has been partly oxidized to acetic acid (Figure S1). As a matter of fact, oxidation of benzyl alcohol to benzoic acid or benzaldehyde with WO_3 powder as a catalyst has been observed in the reaction of benzyl alcohol with WCl_6 in the presence of deferoxamine mesylate. The produced benzoic acid molecules can even intercalate in the oxides to form organic-inorganic hybrid materials (J. Polleux et al. *J. Am. Chem. Soc.* 2005, 127, 15595; J. Polleux et al. *Angew. Chem. Int. Ed.* 2006, 45, 261; N. Pinna et al. *Small*, 2005, 1, 112). A similar oxidation step is expected to occur in our system. Ethanol can interact with WO_3 catalyst, chemisorbing both molecularly or dissociatively. Dehydrogenation may occur on some surfaces, and ethanol is eventually oxidized to acetic acid. The acetic acid molecules can be incorporated into the hybrid structure, which increases the carbon percentage in the TOI microflowers content.

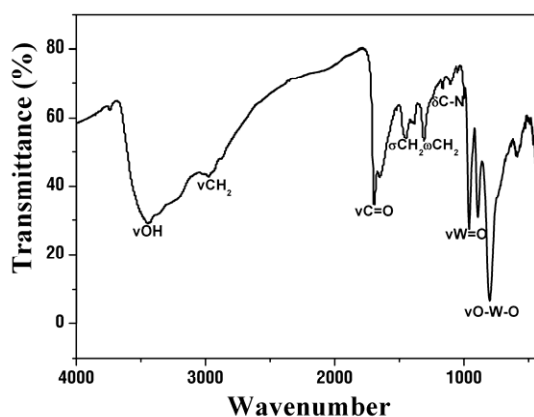


Figure S1: FTIR spectrum of the obtained TOI microflowers

The thermogravimetric and derivative curves for the hybrid material are shown in Figure S2. As can be seen in Figure S2, the curves for the TOI microflowers show three typical steps at ca. 50-150 °C, ca. 380 °C and ca. 485 °C with different weight loss, that is 6.8 %, 18.8 % and 7.6 %, respectively, which may be associated with the release of the adsorbed water or ethanol, HMT and acetic acid. It should be noticed that the weight loss of the reported lamellar yttrium oxide hybrid nanomaterials, consisting of yttrium oxide layers with intercalated benzoate molecules, occurs between 420-700 °C due to the release of the benzoate molecules intercalated in the lamellar structure (N. Pinna et al. *Small*, 2005, 1, 112). The HMT-intercalated Ni(OH)₂ undergoes a mass loss at 350 °C due to the release of HMT (B. H. Liu et al. *J. Phys. Chem. B*. 2006, 110, 4039). Thus it is reasonable to attribute the mass loss at 380 °C and ca. 485 °C to the release of HMT and acetic acid, respectively. The total mass loss percentage for TOI microflowers is 33.2 %, in good agreement with elemental analysis result. Based on the results of elemental analysis, TGA, XRD and FTIR, the hybrid material can be reasonably assumed to consist of WO₃ layers with intercalated HMT and acetic acid molecules, and the formula was determined to split up into WO_{2.34}(C₆H₁₂N₄)_{0.52}(C₂H₄O₂)_{0.49}(H₂O)_x(C₂H₆O)_y (0.5 < x, y < 1).

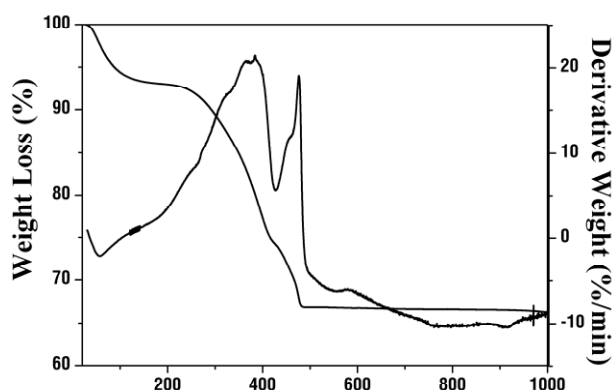


Figure S2: Thermal gravimetric analysis of TOI microflowers.

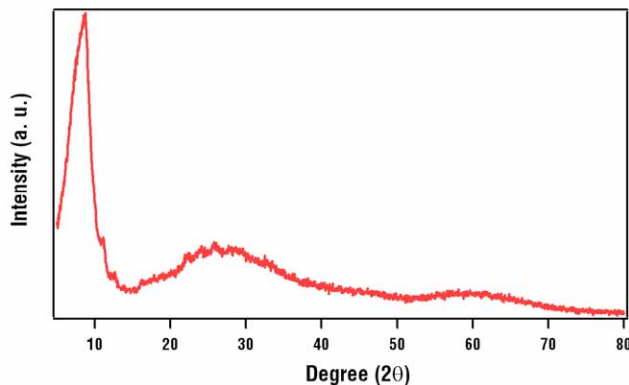


Figure S3: XRD pattern of TOI microflowers.

As can be observed in Figure S3, the diffraction pattern of TOI microflowers exhibits a sharp diffraction peak at 8.7° ($d=1.02$ nm) and a broad diffraction peak at ca. 25.6° ($d=3.47$ nm). The 8.7° could be attributed to organic species intercalation, while the ca. 25.6° may be due to the overlapping of several strong peaks of tungsten oxide. The great difference in diffraction patterns between TOI microflowers and WO_3 indicates that WO_3 lattice is distorted by the inserted organic molecules

[3] The coloration-decoloration cycles of TOI microflowers

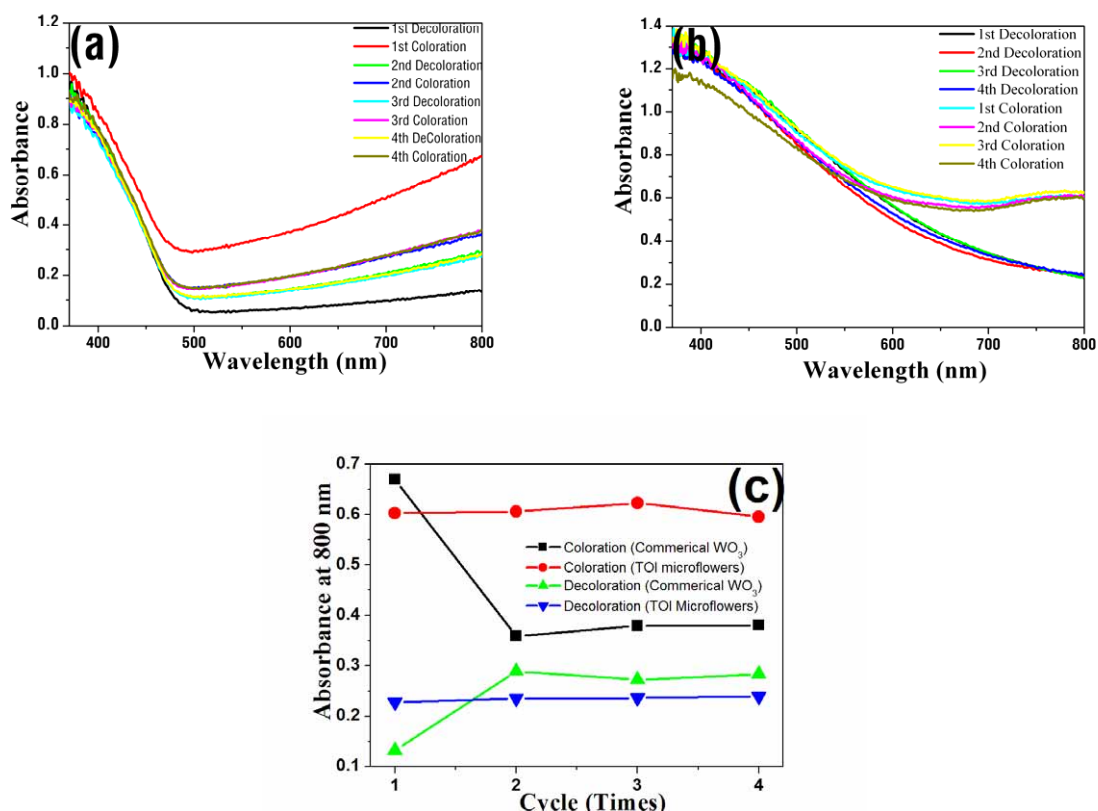


Figure S4: the coloration-decoloration cycles of (a) commercial WO_3 and (b) TOI microflowers; and photochromic response at 800 nm vs. cycle

[4] W4f level XPS of TOI microflowers before and after light irradiation.

To investigate the photochromic and bleaching mechanism of TOI microflowers, the X-ray photoelectron spectra (XPS) measurements on the flower-like hybrid structure were performed to identify the binding energy of the W atoms. The observed signal peaks confirmed the presence of W, C, O, and N. The XPS peaks of the W element before coloration and after light irradiation are shown in Figure S5 for the hybrid microflowers. The variation between the spectrum in (a) and that in (b) is due to the change in binding energy of the W 4f states, namely, the tungsten atom is reduced. Figure 5Sa is the Gaussian

deconvoluted XPS spectrum of the W4f core-level for the hybrid microflowers before coloration. The W4f spectrum can be deconvoluted into two doublets where the main doublet has a W 4f_{7/2} line at 35.5 eV and a W 4f_{5/2} line at 37.6 eV, which correspond to the W⁶⁺ formal oxidation state. The second doublet has a lower binding energy with W 4f_{7/2} at a line at 34.5 eV and a W 4f_{5/2} line at 36.6 eV corresponding to the W⁵⁺ oxidation state. The percentages of W⁶⁺ and W⁵⁺ for the hybrid microflowers before coloration were 56% and 44%, respectively. After light irradiation both the W4f doublet of W⁶⁺ and the W4f doublet of W⁵⁺ as well as W⁴⁺ were detected. Additionally, it should be noted that the percentages of W⁵⁺ and W⁴⁺ increase to 58% and 5%, respectively, while W⁶⁺ decreases to 37%, although the sample after light irradiation was maintained in a vacuum for about 24 hours during XPS measurements. Obviously, part of W⁶⁺ is reduced to W⁵⁺ and W⁴⁺ after the sample is exposed to light, and the optical contrast of the two states is responsible for the appearance of the distinct absorption bands in visible light region after coloration.

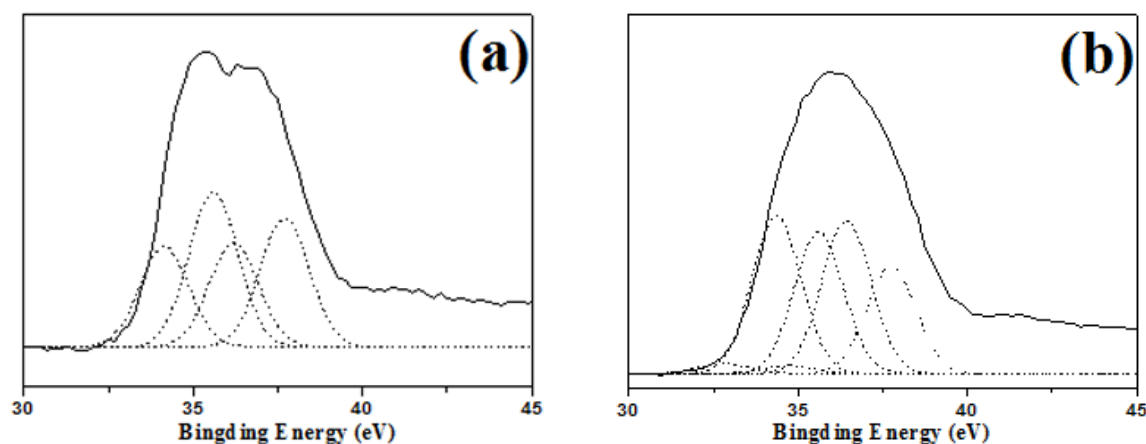


Figure S5: W_{4f} level XPS of TOI microflowers before and after light irradiation