

Photochromic Thermoplastics Doped with Nanostructured Tungsten Trioxide

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Supporting Information

Experimental Details:

Materials

Sodium tungstate dehydrate ($\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$) was provided by the Shanghai Chemical Reagent Company. Dimethylformamide (DMF) (99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Nitric acid (65%) was supplied by the Shanghai Chemical Reagent Company. Cupric bromide (99.95%) and Copper (AR,99.5%) were provided by the Aladdin Industrial Corporation. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA) (>98.0%) and 2-Bromoisobutyric acid ethyl ester (>98.0%) were purchased from the TCI (Shanghai) Development Co.,Ltd. Butyl acrylate (BA) (99%, Aladdin) and methyl methacrylate (MMA) (99.0%, Aladdin) were purified through alumina oxide columns before using. All other reagents were used as received without further purification.

Instrumentation

Gel Permeation Chromatography (GPC) The PL-GPC 220 (Polymer Laboratories) was used to measure samples. These samples were performed on a at 40 °C in THF. Polystyrene (PS) was used as the calibration standard. The detection was operated with a low rate of 1 mL/min.

¹H NMR The test was performed on a Bruker Av400III HD instrument at 400 MHz, Chloroform-D as the solvent for ¹H NMR measurement.

Ultraviolet-visible Light Detector (UV) Samples were prepared through the melt-compounding approach by a circular mold. The diameter and the thickness of the specimens were 25 mm and 1 mm respectively. Then, these samples were irradiated under ultraviolet lamp whose power was 500 W and wave length range was 350~450 nm, for a certain time interval. A Shimadzu Autograph UV-2450 with the wavelength range from 200 to 800 nm was used to collect UV-vis diffusion reflectance spectrum.

Solid Mechanical Property Experiments Samples were prepared by melt-compounding at 150 °C to form uniform dog-bone shaped specimens (length: ~38 mm, width: ~15 mm, thickness: ~0.5 mm) following ASTM standard D1708. The SANS E42.503 tensile tester was used to measure uniaxial tensile tests with a displacement-speed control of 5.0 mm/min at room temperature. The reported results for tensile properties represented an average over at least three independent measurements on three identical specimens for each polymer sample.

Scanning electron microscopy (SEM) Samples for SEM were thin films with 1 mm in thickness, which were prepared through melt-compounding approach, and then cryofractured in liquid nitrogen. The cross-sectional morphologies of the as-prepared films were observed under a Zeiss Ultra Plus microscope.

Transmission electron microscopy (TEM) The size and morphology of WO₃ were measured by transmission electron microscopy (TEM, Hitachi H-600, FEI Tecnai G2 F30).

Differential Scanning Calorimetry (DSC) Thermal transitions were determined by a SDT-Q600 thermal analyzer (TA). Samples (5~10 mg) were loaded into hermetically-sealed aluminum pans. They were first heated to 150 °C at a rate of 30 °C/min and held at 150 °C to erase any thermal history, then quenched to -40 °C, and reheated to 150 °C at a rate of 10 °C/min. Glass transition temperatures were determined during the second heating run.

Thermogravimetric Analysis (TGA) Thermogravimetric analysis was accomplished by a SDT-Q600 instrument. The samples (3 - 5 mg) were loaded into open aluminum pans and then were heated to 800 °C at a rate of 10 °C/min from room temperature in the air atmosphere.

Experimental

Preparation and surface modification of WO₃ Nanosheets. The prior art has provided a hydrothermal method to prepare WO₃ nanosheets.¹ Specifically, 7 mL of nitric acid was added in 30 mL of water and Stirred the mixture for 10 min. 2 g of NaWO₄ · 2H₂O was dissolved in 30 mL of water with ultrasonic treatment for 5 min, and then the solution was slowly added to the prepared nitric acid solution, and immediately light yellow precipitates appeared. The suspension was stirred for 30 min and then hydrothermally treated at 180 °C for 3 h. After being cooled to room temperature, the yellow product was centrifuged. The product was washed for four times with distilled water and dried in a vacuum oven overnight. SEM and TEM images of the WO₃ nanosheets was shown in Figure 2A and Figure S1(A). Finally, the generated WO₃ nanosheets were calcined at 600 °C in air at a heating rate of 5 °C per minute.

Preparation and surface modification of WO₃ Nanorods. A hydrothermal method to prepare WO₃ nanorods was provided by the prior literature.² Firstly, 1.5 g of NaWO₄ · 2H₂O and 0.2 g of NaCl were dissolved in 40 mL of water with ultrasonic treatment for 5 min. 1.2 mol/L HNO₃ was added dropwise into the above solution until light yellow precipitates was formed, which consumed about 7 ml of 1.2 mol/l HNO₃ during the while process. The suspension was stirred for 30 min and then hydrothermally treated at 180 °C for 12 h. The yellow product was centrifuged after being cooled to room temperature. The product was washed for four times with distilled water and dried in a vacuum oven overnight. SEM and TEM images of the WO₃ nanofibers was shown in Figure S2(A) and Figure S2(B). Finally, the generated WO₃ nanofibers were calcined at 600 °C in air at a heating rate of 5 °C per minute.

Synthesis of random copolymer P(MMA-*co*-PBA). P(MMA-*co*-BA) was prepared by adding MMA (15 g, 150 mmol), BA (12.8 g, 14.4 mL, 100 mmol) and 2-Bromoisobutyric acid ethyl ester(9.5 mg, 0.05 mmol) into a Schlenk flask with DMF(15 mL) as the solvent. The catalyst Cu(II)Br₂ (6.5 mg, 0.029 mmol) and ligand PMDETA (25.2 mg, 0.145 mmol) were added. Subsequently, three fresh copper wires

(20 mm in length) were introduced into the flask. After the solution was degassed by three freeze–pump–thaw cycles and backfilled with nitrogen, the solution was placed in a water bath at 70 °C and stirred for 4.5 h. To stop the copolymerization, the flask was opened to contact with air and rapidly cooled in liquid nitrogen. The product was collected by sedimentation in excessive cold methanol for three times and drying under vacuum at 40 °C for two hours to obtain transparent solids. Yield: 12.3g, 44.2%. ¹H NMR (Chloroform-D, δ, ppm) (Figure 1B): 4.0 (-COOCH₂-, 2H), 3.6 (-COOCH₃, 3H), 1.8 (-OCH₂CH₂-, 2H), 1.4 (-CH₂CH₂ CH₃, 2H). GPC curve was shown in Figure 1C.

Preparation of the WO₃/P(MMA-co-BA) nanocomposites. A series of WO₃/P(MMA-co-BA) nanocomposites were prepared in the same procedure, but with different weight percentages and types of WO₃. For example, WO₃-Sheet(0.5) and WO₃-Sheet-C(0.5) was prepared by adding 6mg pristine WO₃ nanosheets and 6mg calcined WO₃ nanosheets into 5mL acetone with ultrasonic treatment for 30 min, respectively. Then 1.2 g of random copolymer P(MMA-co-BA) was added into the above solution and subsequently stirred for 24 h. Finally, the mixture was transferred to a Teflon mold and the solvent was allowed to evaporate for 24 h under ambient conditions. The sample was further dried at 45 °C for 4 hours in a vacuum oven.

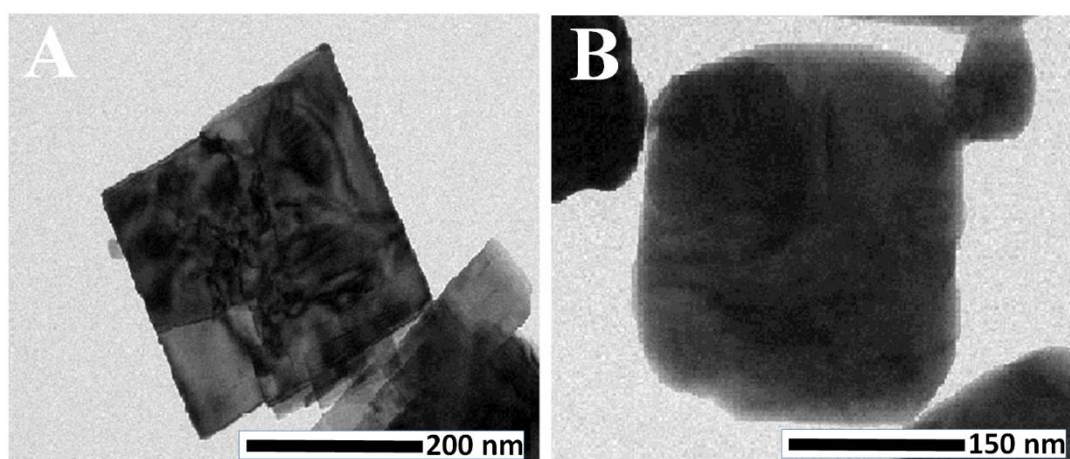


Figure S1. Representative TEM image of (A) pristine WO₃ nanosheets and (B) calcined WO₃ nanosheets.

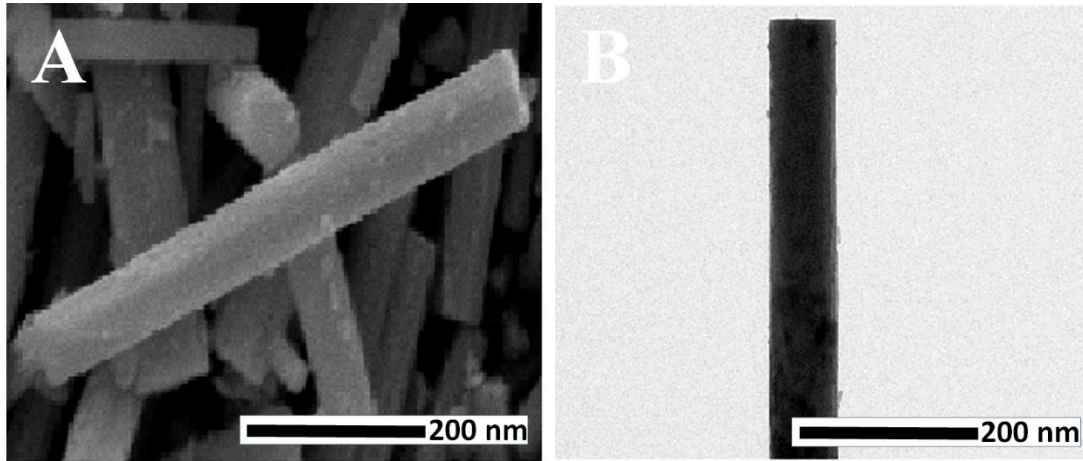


Figure S2. Representative (A) SEM and (B) TEM image of pristine WO_3 nanorods before any further treatment.

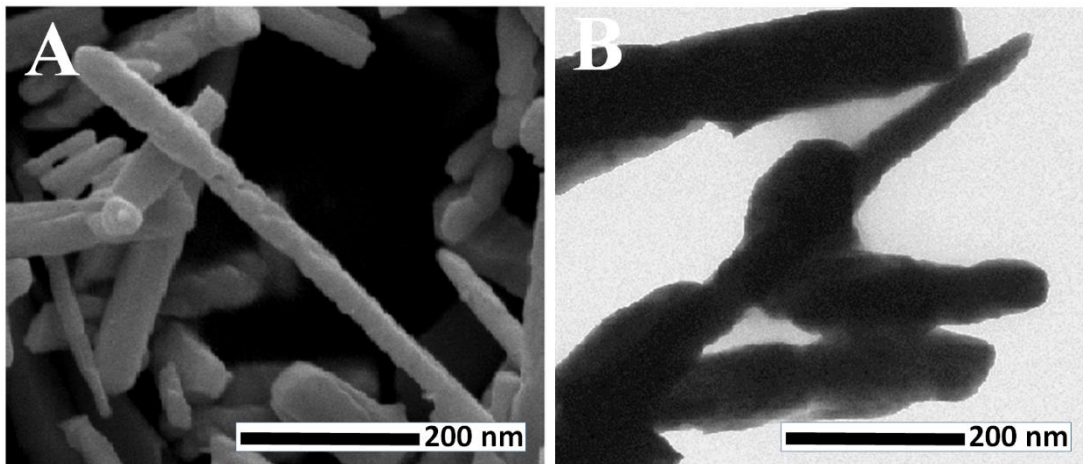


Figure S3. Representative (A) SEM and (B) TEM image of calcined WO_3 nanorods.

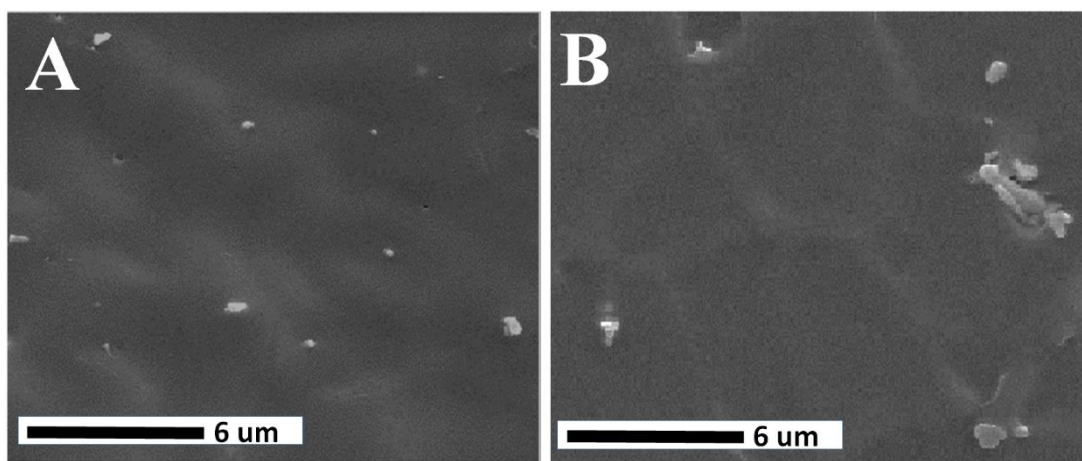


Figure S4. Representative SEM image (cross-section of the sample) of (A) the blends of pristine WO_3 nanorods and the random polymer, P(MMA-*co*-BA); and (B) calcined WO_3 nanorods and P(MMA-*co*-BA). The weight percentage of WO_3 was controlled at 1.5%. The weight percentage of WO_3 in both samples was controlled at

1.5%.

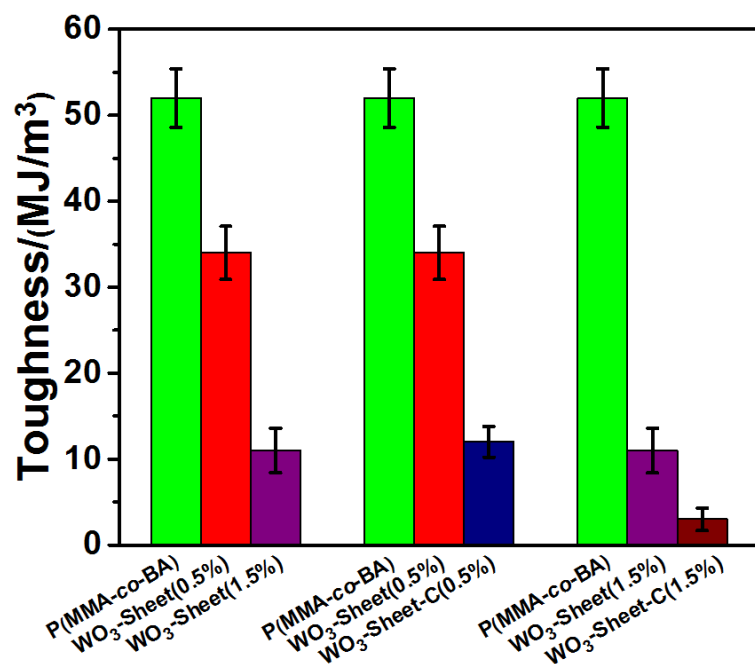


Figure S5. Tensile toughness of WO₃ nanosheets/ P(MMA-co-BA) nanocomposites.

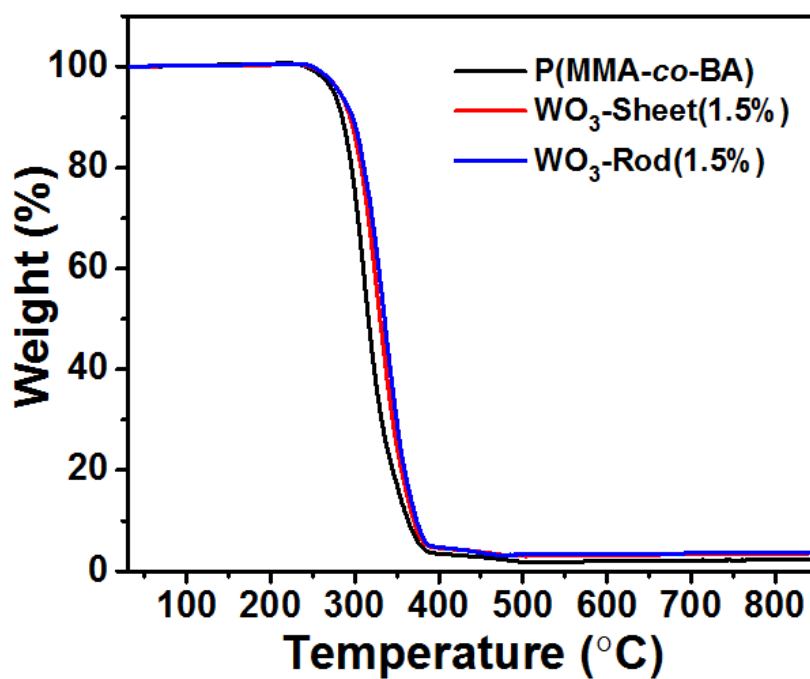


Figure S6. Thermogravimetric analysis (TGA) in air flow for P(MMA-co-BA), WO₃-Sheet(1.5%) and WO₃-Rod(1.5%).

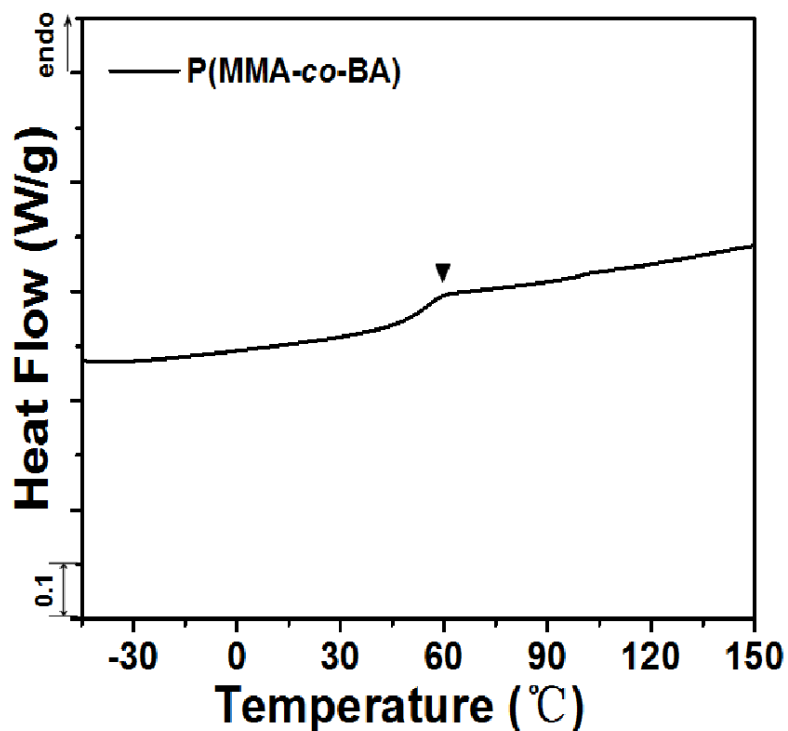


Figure S7. Differential scanning calorimetry (DSC) curves of P(MMA-co-BA). Arrow indicates the glass transition temperature.

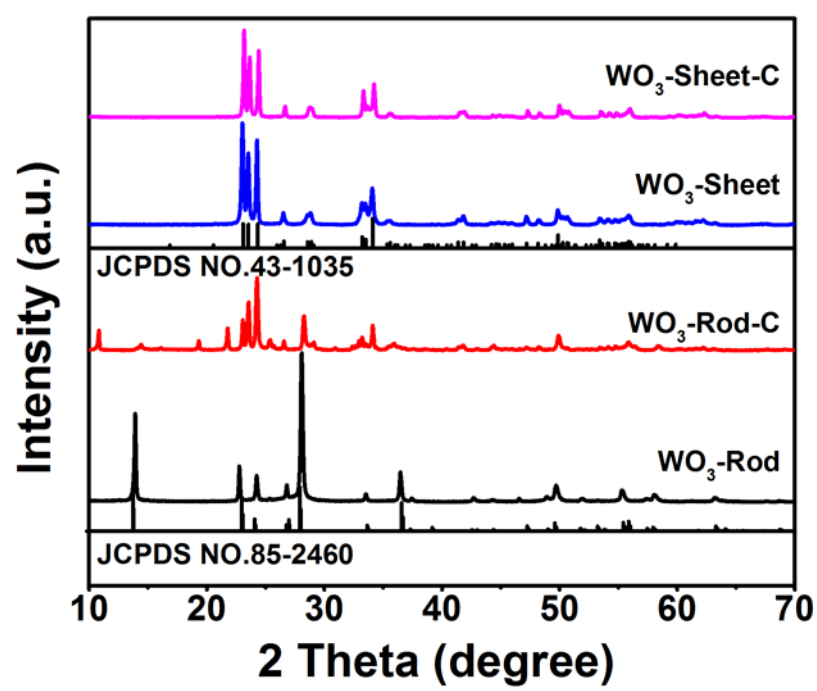


Figure S8. The X-ray diffraction (XRD) spectra of WO₃-Rod, WO₃-Rod-C, WO₃-Sheet and WO₃-Sheet-C. Pattern WO₃-Rod and WO₃-Sheet include the calculated diffraction lines from the corresponding JCPDS databases 43-1035 and 85-2460.

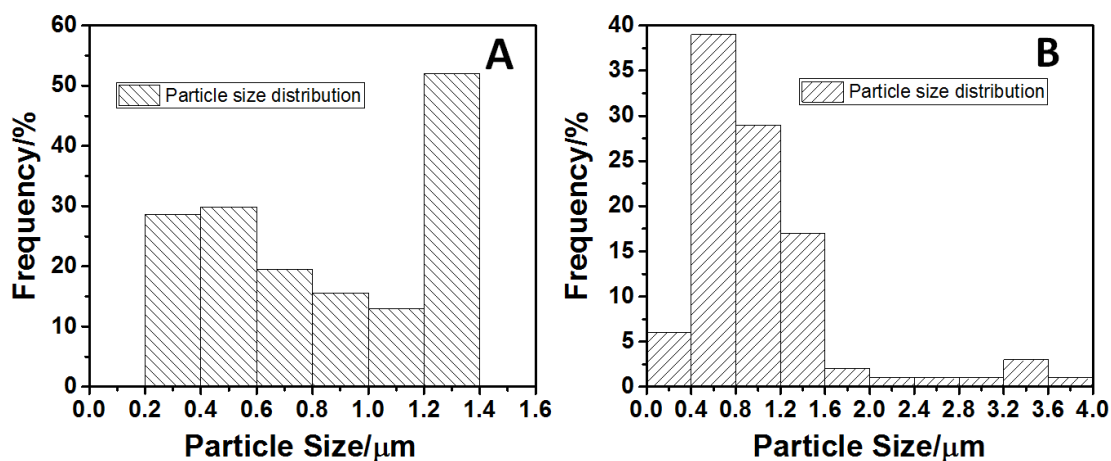


Figure S9. (A) The particle size distribution of embedded pristine WO₃ nanosheets. (B) The particle size distribution of embedded calcined WO₃ nanosheets. The weight percentage of WO₃ nanosheets in both samples was maintained at 1.5%.

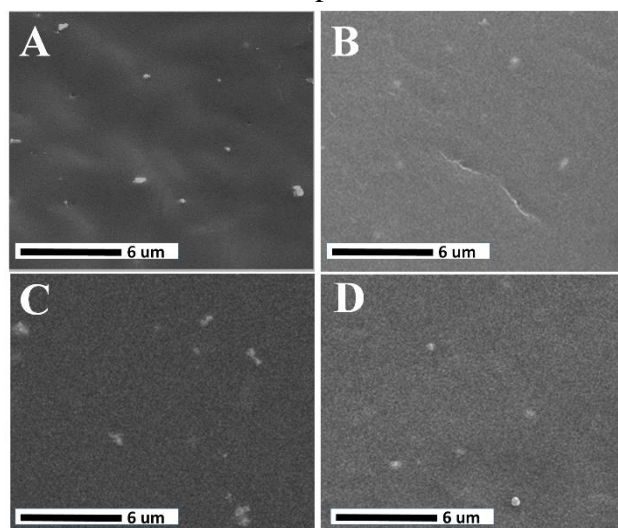


Figure S10. Representative SEM images for (A) WO₃-Sheet(1.5%) and (B) WO₃-Sheet(0.5%)(cross-section); (C) WO₃-Sheet (1.5%) and (D) WO₃-Sheet (0.5%) (surface).

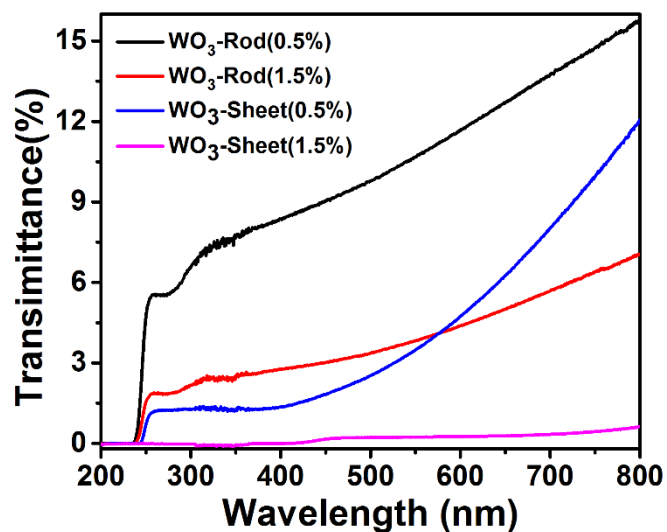


Figure S11. The intensity of transmission for WO₃-Rod(0.5%), WO₃-Rod(1.5%), WO₃-Sheet(0.5%), and WO₃-Sheet(1.5%).

WO₃-Sheet(1.5%) and WO₃-Sheet(0.5%).

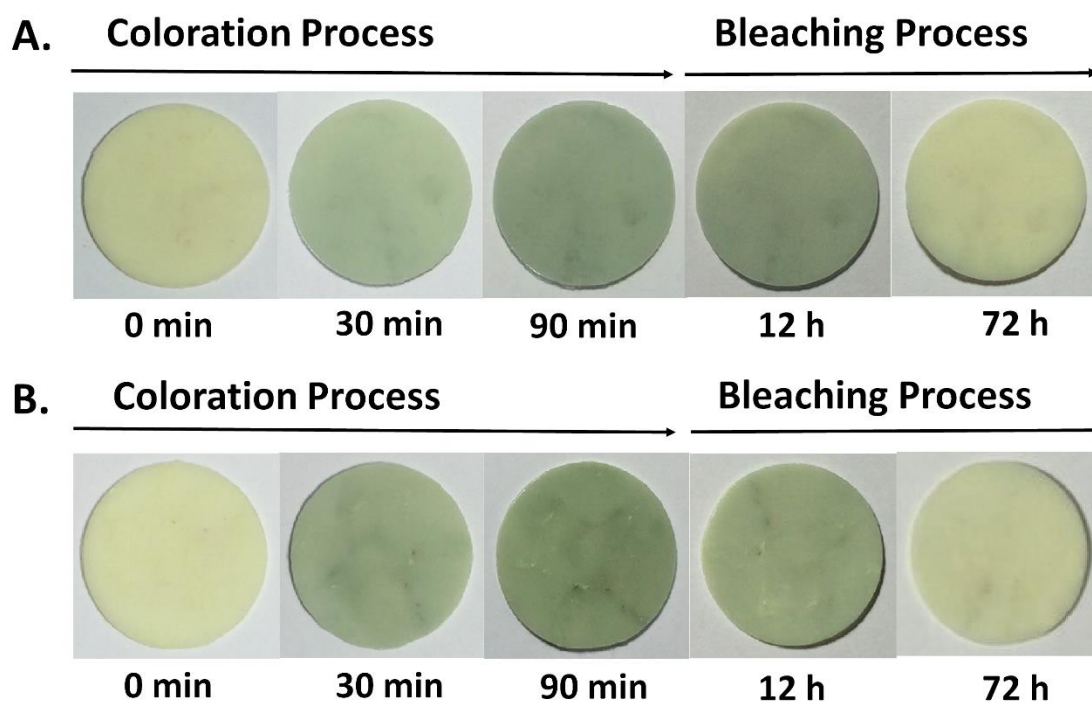


Figure S12. (A) Photos of WO₃-Sheet(0.5%) during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature (25 °C) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 90 min, and the last one on the right corresponds to recovery after 72 h. (B) Photos of WO₃-Sheet-C(0.5%) during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature (25 °C) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 90 min, and the last one on the right corresponds to recovery after 72 h.

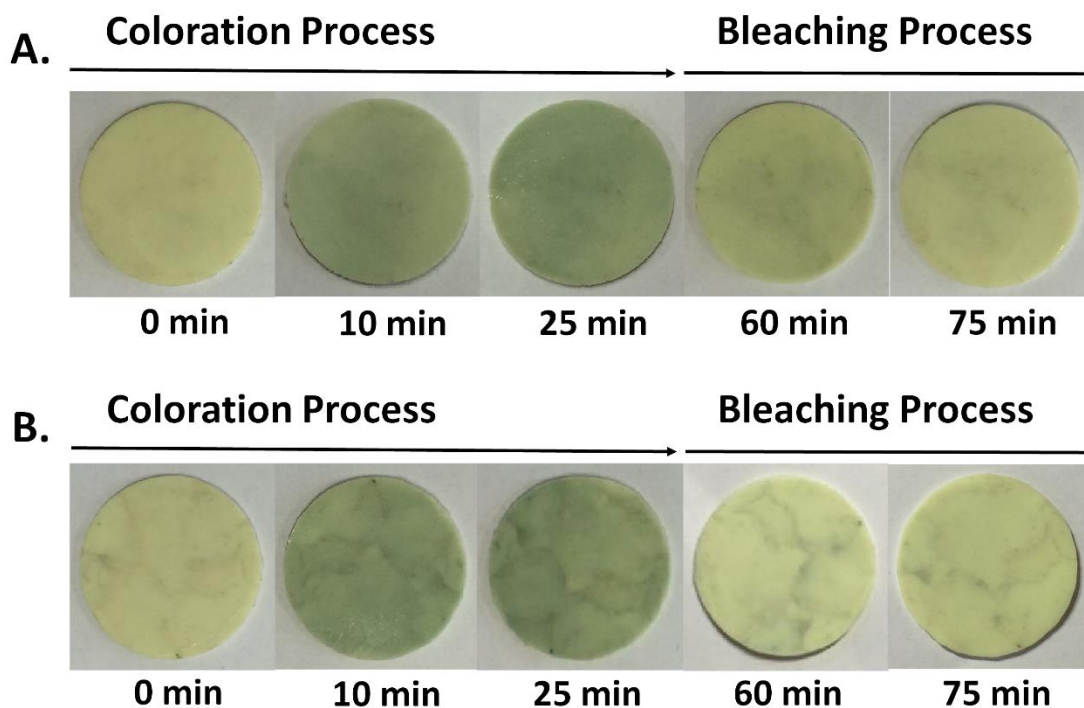


Figure S13. (A)Photos of WO_3 -Sheet(1.5%) during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature (25 °C) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 25 min, and the last one on the right corresponds to recovery after 75 min. (B)Photos of WO_3 -Sheet-C(1.5%) during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature (25 °C) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 25 min, and the last one on the right corresponds to recovery after 75 min.

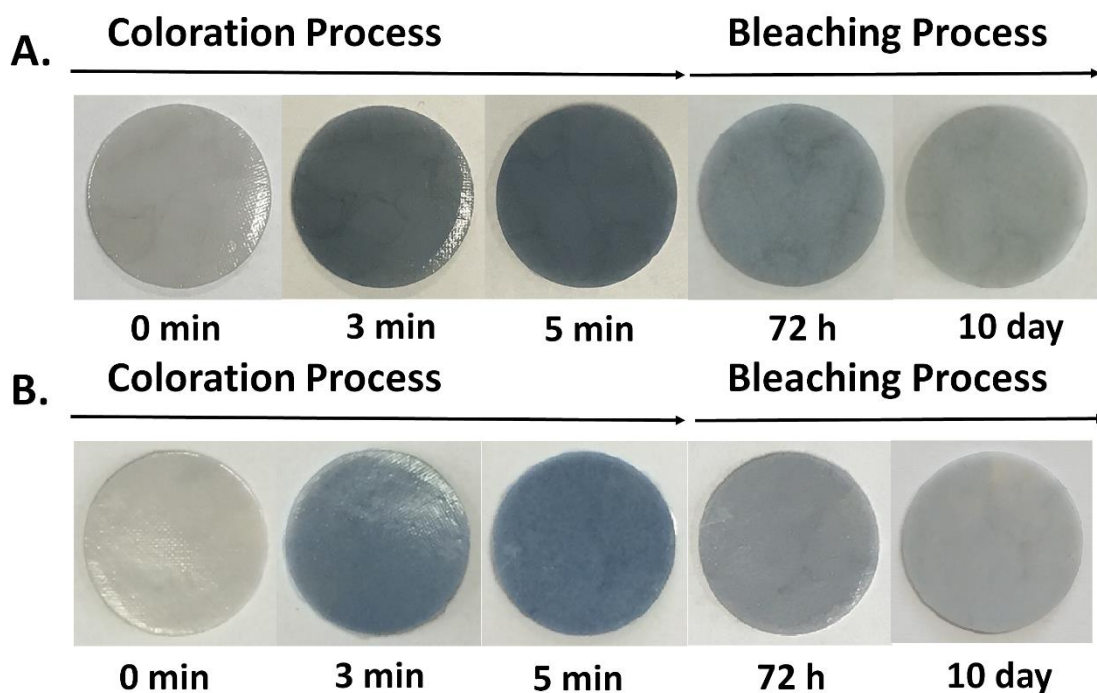


Figure S14. (A) Photos of $\text{WO}_3\text{-Rod}(0.5\%)$ during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature ($25\text{ }^\circ\text{C}$) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 5 min, and the last one on the right corresponds to recovery after 10 day. (B) Photos of $\text{WO}_3\text{-Rod}(1.5\%)$ during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature ($25\text{ }^\circ\text{C}$) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 5 min, and the last one on the right corresponds to recovery after 10 day.

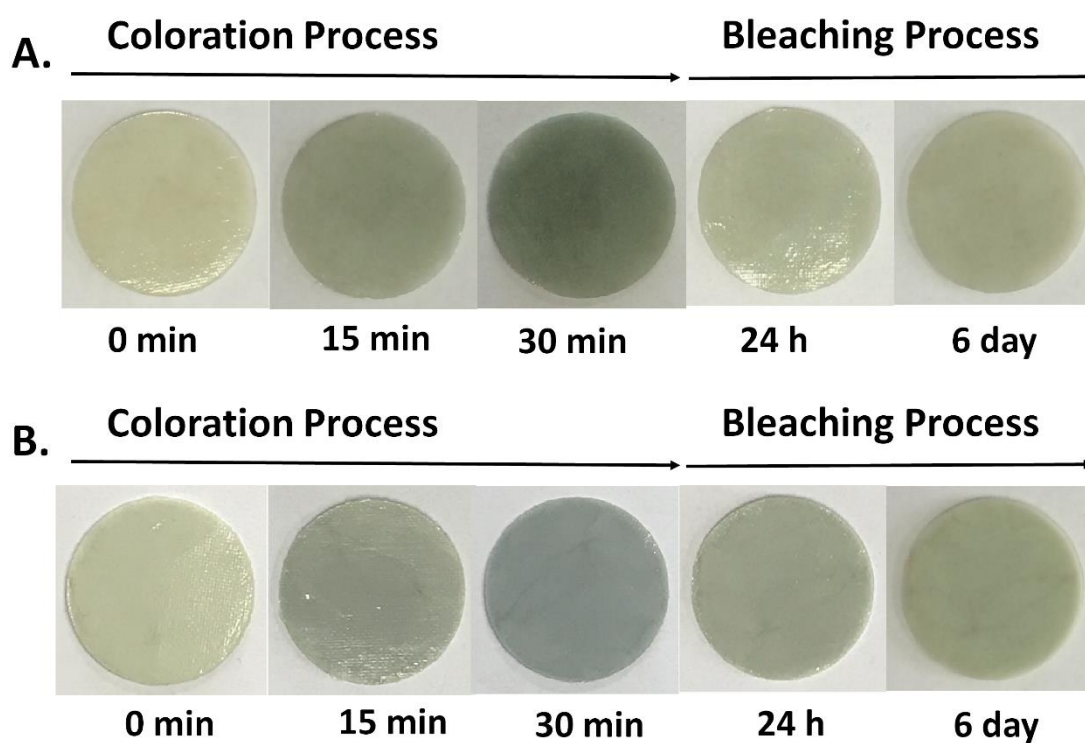


Figure S15. (A) Photos of $\text{WO}_3\text{-Rod-C}(0.5\%)$ during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature ($25\text{ }^\circ\text{C}$) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 30 min, and the last one on the right corresponds to recovery after 6 day. (B) Photos of $\text{WO}_3\text{-Rod-C}(1.5\%)$ during the coloration process after different exposure time to UV radiation and bleaching process after different recovery time at room temperature ($25\text{ }^\circ\text{C}$) in air. The first one on the left corresponds to 0 min of exposure, while the third one in the middle is for 30 min, and the last one on the right corresponds to recovery after 6 day.

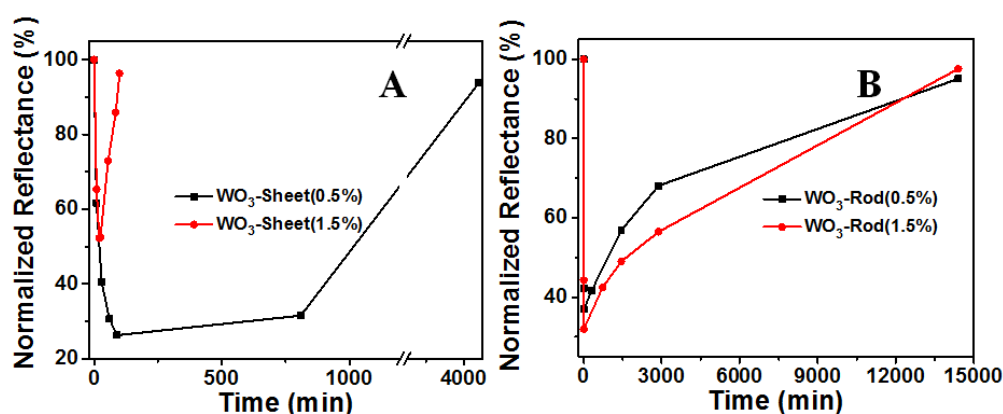


Figure S16. The effect of different contents of pristine WO₃ nanosheets and nanorods on the photochromic properties of WO₃/P(MMA-*co*-BA) nanocomposites. The intensity of reflectance for (A) WO₃-Sheet(0.5%) and WO₃-Sheet(1.5%); (B) WO₃-Rod(0.5%) and WO₃-Rod(1.5%) at 800 nm wavelength during the coloration and bleaching processes.

Table S1. Tensile properties of nanocomposites of WO₃ and P(MMA-*co*-BA) copolymer.

Samples	σ_y (MPa)	E^a (MPa)	ϵ_b (%)	Toughness ^b (MJ/m ³)
P(MMA- <i>co</i> -BA)	30.5 ± 1.5	356.1 ± 59.7	190 ± 15	52
WO ₃ -Rod(0.5%)	33 ± 3.7	390 ± 61.1	187 ± 13	63
WO ₃ -Rod(1.5%)	30.8 ± 1.4	379.9 ± 21	127 ± 15	44
WO ₃ -Rod-C(0.5%)	27.5 ± 1.4	334.6 ± 4.9	126 ± 15	40
WO ₃ -Rod-C(1.5%)	27.5 ± 1.1	368.7 ± 55.6	71 ± 1	21
WO ₃ -Sheet(0.5%)	28.8 ± 0.7	323.3 ± 5.3	105 ± 6	34
WO ₃ -Sheet(1.5%)	23.5 ± 2.0	342.2 ± 66.7	41 ± 2	11
WO ₃ -Sheet-C(0.5%)	23.8 ± 0.7	331.3 ± 16.4	40 ± 6	12
WO ₃ -Sheet-C(1.5%)	40.2 ± 1.1	367.3 ± 82.0	15 ± 4	3

^a Room temperature Young's modulus (E) determined from the slope of the fitting line to the linear elastic regime of stress-strain curves. ^b Tensile toughness determined by integrating the area under stress-strain curves up to the specimen breaking point.

Table S2. Summarized coloration and bleaching time of WO₃/P(MMA-co-BA) nanocomposites.

Samples	Coloration process	Bleaching process
WO₃-Rod(0.5%)	5 min	10 day
WO₃-Rod(1.5%)	5 min	10 day
WO₃-Rod-C(0.5%)	30 min	6 day
WO₃-Rod-C(1.5%)	30 min	6 day
WO₃-Sheet(0.5%)	90 min	72 h
WO₃-Sheet(1.5%)	25 min	75 min
WO₃-Sheet-C(0.5%)	90 min	72 h
WO₃-Sheet-C(1.5%)	25 min	75 min

Reference

- [1] Naixu Li, et al. Metal nanoparticles supported on WO₃ nanosheets for highly selective hydrogenolysis of cellulose to ethylene glycol. *Green Chemistry*. 2016.
- [2] Fu, L., et al., Photocatalytic hydrogenation of nitrobenzene to aniline over tungsten oxide-silver nanowires. *Materials Letters*, 2015. 142: p. 201-203.