Supporting information for

Ordered mesoporous WO_3 film with outstanding gasochromic properties

[a,b] Wei Feng, [a] Guangming Wu and [b] Guohua Gao

[a] Shanghai Key Laboratory of Special Artificial, Tongji University, Shanghai, China P.R. China. Fax: 86 02165986071; Tel: 86 02165982762; E-mail: wugm@tongji.edu.cn; fengwei3166@163.com,

[b] Microstructure Materials and Technology, Tongji University, Shanghai, P.R. China. Fax: 86 02165986071; Tel: 86 02165982762; E-mail: gao@tongji.edu.cn

Experimental Section

Preparation of the mesoporous WO_3 film. In a typical synthesis, 5 g of W powders (99.8%) was completely reacted with 30 ml of H_2O_2 (30%) and EtOH. After refluxing at 80℃ for 2 h, a transparent orange PTA sol was obtained. Subsequently, 2.35 g tri-block copolymer (Pluronic F127, EO_{106}-PO_{70}-EO_{106}, M_w=12600, Aldrich) was added into the former sol under strong stirring for 2h and then aging 2h in an incubator at a stable temperature of 45 ℃. Then, all films were deposited on glass slides or Si wafers through dip-coating technique with a withdraw speed of 2 cm/s. After deposition, the film needs to be aging overnight to stabilize and cross-link the inorganic network. At last, a rapid thermal process system (RTP-AG610, Allwin21 Co.) was used to remove the copolymer and form mesoporous feature. The heating rate and annealing time is 20 ℃/s and 2 min, respectively.

Characterization. For the most part, film was characterized. However, in those instances where film was not convenient to use because of the limited amount of materials, the corresponding powder derived from xerogel (completely drying of the sol under ambient condition) was analyzed. Specifically, the thermogravimetric-differential scanning calorimetry (TG-DSC) analysis of WO_3 xerogel powder was performed by using a TG/DSC NETZSCH STA99C instrument. The analysis was carried out with a heating rate of 10 ℃/min in static air up to 600 ℃. For IR analysis, the film was deposited on Si wafer and the infrared spectra was obtained using a FT-IR Perkin Elmer 2000 system spectrometer (Spectral range 4, 000~400 cm^{-1}). The crystalline phase evaluation was followed by X-ray Diffraction, which was conducted on Siemens D500 with Cu Kα radiation in the range of 5 ~ 60° with a scanning speed of 0.08 °/min. Structural property was further examined by LabRAM HR 800, HORIBA Jobin-Yvon Raman system. TEM measurement was taken by using JEOL-TEM-2010 instrument, where the sample was obtained by scratching off film on the glass. SEM photograph was obtained using S3400 N Scanning Electron Microscope operated at 30 kV. An UV-visible/NIR

spectrophotometer (Jasco-V570) was used to measure the optical transmittance and the coloring/bleaching response toward hydrogen gas. N_2 adsorption isotherms were recorded with an AUTOSORB-1 Surface Area Analyzer (Quantachrome Instrument Corporation) at -196 ℃. Surface area was determined by the Brunauer-Emmett-Teller (BET) method. Pore volume and size were determined by the Barrett-Joyner-Halenda (BJH) method. The corresponding powder sample was got after the same rapid thermal process like the film.

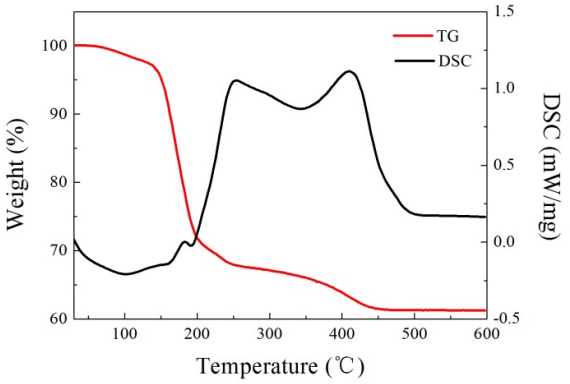

Fig.1S. TG-DSC curves of the PTA/F127 xerogel powder

The TG-DSC curves of the PTA/F127 xerogel are shown in Fig. 1S. It can be seen that there is a 39 % total weight loss on heating up to 600 ℃. At less than 200 ℃, there is a remarkable mass loss of 30 %, which should be ascribed to the desorption of copolymer and solvent on the surfaces. After being heated at 450 ℃, the sample kept a constant weight, which indicated that F127 had been completely removed and WO_3 particles began to crystallize. So, we select the ranges of 250 ~ 450 ℃ as the annealing temperature.

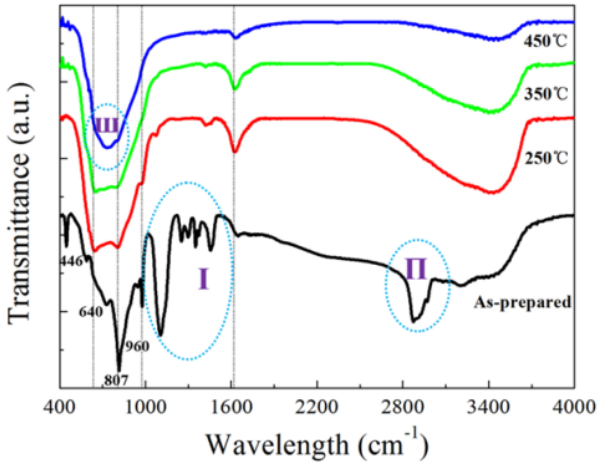

Fig.2S. FT-IR spectra of the hybrid films annealed at different temperatures

As shown in Fig. 2S, the present of F127 in the hybrid film can be affirmed from the strong absorption bands assigned to C-C, C-H, -CH_2-, and C-O-C (as marked in zone I and Π). Even though the annealing time is only 2 minutes, the copolymer visibly decompose after annealing at 250 ℃ and totally disappear after 450 ℃. That is agreement with the result of TG-DSC. Therefore, the rapid thermal process is a much energy-saving and effective calcination process than conventional furnace annealing method in this experiment.

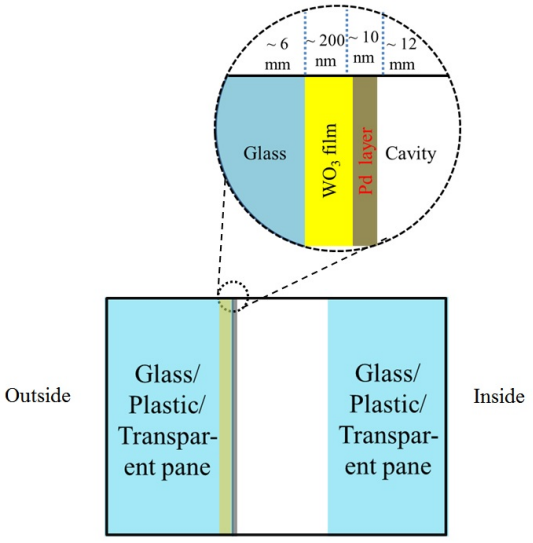

Fig.3S. Schematic of the gasochromic device

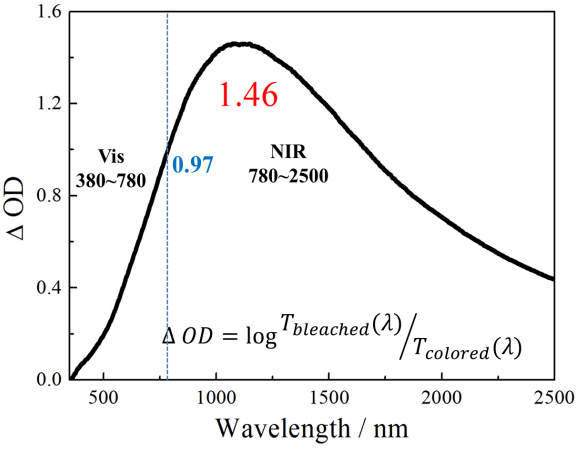

Fig.4S. Optical density change of mesoporous WO_3-based device

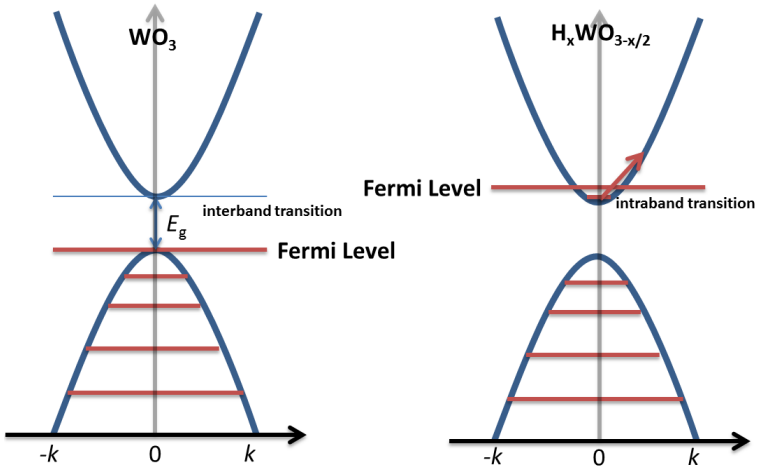

Fig. 5S Schematic of the band structures for WO_3 (bleached) and $H_xWO_{3-x/2}$ (colored)

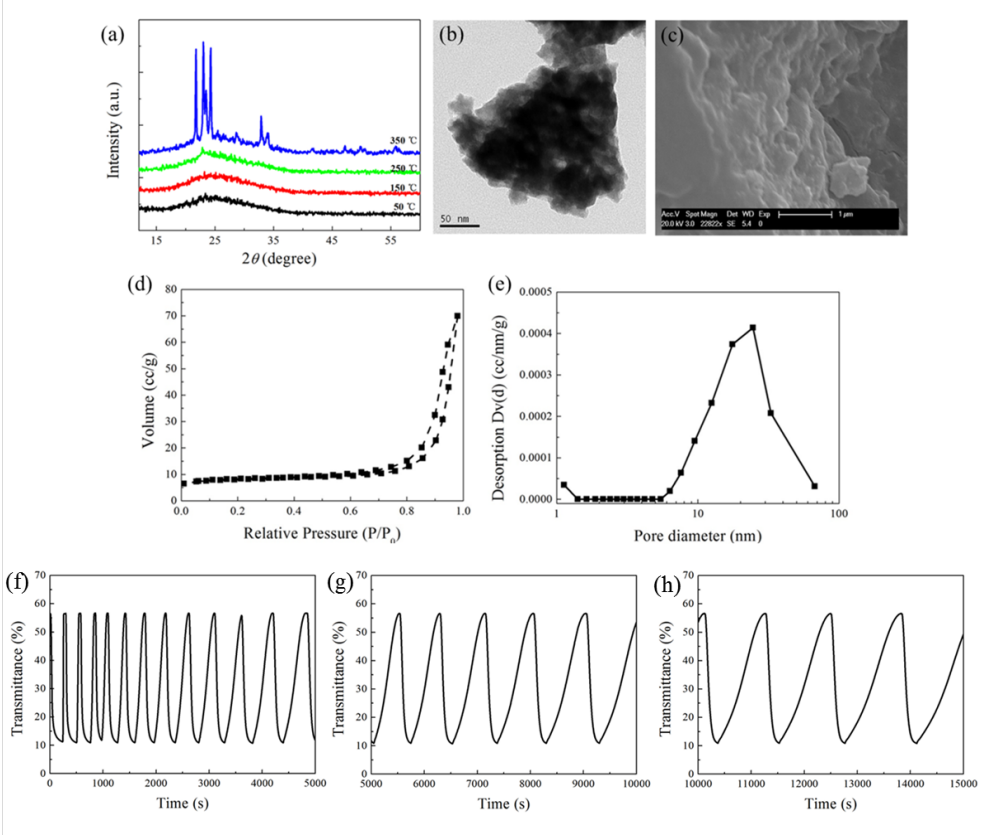

Fig. 6S Crystallinity and morphology of the standard WO_3 film (a) XRD; (b) TEM; (c) SEM; the representative N_2 desorption isotherms (d) and pore size distribution (e); as well as the corresponding coloring/bleaching behaviors (f) ~ (h)