

Photochemical Construction of Free-Standing Sn-Filled SnO₂ Nanotube Array on a Solution Surface for Flexible Use in Photocatalysis

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Electronic Supplementary Material

The array on the film-substrate could be reversed by directly taking the solution as medium. As shown in Figure S1, after the array formed on the surface of the solution (Figure S1 A), a glass rod touched it with a tiny force from the above, and the array would be immersed and suspended in the solution (B). Subsequently, it could be reversed easily in the solution by the glass rod. And then the reversed array could be picked up with a glass substrate (C). Finally, the glass substrate covered with nanotube array was immersed into the deionized water slowly and the array would be peeled off and floated on the surface of water. The SnO₂ nanotube array with end toward to the air was obtained. It could be picked up according to the practical applications.

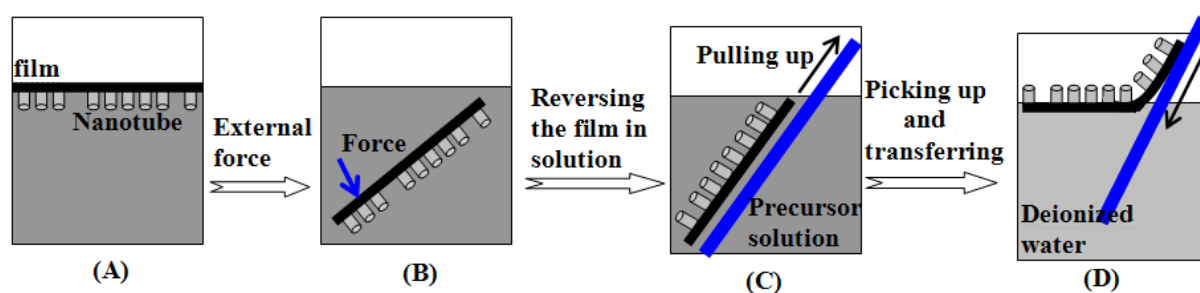


Figure S1 A strategy for reversing the Sn-filled SnO₂ nanotube array. (A) Nanotube array with end towards down floating on the solution. (B) Nanotube array suspending in the solution with a tiny force. (C) Picking

up the reversed array with a glass substrate. (D) Transferring the array with tube end towards the air on the surface of deionized water.

The N₂ adsorption-desorption isotherm (Figure S2) for the obtained array (shown in Figure 1 in the main text) with a hysteresis loop indicates the sample has porous structure and the BET specific surface area for the sample is 28.78m².g⁻¹.

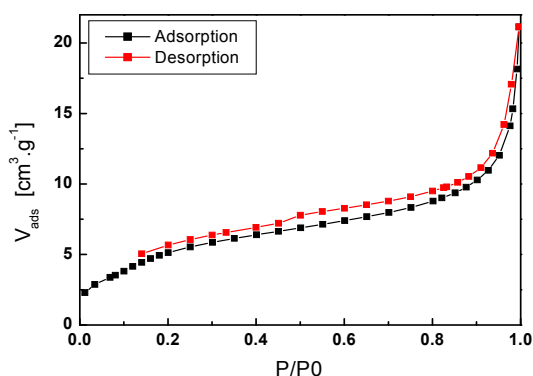


Figure S2 Nitrogen adsorption-desorption isotherm plot for the typical Sn-filled SnO₂ nanotube array

The formation of Sn-filled SnO₂ nanotube arrays was closely related to the ambient atmosphere. When the same precursor solution was put in a sealed quartz test tube filled with N₂, some gray cotton-like aggregates and white particles (SnO₂ from the hydrolysis of Sn⁴⁺) appeared in the solution. The gray aggregates could be separated from the white particles and collected assisted with a nipper in water. The XRD pattern (Fig. S3) showed the admixture were composed of SnO₂ and metallic tin; the gray aggregates were composed of nearly pure metallic tin. This explained, in N₂ atmosphere, when UV light irradiating SnSO₄ solution, the metallic Sn can produced just like reaction (1) in the paper shows. Owing to absence of oxygen, it can't be oxidized to SnO₂ but the Sn⁴⁺ coming from reaction (1) still can hydrolyze to form SnO₂.

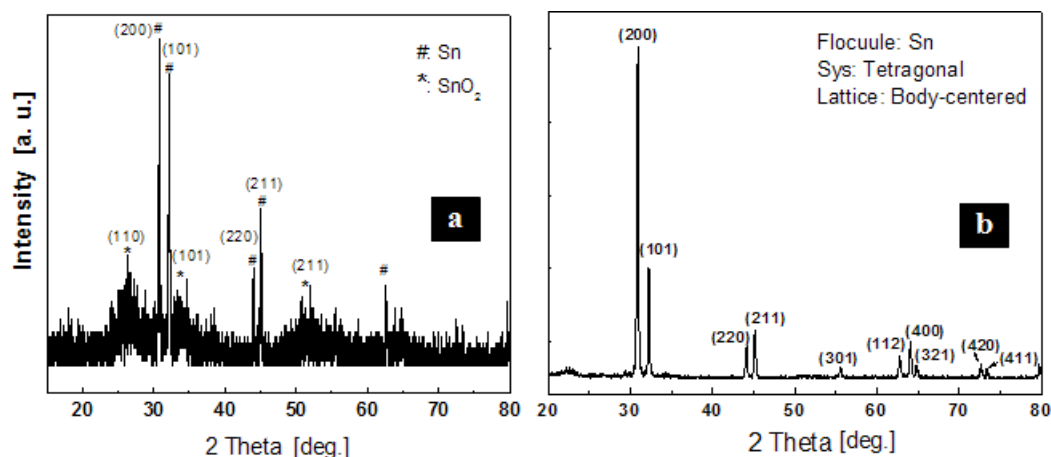


Figure S3. XRD patterns of the obtained sample in N₂ atmosphere after UV light irradiation. (a) mixture of gray aggregates and white particles; (b) gray aggregates.

The air-water interface is the key factor to form Sn-rich SnO₂ nanotube arrays. When put the same precursor solution in the air with continuous agitating under the irradiation of UV light, only amorphous SnO₂ particles could be obtained (see Fig. S4). Because of the agitation, the air-water interface was fluctuant, so that no SnO₂ film substrate could be formed to further induce the formation of nanotubes array. In addition, under the agitation, the oxygen in the air would quickly oxidize the produced metallic tin to form SnO₂.

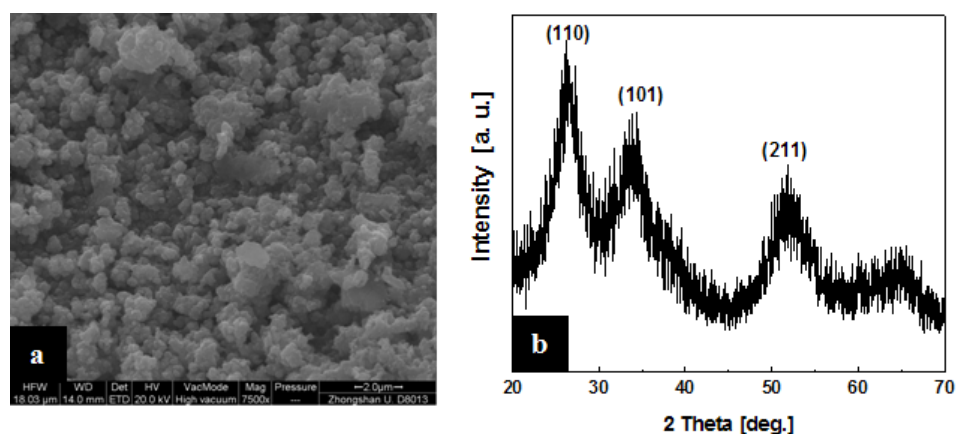


Figure S4. SEM(a) and XRD(b) pattern of the obtained sample in air with continuous agitation after UV light irradiation.

Since the as-prepared metallic Sn was easy to be oxidized, the choice of drying method was important to obtain the Sn-filled SnO₂ nanotubes. When the film as shown in Fig. 1a was dried at 80°C in a surrounding rich in oxygen, a yellowish film would be obtained. SEM image is shown in Fig.S5a. Compared with the sample dried in vacuum (Fig.1c), the array structure is not changed, but Sn peaks in XRD pattern (Fig.S5b) disappear. This indicates drying in vacuum or natural drying at room temperature should be the preferentially considered drying manner.

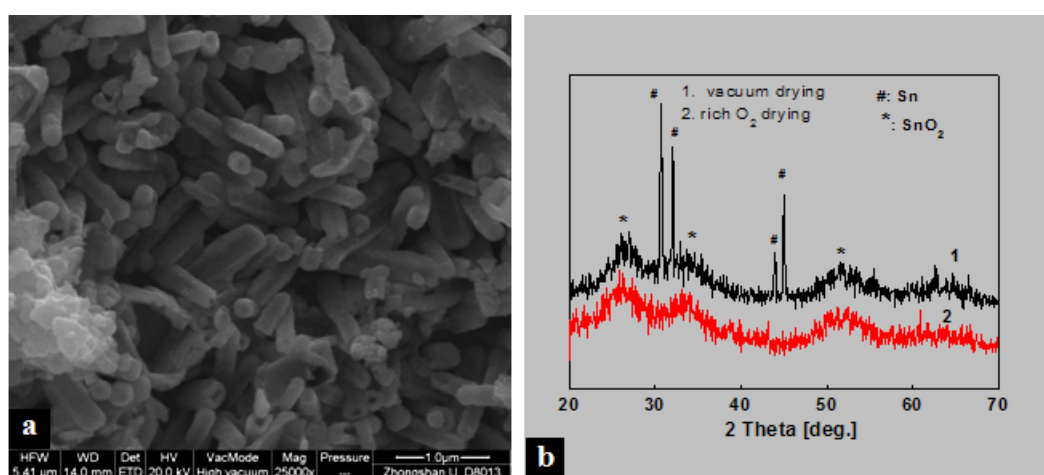


Figure S5 SEM image (a) of SnO₂ array after dried in air at 80 °C and the corresponding XRD pattern (b-2). b-2 shows the XRD pattern of the sample after dried in vacuum.

The formation of Sn-filled SnO₂ nanotube arrays was also related to the concentrations of the precursor solutions. When the precursor solutions with different concentration of SnSO₄ were put under the same UV light source for the same time, products with different morphologies could be obtained. When the concentration of SnSO₄ was kept at 0.0025M, no array and substrate but only some amorphous particles could be formed, because the amount of Sn²⁺ was too low in the precursor to form SnO₂ film substrate (Figure S6a). When the

concentration was increased to 0.005M, the substrate and array could form, however, because Sn resource was not rich, the formed array could not cover the substrate fully and there are still a few incompletely formed nanotubes (Figure S6b). After the concentration of SnSO₄ was increased to 0.01M or higher than 0.01M, perfect nanotube array could always be obtained (Figure S6c, d).

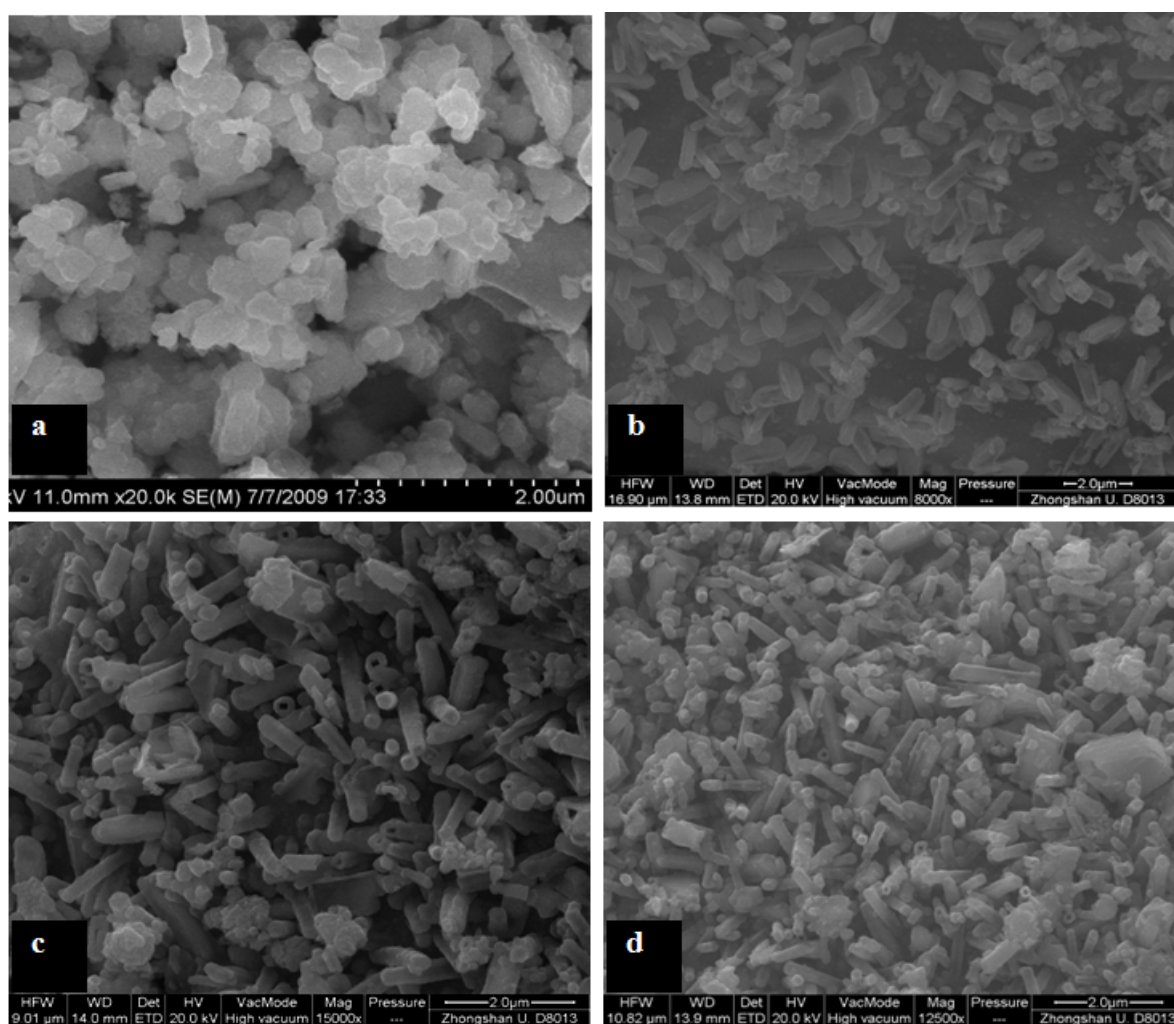


Figure S6 SEM image of samples obtained at different SnSO₄ concentration: (a) 0.0025M, (b) 0.005M, (c) 0.01M, (d) 0.05M

The Sn^{2+} in the precursor solution could absorb UV light, which was essential for the photochemical reactions. As shown in Figure S7, the precursor solution has an evident absorbance band between 350nm and 200nm. The highest absorbance is located at around 250nm and there is nearly no absorbance at higher than 360 nm. Therefore, we chose a UV lamp with wavelength of 254 nm as the light source.

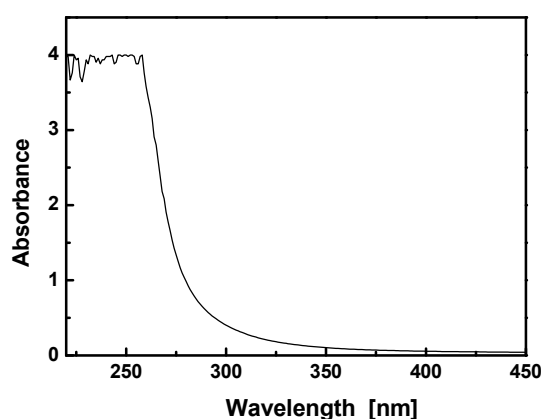


Figure S7 Absorption spectra of the SnSO_4 precursor solution

In our work, we found SLS was very important for the growth of nanotube array. If there was no any surfactant in the precursor solution, as before discussed, only amorphous nanoporous SnO_2 could be obtained. When other but SLS surfactants were employed, different Sn-filled SnO_2 products would be obtained as Figure S8 shows. Obviously, no any nanotube or other regular structures were obtained. According to the molecular structures of the surfactants (f), we found the SLS contained a $-\text{SO}_4$ group. The ability of SLS to form micelle might not be changed in the precursor solution containing H_2SO_4 . The micelle could induce the formation of SnO_2 nanotubes. However, other surfactants couldn't form regular shape micelles because of the influence of their own polarity and structure, and the

H₂SO₄-contained precursor solutions. As a result, no nanotube array could form in the solution.

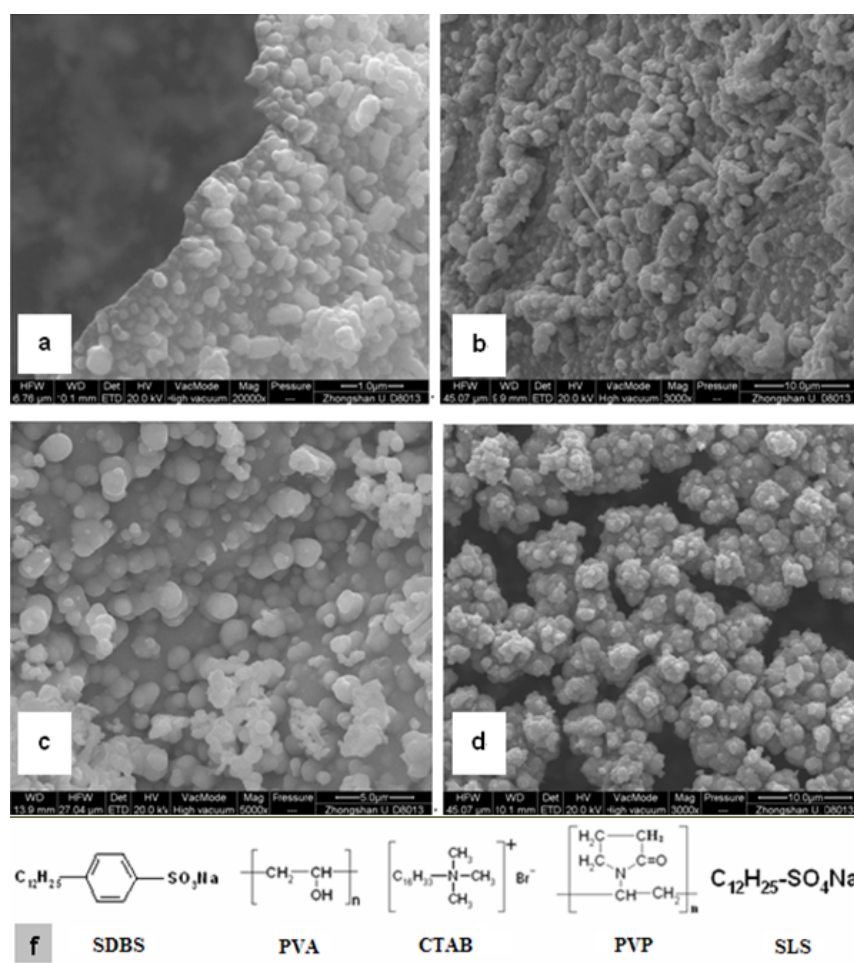


Figure S8 The product with other surfactants (a) SDBS, (b) PVA, (c) CTAB, (d) PVP. And (f) the molecule structure of the different surfactants

The Sn-filled SnO₂ nanotube arrays could be used in photodegradation of various dye pollutants in addition to MO. Figure S9 shows the kinetic of photodegradation of 200 ml 1×10⁻⁴ M RhB, eosin B and MB in 30 minutes under the irradiation of a 300 W high-pressure mercury lamp. Compared with the samples without catalysts, the nanotube arrays obviously enhance the photodegradation rate.

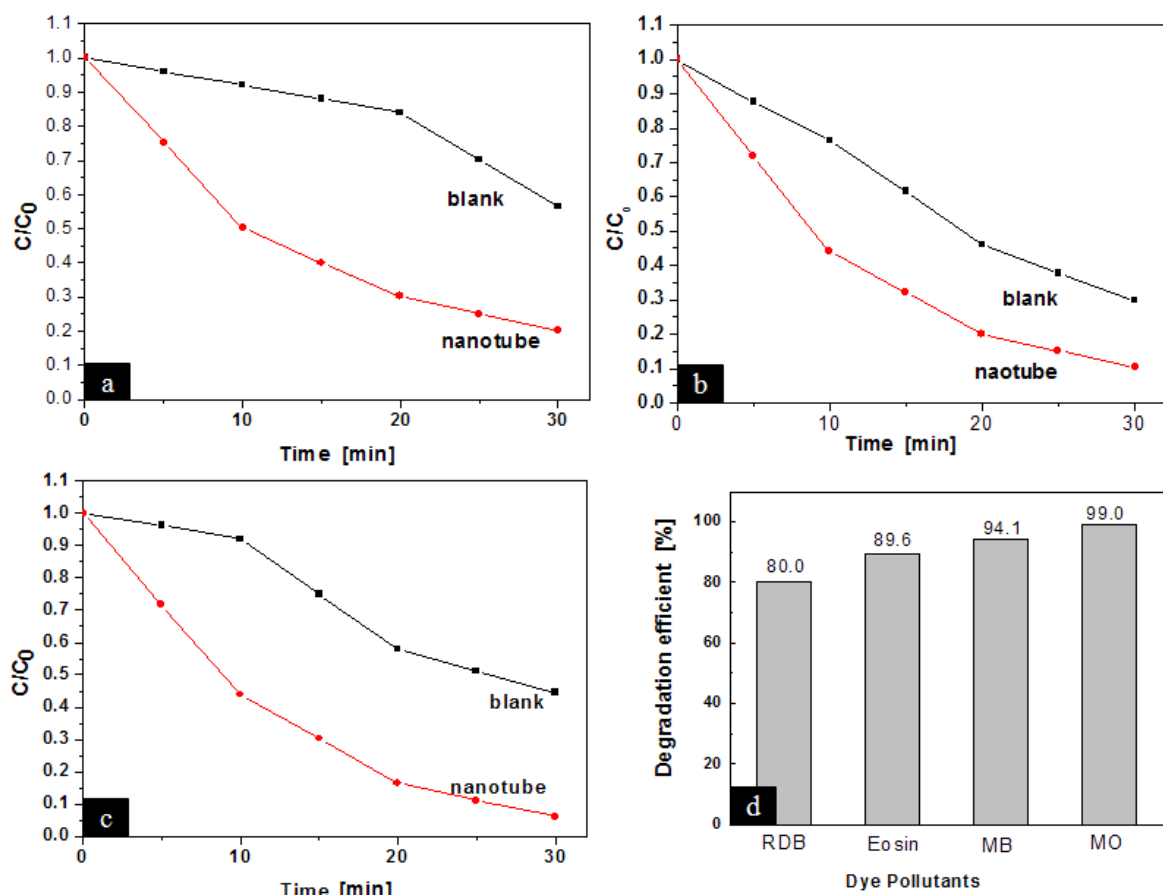


Figure S9 Kinetic of photodegradation of (a) RhB, (b) eosin B and (c) MB in the presence of or without SnO_2 nanotube arrays. And (d) the final degradation rate of all pollutants including MO in 30 minutes.