Amphiphilic Block Copolymer Templated Synthesis of Mesoporous Indium Oxides with Nanosheet-Assembled Pore walls

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Experimental details for micro-sensor fabrication and sensing performance measurement

Chip fabrication : In the clean room, micro-hotplate chips (Figure 5a,b) can be low-cost fabricated in batches by using micro-electro-mechanical-systems (MEMS) technologies. The chips were fabricated on a normal single-side polished silicon wafer. In order to improve the accuracy of working-temperature and reduce the power consumption, suspended structure of the micro-hotplate was designed. In the fabricated micro-hotplate chips, four functional components including comb-finger electrodes, poly-Si heater, insulating layer and suspended plate were integrated. With the FEM analysis tool COMSOL, thermal simulation was implemented to validate the design of the micro-hotplate. Besides thermal simulation, the temperature coefficient of resistance of the Poly-Si heater is further calibrated in a temperature programmable oven. Based on the linear fitting relationship between temperature versus heating voltage, the working temperature on sensing area of the micro-hotplate can be well controlled by adjusting the voltage supply.

Sensor preparation: 0.01 g of the mesoporous In_2O_3 sample was added into 1.0 mL of deionized water and dispersed under ultrasonic to form a crude suspension. After that, 1.0 μL of the suspension was loaded onto the sensing area (i.e. comb-like electrode) of the micro-hotplate chip to form a chemiresistor-type microsensor. Then, the microsensor was dried in an oven at 80 ^oC for about 2 h (Figure S9). The sensing response was defined as the resistance change of $\Delta R = R_{NO2}/R_0$. The working temperature of the sensor was induced by a voltage adjustable DC power source, which was connected to the micro-heater. The resistance of the microsensor was real-time recorded by using a commercial multimeter (model: Agilent-34410A). The gas sensing tests were carried out in a lab-made testing chamber (20 L in volume), where the microsensor was previously put inside. In order to obtain NO_2 with a desired concentration, the standard NO_2 gas with known volume was injected into the testing chamber and, thereafter, rapidly diluted by ambient air. When NO_2 gas was introduced to the testing chamber, the NO_2 molecules adsorbed by the mesoporous In_2O_3 will capture electrons from the material that can be detected by the signal of resistance increase. After each test for a concentration, the cover of the testing chamber was removed and the atmosphere of the testing chamber was switched to fresh air for signal recovery. Under fresh air, the NO_2 molecules desorbed from the mesoporous In_2O_3 and released the captured electrons. The released electrons made the resistance of the mesoporous In_2O_3 decreased.

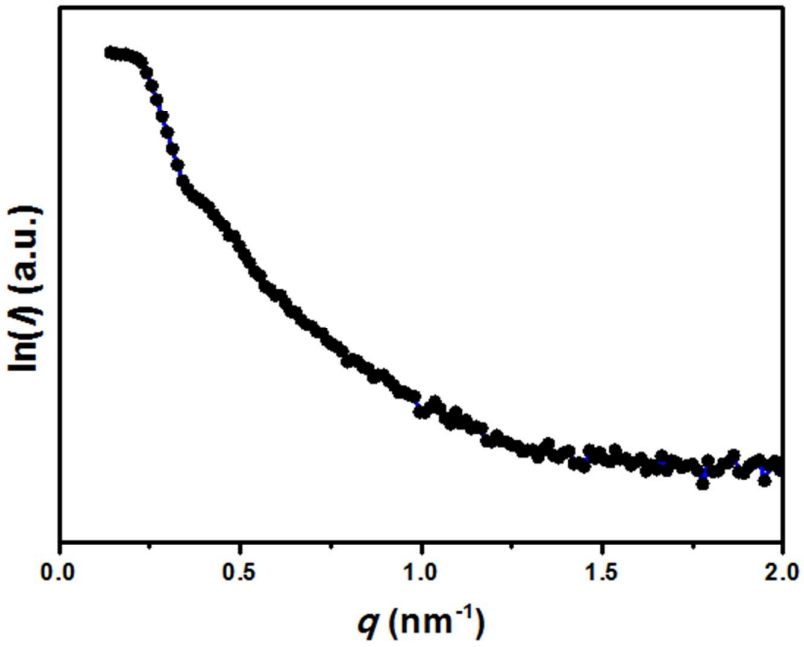

Figure S1. SAXS patterns of the as-made PEO-*b*-PS/In_2O_3 hybrid sample with a weight ratio (PEO-*b*-PS: In_2O_3) of 3.0.

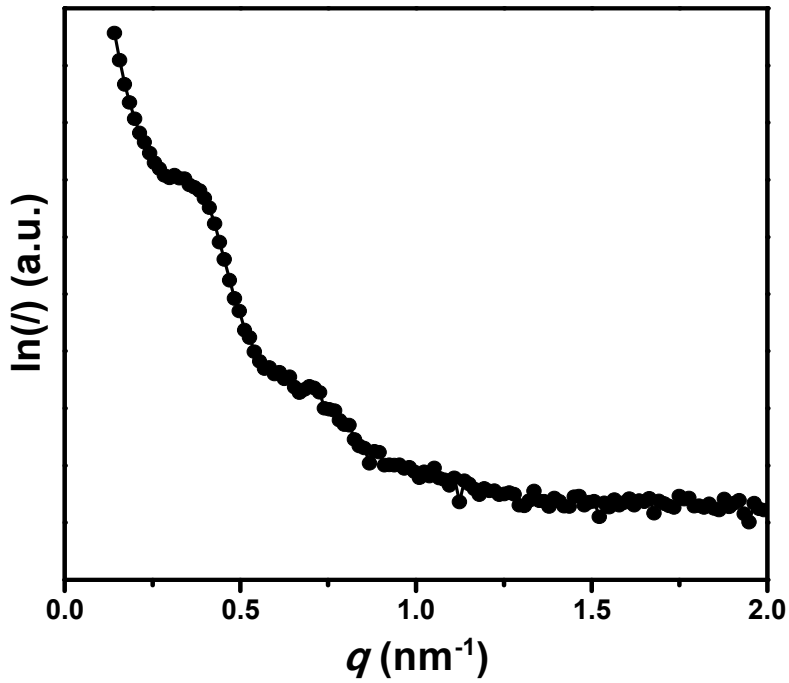

Figure S2. SAXS patterns of the In_2O_3-2.5-400-0.5 sample obtained after calcination of the as-made organic-inorganic composite with a weight ratio ($InCl_3$:PEO-*b*-PS) of 2.5 at 400 ºC for 0.5h in the presence of comburent CaO_2 in a muffle furnace.

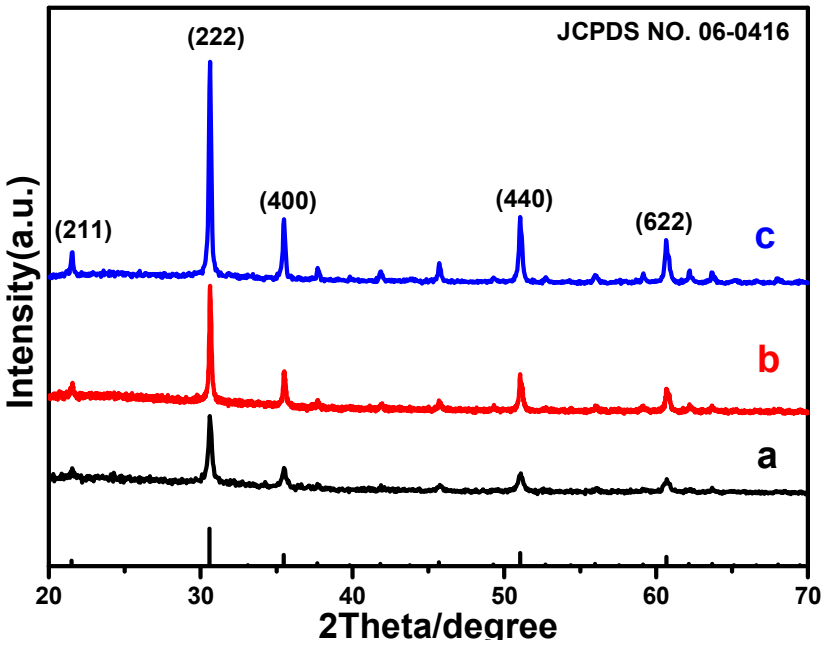

Figure S3. Wide angle XRD patterns of the In_2O_3-2.5-400 samples obtained after CaO_2 assisted calcination of the as-made organic-inorganic composite with a weight ratio (PEO-*b*-PS: In_2O_3) of 2.5 in air at 400 ^oC for 0.5 h (a), 1h (b), and 1.5h (c), respectively.The gradual increase of diffraction intensity indicates an ever-increasing degree of crystallization of In_2O_3 with the prolonging calcination treatment time from 0.5 to 1.5 h.

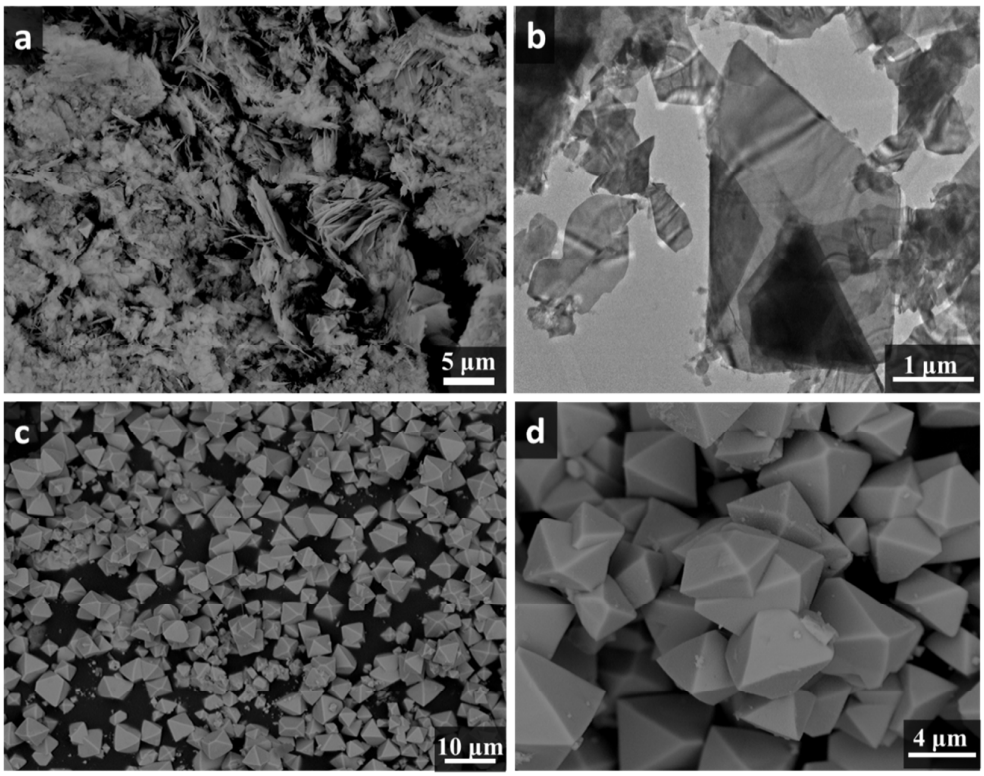

Figure S4. SEM (a, c, d) and TEM (b) images of the In_2O_3 sample obtained by direct calcination of $InCl_3$ in air at 400 ^oC for 0.5h (a, b) and at 450 ^oC for 0.5h (c, d).

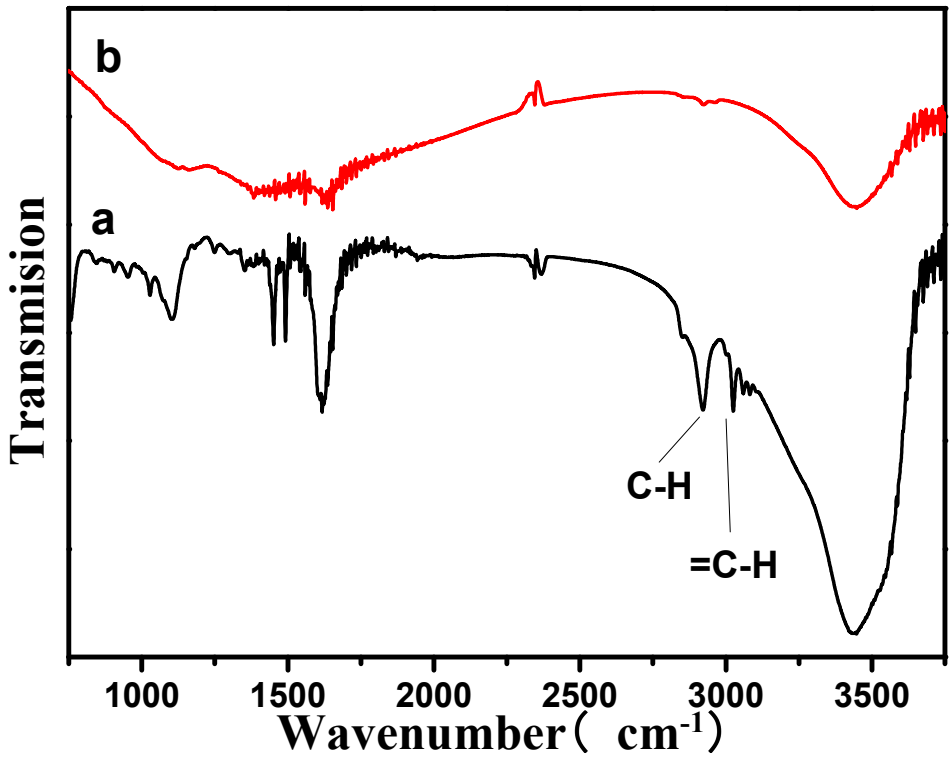

Figure S5. FTIR spectrum of (a) as-made PEO-*b*-PS/In_2O_3 composite and (b) the mesoporous In_2O_3 -2.5-400-0.5 obtained after calcination at 400 ^oC in air for 0.5h. Before calcination, typical absorption peaks at 2918 cm^{-1} and 3024 cm^{-1} can be clearly visible in the as-made PEO-*b*-PS/In_2O_3 composite. While after calcination at 400 ^oC in air for 0.5h, all these peaks disappear, implying a complete removal of the PEO-*b*-PS copolymers.

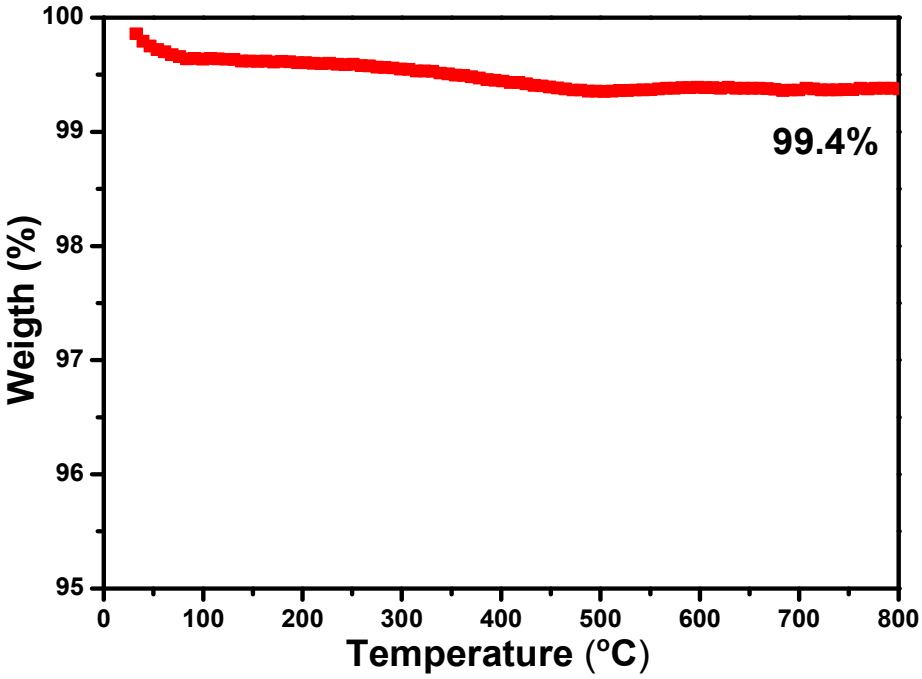

Figure S6. TG curves of the mesoporous In_2O_3-2.5-400-0.5 sample obtained after calcination at 400 ^oC in air for 0.5 h. It indicates a negligible weight loss of about 0.6% until 800 ^oC, confirming the complete removal of PEO-*b*-PS molecules after calcination at 400 ^oC in air with the assistance of CaO_2.

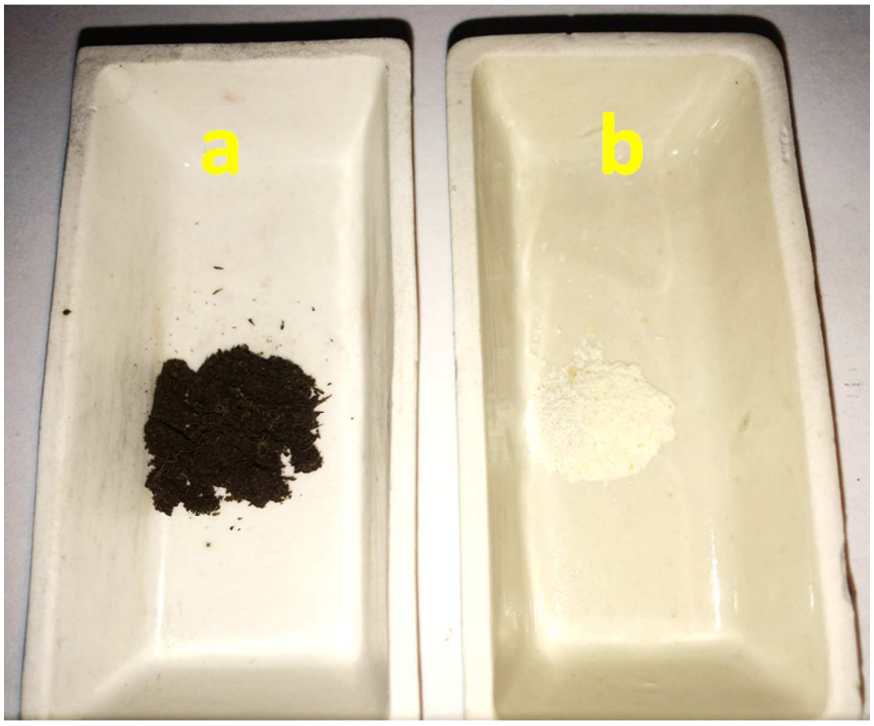

Figure S7. optical photographs of the mesoporous In_2O_3 obtained after calcination in air at 400 ºC for 0.5 h with the absence of CaO_2 (a) and with the presence of CaO_2 (b). It clearly indicates that without the use of CaO_2, the PEO-b-PS copolymers can be carbonized after quick calcination at 400 ºC even in air due to the incomplete combustion, yielding a black sample. By contrast, with the presence of comburent CaO_2, the PEO-b-PS copolymer can be quickly decomposed, resulting in a light yellow powder sample.

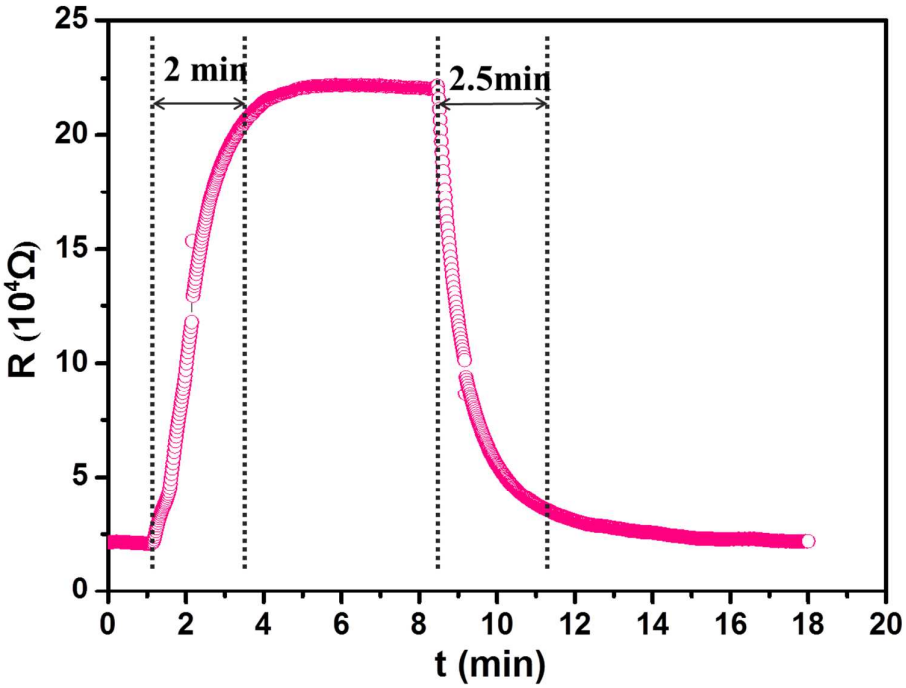

Figure S8. The response-recovery curve of the crystalline mesoporous indium oxides-based sensor to 250 *ppb* of NO_2 at 150 ^oC.

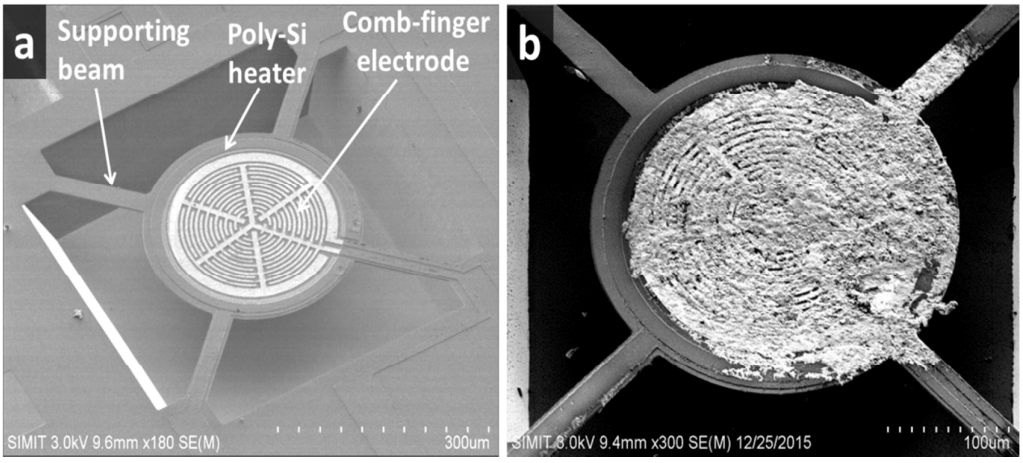

Figure S9. SEM images of the micro-hotplate chips before (a) and after depositing mesoporous In_2O_3 (b).

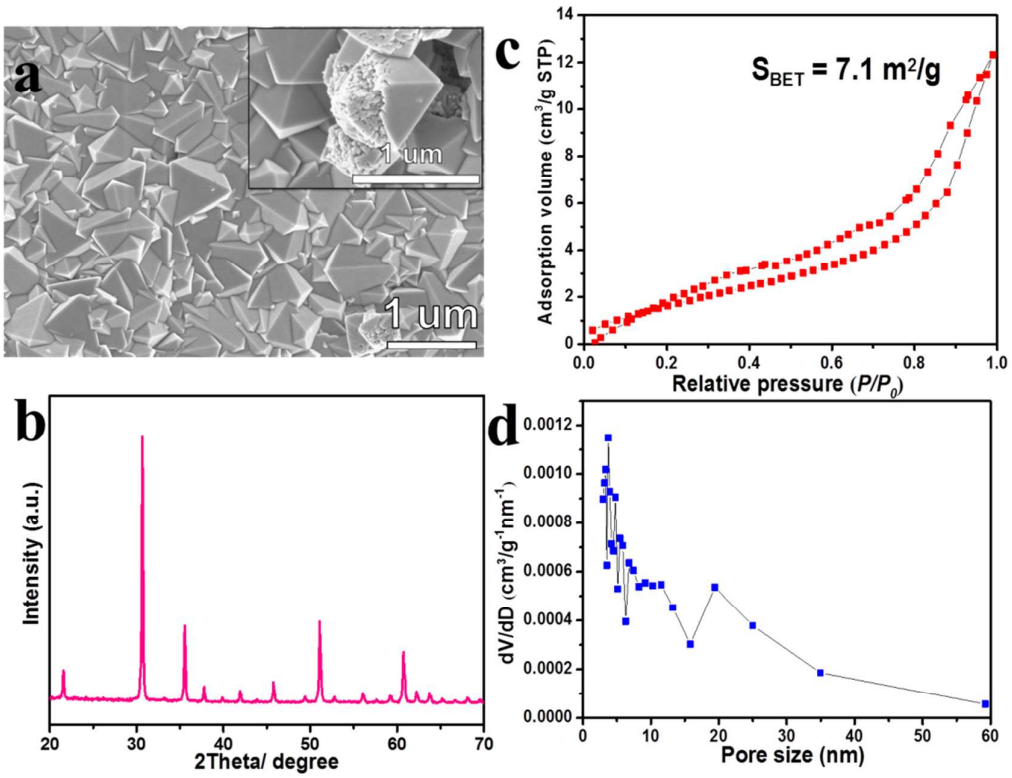

Figure S10. (a) SEM image, (b) XRD pattern, (c) the nitrogen adsorption-desorption isotherms and (d) the corresponding pore size distribution profile of the In_2O_3-2.5-450-1.0 sample.