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Supporting Information

Surfactant-assisted photochemical deposition of three-dimensional nanoporous nickel oxyhydroxide films and their energy storage and conversion properties

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Experimental details

Preparation of TiO₂ films

TiO₂ films were synthesized by a hydrothermal method.¹ A mixture of 7.5 mL hydrochloric acid (37 wt%) and 7.5 mL saturated NaCl solution was stirred at ambient conditions for 5 min in a Teflon-lined stainless steel autoclave (30 ml volume), and 0.15 mL tetrabutyl titanate was added into the mixture and stirred for another 5 min. The fluorine-doped tin oxide (FTO) substrate (F: SnO₂, TCO-15, 5 Ω cm⁻², NSG group), was ultrasonically cleaned for 30 min in isopropanol and for another 30 min in the mixture of ammonia and hydrogen peroxide (1:1 in v:v), then washed by deionized water and dried under a mild N₂ flow. Then one piece of cleaned FTO (1cm×3cm) was placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 150 °C for 15 h in an electric oven. After synthesis, the autoclave was naturally cooled down to room temperature. The FTO substrate was taken out and washed with deionized water. After dried under mild N₂ flow, the FTO substrate was annealed at 450 °C for 30 min in a Muffle furnace. The TiO₂/FTO electrode was obtained by the above procedure.

Measurement of surface tensions

A bubble pressure tensiometer BP (Kruss, Germany) based on the principle of maximum bubble pressure was used to test the surface tensions of the photodeposition solutions consisting of 0.13 M sodium acetate, 0.13 M nickelous sulfate, 0.1 M sodium sulfate and various contents (0 ~ 1.5 wt%) of the surfactant (sodium lauryl sulfate, SDS). At minimum bubble radius the gas pressure necessary to create the bubble is maximum and can be related to surface tension using the Young-Laplace equation.²

The dependence of surface tension on SDS concentration for the photodeposition solutions at 40 °C is illustrated in Fig. S1. The surface tension sharply decreases with increasing SDS concentration in the range of 0 ~ 0.3 wt%, and henceforth tends to level off with further increase of SDS concentration.

Spectrophotometric measurements of formaldehyde concentrations

In the presence of excessive ammonium acetate, formaldehyde can react with acetylacetone to form 3,5-diacetyl-1,4-dihydropyridine complex, which is yellow in color.³ The color becomes deeper as the concentration of formaldehyde increases, so the concentration of formaldehyde can be determined by measuring the absorbance of the complexes.

The absorption spectra in the wavelength range of 350–600 nm were measured with a Perkin Elmer Lambda-15 UV–VIS spectrophotometer. All chemicals from commercial sources were of analytical reagent grade, and were used as received. Deionized water was used for preparation of the solutions.

A $\sim 4.0 \mu\text{g mL}^{-1}$ standard stock solution of formaldehyde was prepared by diluting formaldehyde solution (36–38%) with deionized water, followed by an accurate concentration determination using the iodometric method.⁴ The detection reagent solution was prepared by adding 25 g ammonium acetate, 3 mL glacial acetic acid and 0.4 mL acetylacetone into 100 mL deionized water. A series of model solutions were prepared to obtain a calibration graph. Each of them contained 2 mL of the detection reagent solution and a certain volume of the standard stock solution of formaldehyde (0.1–2.5 mL), and its total volume was diluted to 10 mL with deionized water. The calibration graph was obtained by measuring the absorption spectra of the model

solutions, as shown in Fig. S3.

Formaldehyde in the sampled gas (5 mL) was absorbed in 10 mL deionized water. 2 mL of the formaldehyde solution and 2 mL of the detection reagent solution was mixed, and the obtained solution was diluted to 10 mL. The concentration of formaldehyde in the gas can be calculated according to the measured absorbance and the calibration graph.

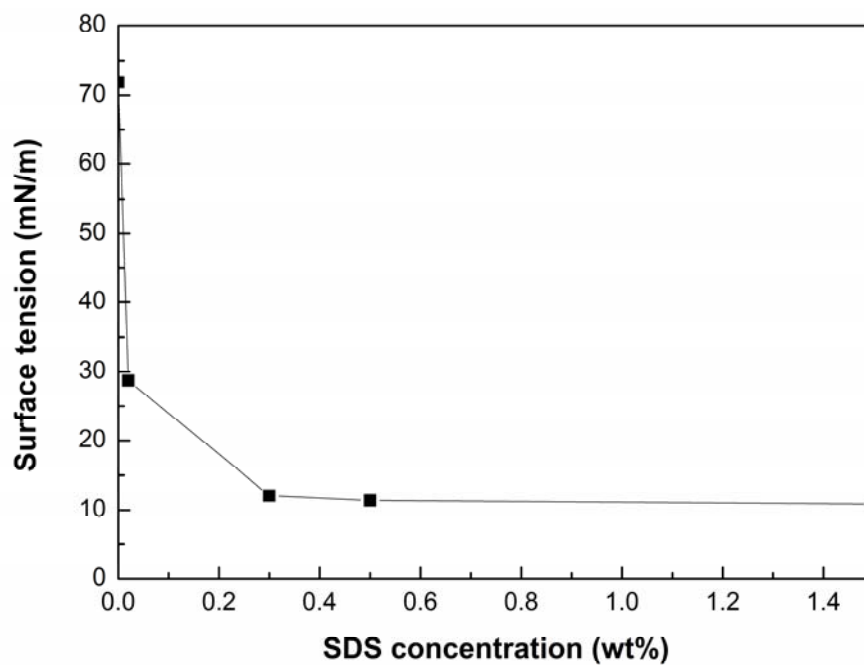


Fig. S1 Dependence of surface tension on SDS concentration for the photodeposition solutions at 40 °C.

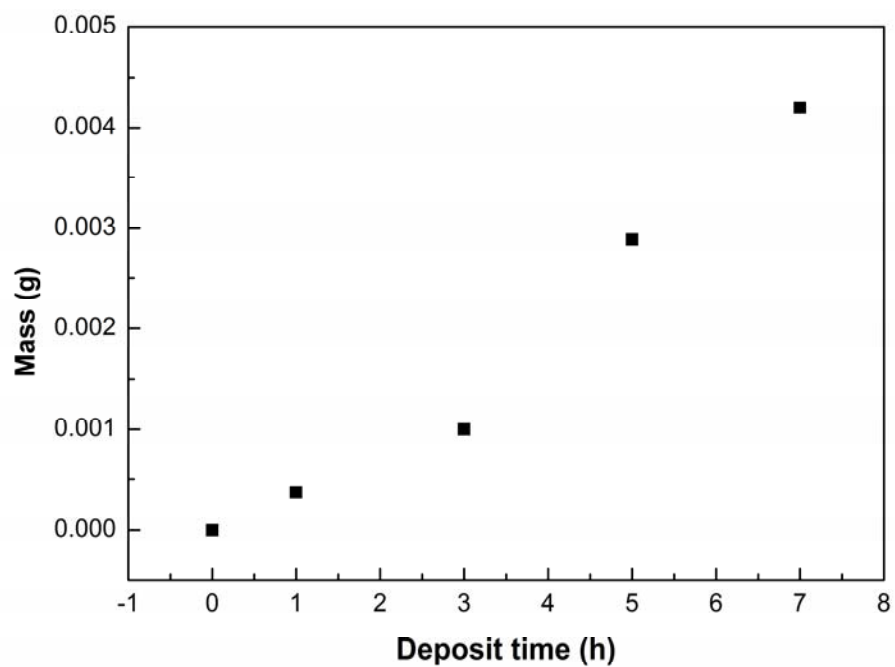


Fig. S2 Dependence of NiOOH mass on photodeposition time. The photodeposition of NiOOH on the TiO₂ nanoarray substrate was conducted in the solution with 0.3 wt% SDS at 40 °C.

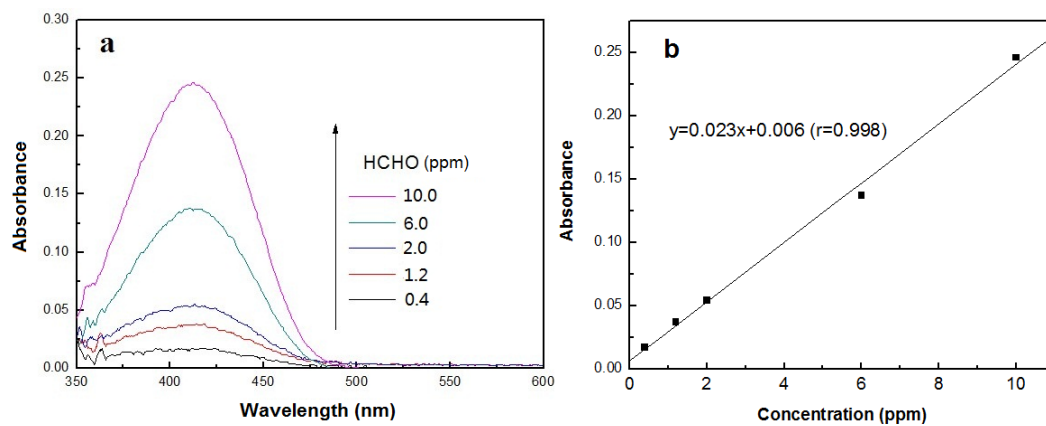


Fig. S3 (a) The absorption spectra of the model solutions prepared by mixing various amounts of standard formaldehyde solution with a certain volume of the detection reagent solution. (b) The calibration graph of concentrations of formaldehyde vs. absorbances at 412 nm.

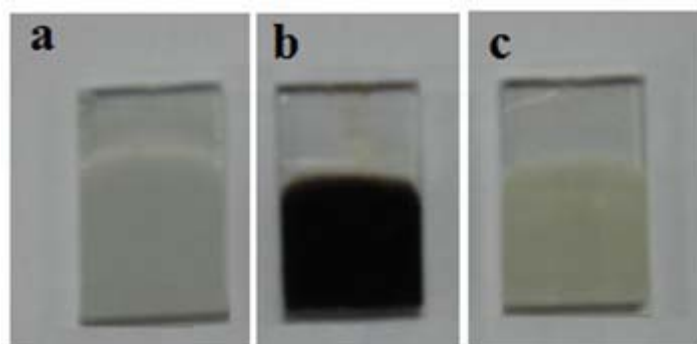


Fig. S4 Photographs of the TiO_2 nanorod array (a) and the photodeposited NiOOH composite films before (b) and after (c) degradation of formaldehyde.

References

1. B. Liu and E. S. Aydil, *J. Am. Chem. Soc.*, 2009, **131**, 3985.
2. S. H. Hsu, W. H. Lee, Y. M. Yang, C. H. Chang and J. R. Maa, *Ind. Eng. Chem. Res.*, 2000, **39**, 1473.
3. P. Sritharathikhum, M. Oshima and S. Motomizu, *Talanta*, 2005, **67**, 1014.
4. Q. Li, P. Sritharathikhum, M. Oshima and S. Motomizu, *Anal. Chim. Acta*, 2008, **612**, 165.