ChemComm

Chemical Communications

www.rsc.org/chemcomm

Volume 48 | Number 98 | 21 December 2012 | Pages 11909–12024

RSC Publishing

ISSN 1359-7345

COMMUNICATION





1359-7345(2012)48:98;1-M

Cite this: Chem. Commun., 2012, 48, 11939-11941

COMMUNICATION

Inverse opal tungsten trioxide films with mesoporous skeletons: synthesis and photoelectrochemical responses[†]

Jung Kyu Kim,^a Jun Hyuk Moon,^b Tae-Woo Lee^c and Jong Hyeok Park^{*a}

Received 26th September 2012, Accepted 22nd October 2012 DOI: 10.1039/c2cc36984b

Inverse opal structured tungsten trioxide (WO₃) films with mesoporous morphology were prepared using self-assembled polystyrene (PS) colloid as an organic template and by addition of polyethyleneglycol (PEG) to a precursor as an organic surfactant. The photoelectrochemical properties of these films were investigated. By adjusting the tungsten to PEG weight ratio in the precursor, an inverse opaline WO₃ film with a nanoparticular skeleton and increased specific surface area was constructed. The unique morphology of this film led to enhanced photoelectrochemical catalytic responses under UV-Visible 1-sun illumination.

Since Fujishima and Honda described the use of titanium dioxide (TiO₂) photoanodes in water splitting in 1972,¹ metal oxide semiconductor materials with photocatalytic activity have become increasingly sought-after for their pollutant-free properties, non-toxicity, low cost of production, and broad applicability in many fields. Indeed, these materials have putative roles in decomposing organic pollutants,² generating hydrogen energy sources,³ anti-corrosion coating,⁴ and photocatalytic lithography.⁵ Among these materials, TiO₂ has been particularly well-regarded as a photocatalytic material capable of decomposing organic pollutants⁶ and functioning as a hydrogen-based alternative energy source.⁷ However, TiO₂based photocatalytic systems, including photoelectrochemical cells, are limited by their low light absorption ability imparted by a relatively wide band gap energy ($\sim 3.2 \text{ eV}$) which causes utilization of the UV region (i.e., under 380 nm) of solar light.⁸

Therefore, one of the major focuses of the photocatalytic research field has been to achieve greater solar light utilization with a material that has a smaller band gap than TiO₂. Many have reported various low band gap materials, such as tungsten

- ^c Department of Materials Science and Engineering,
- Pohang University of Science and Technology (POSTECH), san 31 Hyoja-dong, Nam-gu, Pohang, Gyungbuk 790-784,

trioxide (WO₃),⁸ cadmium sulfide (CdS)⁹ and iron oxide (Fe₂O₃).¹⁰ Although WO₃ is not the most ideal material in terms of its band gap energy (WO₃: 2.5 eV, CdS: 2.4 eV and Fe₂O₃: 2.2 eV), we nevertheless adapted it to the photoanode in this study because it has outstanding stability under acidic conditions, resistance against photocorrosion in aqueous solutions, and stronger visible light absorption ability than TiO₂.

To improve the photocatalytic ability of metal oxides, many researchers have focused on synthesizing nanostructures of materials to increase active reaction sites between the photocatalyst and the substrate medium.¹¹ In recent years, various nanostructured metal oxides have been synthesized to increase both hydrogen generation by water splitting and photo degradation of organic dyes or pollutants.⁷ In particular, studies on fabricating three-dimensionally ordered inverse opal WO₃ films with a sub-micrometer range of pore size have attracted much attention, as these films may have a role as electrochemical devices due to their high specific surface area.¹² Furthermore, Chen et al.¹² found that the light absorption properties of these films can be altered by adjusting the macropore size of the three-dimensionally ordered macroporous tungsten oxide structure. Unfortunately, in spite of the large specific surface area and enhanced light absorption performance of the inverse opal structured films, the solarto-hydrogen conversion efficiency of the inverse opal structured films is lower than that of the assembled nanoparticulate films.¹³ As Kwak et al. reported, this is presumably because the amount of metal oxide incorporated in the inverse opal structure is only about one third of the amount of it in the assembled nanoparticle structure.

In this study, polyethylene glycol (PEG) 300 was used as an organic additive in fabricating mesoporous inverse opal WO_3 film to overcome the aforementioned drawbacks of the inverse opal structure. We created an inverse opal structured film with a mesoporous skeleton composed of WO_3 nanoparticles using the sol–gel reaction method, with tungsten acid precursors containing PEG as a structure-determining template. We then filled the precursors into the PS colloid templates, as shown in Fig. 1. By controlling the weight ratio of tungsten to PEG in the precursor solution, we observed higher photocurrent density in PEC, as well as enhanced photodecomposition efficiency.

Fig. 1 shows the process of fabricating the inverse opal structured mesoporous WO_3 films on the TCO substrate. These inverse opal films were obtained using a simple spin

^a SKKU Advanced Institute of Nano technology (SAINT) and School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea. E-mail: lutts@skku.edu; Fax: +82-31-290-7272; Tel: +82-31-290-7346

^b Department of Chemical and Biomolecular Engineering, Sogang University, 1 Shinsu-dong, Mapo-gu, Seoul 121-742, Republic of Korea

Republic of Korea

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc36984b



Fig. 1 Schematic of (a) self-assembled polystyrene colloid film on FTO glass, (b) spin cast tungstic acid precursor solution on colloid film, (c) WO₃ inverse opal structures from organic additive-free tungstic acid precursor solution, and (d) mesoporous WO₃ inverse opal structures from tungstic acid precursor solution with organic additives.

coating method. Twenty microliters of precursor solution was dropped on the PS colloid template, deposited on the FTO glass (dimensions: 1.5 cm \times 1.5 cm), and infiltrated by a spin coater for 30 s at 1500 rpm. Then, as-deposited films were annealed at 550 °C for 30 min to remove the PS colloidal template and to construct solid wall skeletons having three-dimensionally packed spherical porous voids. The samples used in this study were prepared using the following tungsten : PEG 300 weight ratios: 1 : 0, 1 : 10 and 1 : 30. Nanoparticulated mesoporous WO₃ film without an inverse opal structure, as well as bare WO₃ film, was also fabricated using precursor solution containing PEG 300 (W : PEG = 1 : 30) and without PEG, respectively.

It is well known that the morphology of tungsten oxide film is highly influenced by the addition of an organic additive or stabilizer.³ When a tungstate precursor solution without PEG was infiltrated into a PS colloidal template with a diameter of 1 μ m, a conventional inverse opal WO₃ film with smooth surface morphology was obtained (Fig. 1c). Fig. 2a and b show the morphologies of the conventional bare type inverse opal WO₃ films with their three dimensionally ordered



Fig. 2 SEM images of spin-casted WO₃ inverse opal structures from tungstic acid precursor solution. The ratios of W : PEG 300 used were 1 : 0 (a and b), 1 : 10 (c and d), and 1 : 30 (e and f) on PS colloid deposited FTO glass.

macroporous structure.¹⁴ In contrast, mesoporous inverse opal WO₃ films were obtained when the precursor solution contained PEG 300, as shown in Fig. 1d. The organic additive played an important role in determining the morphology of the skeleton in the inverse opal structure. Fig. 2c-f show the morphologies of the inverse opal structure fabricated from solutions prepared by mixing PEG in pure tungstic acid solution with tungsten to PEG weight ratios of 1:10 and 1: 30, respectively. In Fig. 2a and b, the skeleton of the inverse opal structure prepared from the PEG free precursor had a flat morphology in the skeleton, which was not porous. Similarly, the inverse opal film prepared from the solution with a 1:10 W : PEG weight ratio had a flat film structure; however, there were many narrow cracks on its surface with a grain size of approximately 100 nm. When the amount of PEG was increased further to a 1:30 W: PEG weight ratio, an inverse opal structured WO₃ film with a nanoporous skeleton was observed. Fig. 2e and f show that the inverse opal skeleton consisted of assembled sphere-like nanoparticles and that this film had mesoporous structure. The diameter of the nanoparticles was less than 50 nm. From these SEM images, one may conjecture that adjusting the combination of the organic additive PEG 300 and self-assembled PS colloid is a means of controlling not only the macro-pore, but also the meso-pore inside the WO₃ films. However, the WO₃ films prepared from precursor solutions of varying W: PEG weight ratios had similar thicknesses of around 2.0 µm.

Fig. 3 shows the photoelectrochemical response of the inverse opal WO₃ film prepared using a PEG-free precursor and inverse opal mesoporous WO₃ film (W : PEG 300 = 1 : 30 wt%). The nanoparticulate mesoporous WO₃ film was prepared using the sol-gel method with the PEG 300-containing precursor, but without the PS template, and bare WO₃ film was also prepared by the PEG free precursor. The thickness of the bare film was controlled to around 2.0 μ m, similar to that of the inverse opal films. The photocurrent density of the inverse opal film (curve B in Fig. 3) was much lower than that of both the mesoporous film (curve F in Fig. 3) and the bare film (inset curve in Fig. 3). The addition of a mesoporous frame increased the photocurrent density from



Fig. 3 Dark current density and photocurrent density of (a) and (b) inverse opal WO₃ film, (c) and (d) inverse opal WO₃ film with a mesoporous skeleton (W : PEG 300 = 1 : 30) and (e) and (f) nanoparticulate mesoporous WO₃ film under 100 mW cm⁻² illumination. The inset data show dark current density and photocurrent density of bare WO₃ film prepared by a PEG free precursor. SEM images show morphology of mesoporous inverse opal WO₃ film (W : PEG 300 = 1 : 30), mesoporous nanoparticulate WO₃ film and bare WO₃ film prepared by a PEG-free precursor from top to bottom, respectively.



Fig. 4 (a) The photoresponse characteristic (photocurrent density–time curve) of inverse opal mesoporous WO₃ film (W : PEG 300 = 1 : 30) under 100 mW cm⁻² illumination. (b) Change in concentration, C/C_0 , at 525 nm as a function of the irradiation time during inverse opal WO₃ (PEG free) and mesoporous inverse opal WO₃ (W : PEG = 1 : 30) photocatalysis of rhodamine B in aqueous solution.

about 0.2 mA cm⁻² (curve B in Fig. 3) to about 0.95 mA cm⁻² (curve D in Fig. 3) at 1 V. Most inverse opal structured films have been reported as having worse performance than the assembled nanoparticulate films.¹³ However, this mesoporous inverse opal structured film (curve D in Fig. 3) was superior to the nanoparticulate films (curve F in Fig. 3) in photocurrent value. This is because the mesoporous inverse opal structured WO₃ film can outstandingly enlarge the tungsten oxide and electrolyte contact area due to the film's unique morphology. However, the photocurrent density values of inverse opal films were not saturated, even at a high bias potential. Presumably, this is due to increased electrical resistance, resulting from loosely bound WO₃ particles on the FTO substrate and an increased number of grain boundaries which originate from the mesoporous inverse opal structure. Moreover, due to the conspicuously enhanced surface area of mesoporous inverse opal structure, the dark current density of mesoporous film (curve C in Fig. 3) was extraordinarily high compared to the dark current density of the other films because of the formation of an electric double layer on it.¹⁵ Under chopping AM 1.5G light, the mesoporous inverse opal WO₃ film showed strong responses to the light. Photocurrent density decreased slightly for the first ten seconds, though it remained constant under illumination thereafter (Fig. 4).

In order to confirm the improved photocatalytic ability of the mesoporous inverse opal structure, we performed organic dye decomposition experiments by monitoring the change in optical absorption of Rh B solution under visible light irradiation (Fig. 4).¹⁶ The photo-decomposition reaction was carried out in 20 ml of 2×10^{-3} mM rhodamine B (Rh B) aqueous solution using the three electrode system described previously, with samples (working electrode), Pt (counter electrode) and Ag/AgCl (reference electrode), at 0.8 V of applied bias and 100 mW cm⁻² of light irradiance from a xenon lamp based solar simulator. The photocatalytic degradation was measured as the time-dependent absorption changes in 550 nm UV spectra with a UV-2401 PC, Shimadzu (UV/visible spectrophotometer). The concentration changes were estimated using a calibration equation with absorbance data measured from a UV/visible spectrophotometer. Degradation of Rh B was enhanced in the presence of the mesoporous inverse opal film as compared to the bare inverse opal film. This

photo-degradation reaction was considered to be first-order, and the rate constants of photocatalytic decomposition were calculated using the following equation: $C/C_0 = \exp(-kt)$ in which k is the apparent rate constant, t is the irradiation time, C is the final concentration and C_0 is initial concentration of Rh B solution. Using this equation, the rate constant k of the mesoporous inverse opal film was calculated to be $1.75 \times 10^{-3} \text{ min}^{-1}$, much larger than the $8.72 \times 10^{-4} \text{ min}^{-1}$ of the bare inverse opal film.

Inverse opal structured tungsten trioxide films with mesoporous skeletons were successfully fabricated using a novel process that involved both a PS colloidal sacrificial template and polyethylene glycol 300 as a structure-determining agent and organic stabilizer. Investigation of their photoelectrochemical characteristics revealed the films' photocurrentpotential responses, indicative of water splitting efficiency, and demonstrated that the mesoporous morphology of inverse opal WO₃ films played a critical role in their photocatalytic activity. The photodegradative abilities on rhodamine B also support this idea and demonstrate the benefits of altering the surface of inverse opal WO₃ films. We believe that this unique approach can be used to maximize the photocatalytic ability of metal oxides.

This work was supported by NRF grants funded by the Korea Ministry of Education, Science and Technology (MEST) (2011-0030254, NRF-2009-C1AAA001-2009-0094157), the NCRC program (2011-0006268) and Future-based Technology Development program (2010-0029321).

Notes and references

- 1 A. Fujishima and K. Honda, Nature, 1971, 238, 37.
- C. A. Martinez-Huitle and E. Brillas, *Appl. Catal.*, *B*, 2009, **87**, 105;
 X. B. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891.
- 3 J. K. Kim, K. Shin, S. M. Cho, T. W. Lee and J. H. Park, *Energy Environ. Sci.*, 2011, **4**, 1468.
- 4 Y.-S. Jung, K.-H. Kim, T.-Y. Jang, Y. Tak and S.-H. Baeck, Curr. Appl. Phys., 2011, 11, 358.
- 5 N. An, H. Liu, Y. Ding, B. Lu and M. Zhang, *Appl. Surf. Sci.*, 2012, **256**, 5052; W. Kubo, T. Tatsuma, A. Fujishima and H. Kobayashi, *J. Phys. Chem. B*, 2004, **108**, 3005.
- 6 C. Sahoo, A. K. Gupta and A. Pal, Dyes Pigm., 2005, 66, 189.
- 7 J. H. Park, S. Kim and A. J. Bard, *Nano Lett.*, 2006, 6, 24; I. Cesar, A. Kay, J. A. G. Martinez and M. Gratzel, *J. Am. Chem. Soc.*, 2006, 128, 4582.
- 8 K. Zhang, X. J. Shi, J. K. Kim and J. H. Park, *Phys. Chem. Chem. Phys.*, 2012, 14, 11119.
- 9 K. Shin, S. Seok, S. H. Im and J. H. Park, *Chem. Commun.*, 2010, 46, 2385.
- 10 A. Mao, J. K. Kim, K. Shin, D. H. Wang, P. J. Yoo, G. Y. Han and J. H. Park, J. Power Sources, 2012, 210, 32.
- 11 G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 2005, **5**, 191; E. Y. Kim, J. H. Park and G. Y. Han, *J. Power Sources*, 2008, **184**, 284.
- 12 K. A. Arpin, M. D. Losego and P. V. Braun, *Chem. Mater.*, 2011, 23, 4783; X. Chen, J. Ye, S. Ouyang, T. Kako, Z. Li and Z. Zou, *ACS Nano*, 2011, 5, 4310.
- 13 E. S. Kwak, W. Lee, N.-G. Park, J. Kim and H. Lee, Adv. Funct. Mater., 2009, 19, 1093.
- 14 A. Stein, F. Li and N. R. Denny, Chem. Mater., 2008, 20, 64.
- 15 S. Yoon, E. Kang, J. K. Kim, C. W. Lee and J. Lee, *Chem. Commun.*, 2011, 47, 1021.
- 16 Z. Xiong, L. L. Zhang, J. Ma and X. S. Zhao, Chem. Commun., 2010, 46, 6099.