Electronic Supplementary Information

A Novel Planarization Method Based on Photoinduced Confined Chemical Etching

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1. Experimental Section

Materials, reagents and apparatus

Reagents: hexamethylenetetramine ($C_6H_{12}N_4$; AR), zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$; AR), glycine (gly; AR), boric acid (H_3BO_3), ethyl alcohol absolute and acetone were purchased from China National Pharmaceutical Group Corporation. Ammonium hexa-fluorotitanate (99.99%) was obtained from sigma-Aldrich Co. LLC. All reagents were used without further purification. All solutions were prepared with Milli-Q-purified water (resistivity was 18.2 M Ω cm).

Materials: Fluorine-doped tin oxide (FTO) conducting glass was purchased from LOF glass company (USA). Cu has a purity of 99.9% from Beijing CUI BO LIN Technique Development Center.

Apparatus: Model 173 Potentiostat (EG&G) was used to carry out the electrochemical preparations. The fluorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. The incident light was obtained from a 500W Xenon lamp (Beijing 7-Star Optical Instruments Co.). SEM images were obtained on a Hitachi S-4800 SEM system operating at 15 kV. Energy dispersive X-ray spectroscopy (EDS) measurements were performed with the spectrometer attached on the S-4800 SEM. The crystal structure was characterized by Panalytical X'pert X-ray diffraction system. The Cu surface was characterized with an atomic force microscope (AFM) (NANOSCOPE IIIa, DJ Co.). The X-ray photoelectron spectroscopy (XPS)

experiments were performed on PHI 2000 model spectrometer equipped with an Al K α monochromator X-ray source. The binding energy was referenced to the C1s level (284.5eV) due to surface contaminants.

Pre-treatment of FTO and the Cu foil

Pre-treatment of FTO: FTO was sonicated in acetone, ethanol and deionized water for several times, while each time takes 10-20min, followed by drying under a N₂ stream.

Pre-treatment of the Cu foil: The Cu foil was lapped with 1500# WA sand-paper, then it was polished successively with alumina powder of 1µm, 0.3µm and 0.05µm diameter, followed by rinsing successively with deionized water and acetone in an ultrasonic bath for several minutes, and finally rinsed with deionized water prior to use.

TiO₂ nanotube arrays prepared by the method of ZnO template

At present, TiO_2 is not the only choice for this photocatalytic oxidation process. However, it is the best choice because of its high photocatalytic activity and chemical stability. TiO_2 is well known as a useful, non-toxic, environmentally friendly, corrosion-resistant and cheap material. TiO_2 nanotube arrays that formed optically transparent films on FTO substrates can be prepared using various methods including the template-assisted approach, hydro/solvothermal methods, and electrochemical anodization. ZnO has been explored as a possible alternative to TiO_2 in dye-sensitized solar cells, and we have also used it. However, ZnO is inferior to TiO_2 in this photocatalytic oxidation process because of its lower chemical and photo-stability in etchant solutions than TiO_2 .¹

ZnO nanorods were galvanostatically deposited on $1 \text{cm} \times 1 \text{cm}$ FTO substrates at 90°C^2 . An aqueous solution of 5 mM zinc nitrate hydrate $(Zn(NO_3)_2 \cdot 6H_2O)$ and equimolar hexamethylenetetramine $(C_6H_{12}N_4)$ was used as electrolytes. The current during deposition was 0.25 mA cm⁻². After a growth time of 50 min, the sample was removed from the solution and immediately rinsed in flowing deionized water to remove any residual salt from the surface. Finally well-crystallized hexagonal ZnO can be obtained.

Preparation of TiO₂ nanotube arrays³: when preparing the TiO₂ photoelectrode, the structure of nanotube was adopted due to its high electron mobility, specific surface area, regularity at the top of tubes and mechanical strength. TiO₂ nanotube arrays were obtained by liquid-phase deposition of the TiO₂ on FTO substrates using ZnO nanorods as a template. The TiO₂ NT arrays were obtained by the immersion of substrates into a solution containing 0.05 M C₆H₁₂N₄ and 0.15 M H₃BO₃ for 4h. The TiO₂ nanotube arrays annealed at 450 °C for 2h and a crystalline anatase phase could be obtained.

Configuration of the photoinduced confined chemical etching system and experimental procedures

The photoinduced reaction cell and Poly(tetrafluoroethylene) (PTFE) holder with a thickness of 2.2mm were designed. One of the PTFE holders with a 8×8 mm square hole allowed the light to pass through. TiO₂ nanotube arrays, PTFE spacer and Cu foil were fixed with screws between two pieces of PTFE holder, as shown in Fig.S1. The fixed device was immersed in the cell with quartz glass. The white light illumination of 1.58W cm⁻² was obtained from a Xenon lamp of 500W.



Fig. S1 Configuration of the photoinduced confined chemical etching system.

2. Detection of •OH using the fluorescence technique

The free •OH is quantitatively and selectively determined by the fluorescence probe technique,⁴ and the photogenerated O_2^- , HO_2^+ and H_2O_2 did not interfere. The selected fluorescence probe, terephthalic acid (TA), reacts with •OH and generates 2-hydroxyterephthalic acid (TAOH), the reaction rate constant is about 3.3×10^9 L mol⁻¹ s⁻¹⁵. The reaction equation of •OH with TA is as follows:



In the fluorescent experiment, the measurements of the amount of •OH were performed as follows. The sample cell containing 0.01 M NaOH and 1 mM TA with or without 1wt% glycine was placed under the white light illumination (1.58W•cm⁻²) for 15min. After the irradiation, the fluorescence spectra of the solution were measured on a Hitachi F-7000 fluorescence spectrophotometer with 312nm excitation. The fluorescence intensity at 424nm, which is the characteristic peak of TAOH, indirectly reflected the amount of •OH. According to the result of the fluorescence spectra in Fig.3, after the glycine was added to the solution of TA, the fluorescence intensity at 424nm declined sharply. This indicates that glycine can capture the etchant •OH and then confine the diffusion of the •OH.

3. SEM and EDS of the pre-treated Cu surface

As shown in Fig. S3a of SEM image of the pre-treated Cu surface, scratches, cracks and small particles, which has been introduced during the lapping process, can be observed all over the surface. The weak signals of Al, O and C, which appear in the EDS analysis (Fig. S3b), are mainly due to the Al₂O₃ polishing powder and other impurities.



Fig. S3 SEM (a) and EDS (b) images of the pre-treated Cu surface

4. Effect of the glycine on the etching of the Cu surface

The effect of the glycine on the etching was investigated by SEM. As seen in Fig. S4a, there were a large number of pits on the unobstructed parts of the Cu surfaces after etching in the solution with glycine. While in the solution without glycine, there were no significant differences compared with the Cu surfaces before etching (Fig. S4c). This can be explained by the fact that Cu can simultaneously react with glycine and form the soluble complex during the oxidation by •OH, resulting in the dissolution of Cu from the surface;⁶ While in the solution without glycine, the oxide layer will be formed on the Cu surface soon after being oxidized by •OH, preventing the Cu surface from the further etching. It indicated that glycine can play the role of the complexing agent well to avoid the formation of the oxide layer on the Cu surface and influence the etching process.

The obstructed parts of the Cu surfaces are difficult to etch by the photoinduced •OH because of the physical barrier of the PTFE spacer. The obstructed Cu surface after etching in the solution with glycine almost remained unchanged, as shown in Fig. S4b. However, as shown in Fig. S4d, the obstructed Cu surface in the solution without glycine changed a lot after etching, which is due to the autoxidation of Cu by the dissolved oxygen.⁷ The possible reason is that the glycine on the Cu surfaces can suppress the autoxidation of Cu to a certain extent. But this kind of suppression would not obstruct the oxidation and etching of Cu by •OH. Herein, another advantage to introduce the glycine is the protection of the Cu surface from the autoxidation, especially on the parts of Cu that do not be immersed in the confined etchant layer.



Fig. S4 SEM images of the Cu surfaces after etching for 4h in solutions (a, b) with and (c, d) without 1wt% gly, a,c: obstructed region; b,d: unobstructed region. The thickness of PTFE spacer was 35 μm.

5. SEM of the Cu surface after etching using spacers of different thickness

As shown in Fig. S5, there were considerable morphology changes of the Cu surface after etching with the PTFE spacer of the thickness of 35 μ m and plenty of pits were observed. While there was no observed morphology change of the Cu surface after etching with the 100 μ m spacer. It can be inferred that the distance of 100 μ m meets or exceeds the thickness of the effective confined etchant layer.



Fig. S5 SEM images of the Cu surface after etching using PTFE spacers with the thickness of(a) 35 μm and (b) 100 μm in1 wt% glycine solution for 4 h.

6. Effect of the etching time



Fig. S6 SEM images of the Cu surface after etching for (a) 4 h and (b) 8 h using PTFE spacers with the thickness of 35 μ m in1 wt% glycine solution.

We did conduct experiments comparing different etching times of 1 h, 2 h, 4 h and 8 h. Compared with etching times of 1h or 2 h, the Cu surface was smoother after etching for 4 h. When the etching time was extended to 8 h, however, uniform nanocubes with sides of about 80 nm were observed all over the surface (see Fig. S6). This surface morphology reconstruction may be caused by the *in situ* deposition of Cu.⁸ Hence, 4 h was selected as a suitable etching time for our experiments.

7. A brief comparison of the running cost

The running cost is one of the factors determining the likelihood of our proposed method being adopted in commercial production. Although this manuscript mainly focused on proposing the concept and investigating the feasibility of photoinduced confined chemical planarization, we also considered the running cost of this method. The running costs of our method and CMP are compared below.

The set-up of CMP is expensive, as are the consumption of slurries and polishing pad.

- ✓ The major components of slurries include oxidizer, abrasive, inhibitor, surfactant, chelating agent and polyelectrolytes.
- ✓ Most commonly used oxidizers are H₂O₂, K₂S₂O₈, NH₄OH and Fe(NO₃)₃ with strong acidity or alkalinity. They cause the apparatus to corrode and increase running cost.
- \checkmark The cost of abrasive is also high.

In our system, no abrasives or polishing pad are needed. Because no oxidizers are added and the oxidizer (•OH) is generated *in situ* and is confined to a thin layer on the surface of the tool, corrosion of the apparatus is minimized, which should reduce running cost. In our present set-up, the consumption of light source and glycine are the main running costs.

- ✓ TiO₂ has good chemical stability and reusability, so it is barely consumed. Synthesis of TiO₂ nanotube arrays is achieved by a simple and cheap route. Hence, the running cost of TiO₂ is low.
- ✓ Glycine is a common, cheap chemical that is widely used in industrial applications; *e.g.*, as a complexing agent in CMP.
- ✓ At present, one of the main running costs was the high-power xenon lamp. In future experiments with a precise approaching device, there will be no need to maintain such a relatively thick CEL. Hence, the light power and energy consumption can be decreased considerably. Another way to reduce energy consumption is to modify TiO₂ to increase visible light harvest and improve light use.

Overall, the running cost of our method is thought to be much lower than that of CMP.

References

- 1. Q. Zhang, C. S. Dandeneau, X. Zhou and G. Cao, Advanced Materials, 2009, 21, 4087-4108.
- Q. Zhang, H. Guo, Z. Feng, L. Lin, J. Zhou and Z. Lin, *Electrochim. Acta*, 2010, 55, 4889-4894.
- 3. J.-H. Lee, I.-C. Leu, M.-C. Hsu, Y.-W. Chung and M.-H. Hon, *The Journal of Physical Chemistry B*, 2005, **109**, 13056-13059.
- 4. T. Hirakawa, K. Yawata and Y. Nosaka, *Applied Catalysis A: General*, 2007, **325**, 105-111.
- 5. M. Anbar, D. Meyerstein and P. Neta, *The Journal of Physical Chemistry*, 1966, **70**, 2660-2662.
- 6. S. Aksu and F. M. Doyle, J. Electrochem. Soc., 2002, 149, G352-G361.
- J. Iijima, J. W. Lim, S. H. Hong, S. Suzuki, K. Mimura and M. Isshiki, *Appl. Surf. Sci.*, 2006, 253, 2825-2829.
- 8. O. Kirino and T. Enomoto, *Precision Engineering*, 2011, **35**, 669-676.