Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Elaborate Fabrication of MOF-5 Thin Films on Glassy Carbon Electrode (GCE) for Photoelectrochemical Sensors

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Experimental Methods

Materials

4-carboxyphenyl diazonium tetrafluoroborate and Tetrabutylammonium tetrafluoroborate (NBu_4BF_4) were synthesized according to the literature methods.[1,2] All other reagents were purchased from Aldrich and used without further purification.

Preparation of the MOF-5 thin films on GCE

After being completely polished with alumina slurry and rinsed with doubly distilled water, the GCE (diameter: 3 mm) was firstly treated in acetonitrile containing 1 mM 4-carboxyphenyl diazonium tetrafluoroborate and 0.1 M NBu_4BF_4 using cyclic voltammetry at a scan rate of $100mVs^{-1}$ for two cycles between +1.0 V and –1.0 V (vs. Ag|AgCl). The 4-carboxyphenyl diazonium tetrafluoroborate solution was degassed using argon for at least 15 min prior to derivatization. The electrode was then rinsed with copious amounts of acetonitrile and then water and dried under a stream of argon.
In a glass reactor equipped with a reflux condenser, 0.2 g of terephthalic acid (1.2 mmol) and 1.09 g of $Zn(NO_3)_2 \cdot 6H_2O$ (3.6 mmol) were dissolved in 30 mL of N,N-dimethylformamide (DMF) and heated to 120 °C for 48h without stirring before the mixture was slowly cooled down to room temperature. After filtering off the colorless crystals, the clear MOF-5 mother liquid was obtained.
The treated GCE was immersed in this clear MOF-5 mother liquid for 24h, and the assembly of thin films was allowed to proceed. After washing completely with DMF and chloroform, and drying at 65 °C for three hours under reduced pressure (<0.2 mbar), the final MOF-5 thin films were obtained.

Photoelectrochemical experiments general

Photoelectrochemical measurements were performed with a home-built photoelectrochemical system. A 500W Xe lamp was used as the irradiation source. Photocurrent was measured on a CHI 760D electrochemical workstation (CH Instruments, Austin, TX). All experiments were carried out at room temperature using a conventional three-electrode system with the modified glassy carbon electrode (GCE) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode.

Characterization of the MOF-5 thin films

Scanning electron microscope and energy dispersive X-ray micro-analysis (SEM/EDX) were performed on a scanning electron microscopy (SEM, Hitachi S-4800, Japan) at an acceleration voltage of 15 kV. X-ray diffraction (XRD) pattern of the sample was recorded on a German Brucker AXS D8 ADVANCE X-ray diffractometer.

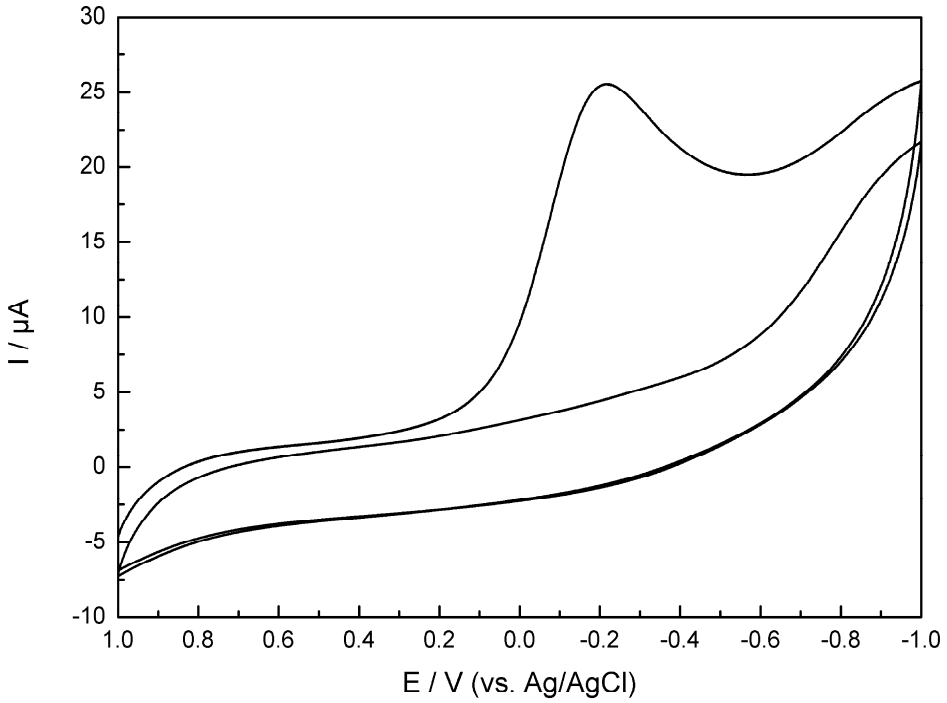

Figure S1. Cyclic voltammograms of the polished GCE in acetonitrile solution containing 1 mM 4-carboxyphenyl diazonium tetrafluoroborate and 0.1 M NBu_4BF_4 at a scan rate of 100 mVs^{-1}.

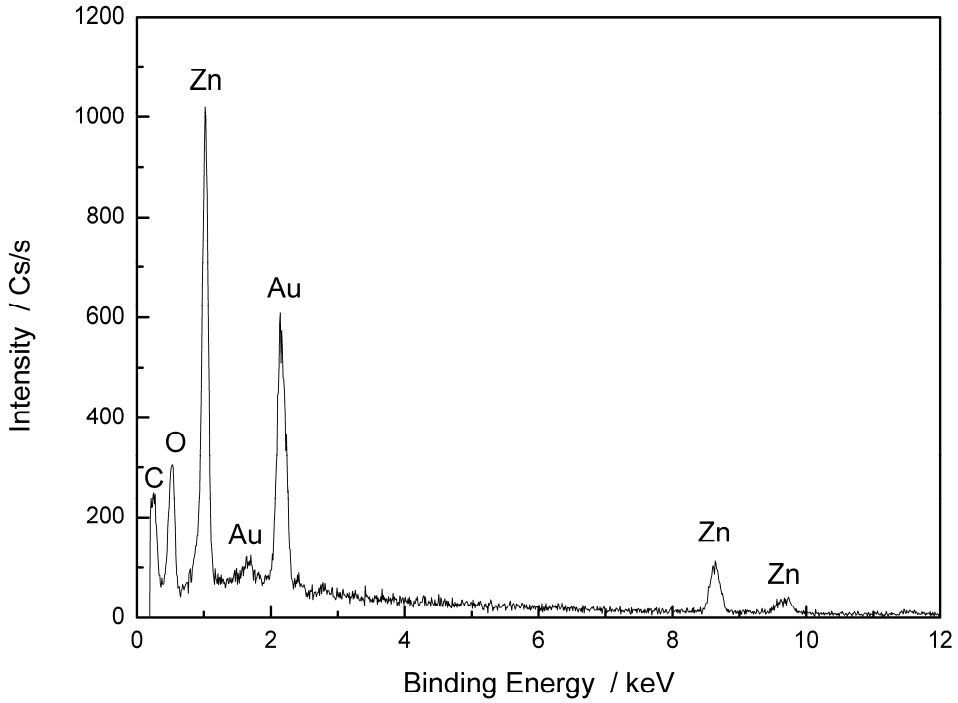

Figure S2. Energy dispersive X-ray analysis (EDX) of the MOF-5 thin films on GCE. The Au signal is related to the Au films sprayed before the SEM measurement.

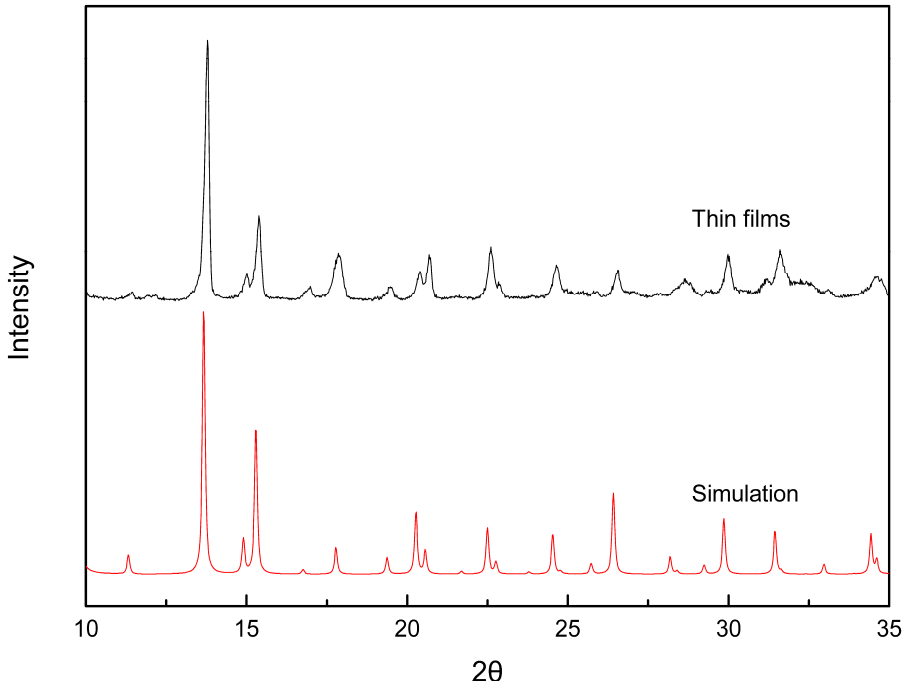

Figure S3. XRD patterns of the as-synthesized MOF-5 thin films and the simulated one from MOF-5 crystal structure data

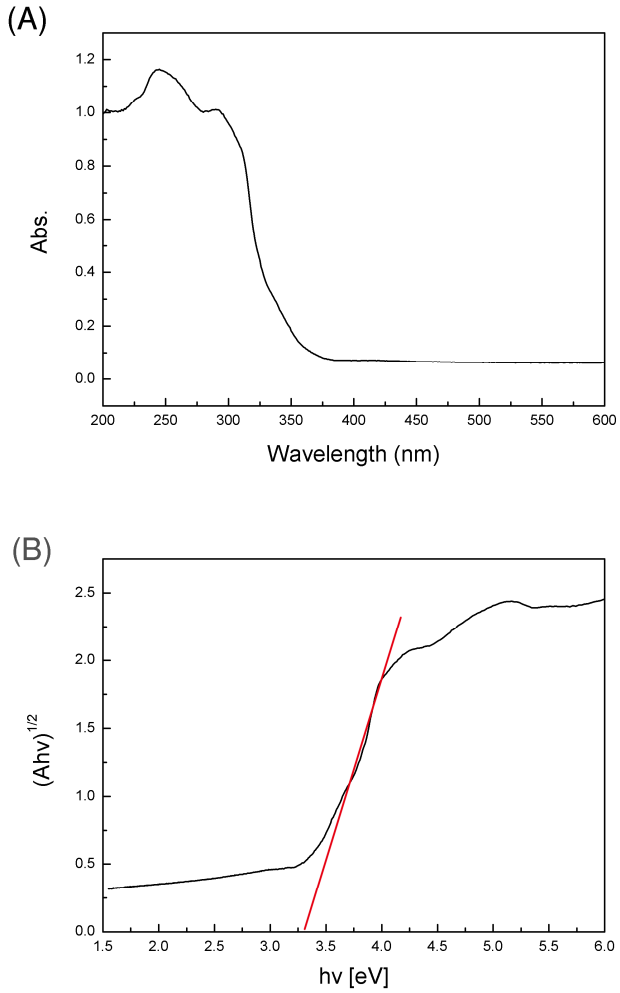

Figure S4. The diffuse reflective spectra (DRS) of MOF-5 (A), and calculation of band gap in MOF-5 of 3.3 eV.

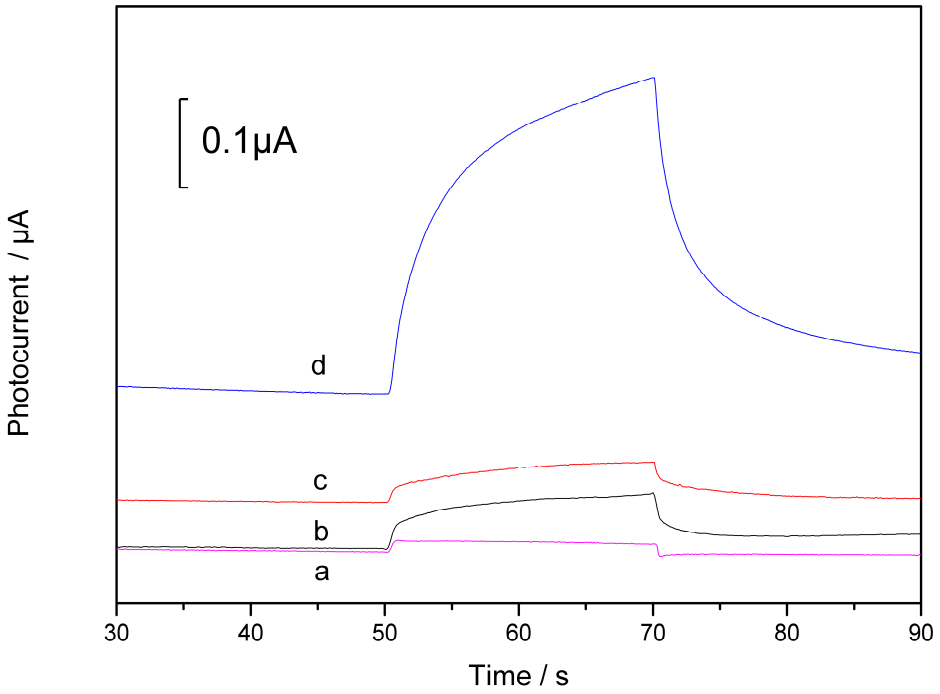

Figure S5. Photocurrent responses of (c) bare, (b) 4-carboxyphenyl, and (a,d) MOF-5 modified GCE in acetonitrile containing 0.1 M NBu_4ClO_4 in the (a)absence and (b, c, d) presence of 1mmol L^{-1} AA at 0 V(vs. SCE) to a light excitation.

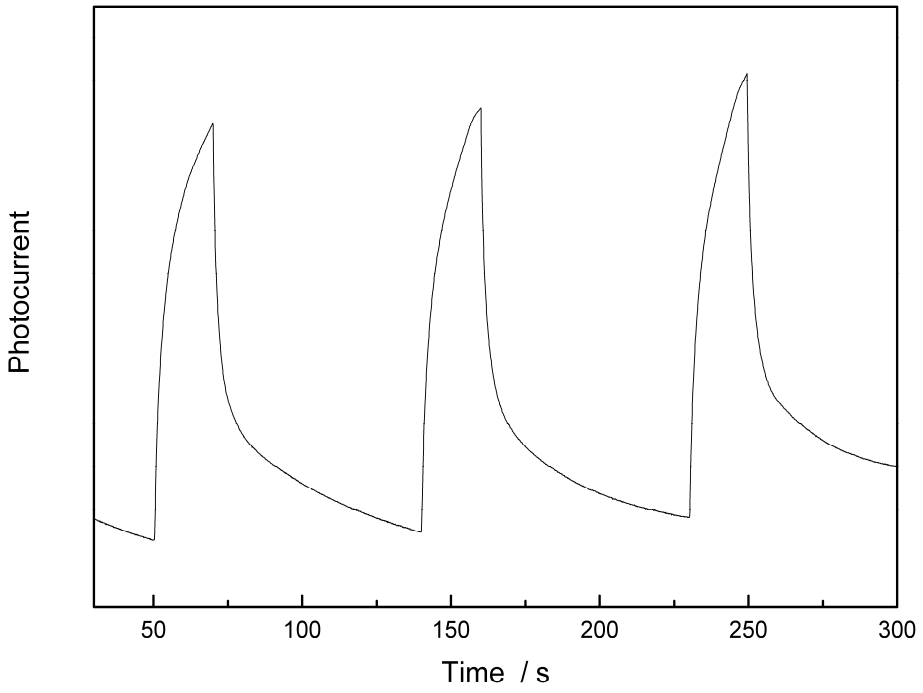

Figure S6. Photocurrent responses of the MOF-5 thin film modified GCE in acetonitrile containing 0.1 M NBu_4ClO_4 in the presence of 1mmol L^{-1} AA under three on/off irradiation cycles

References

(1) Saby, C.; Ortiz, B.; Champagne, G. Y.; Bélanger, D. *Langmuir* 1997, **13**, 6805-6813.
(2) Downard, A. J.; Tan, E. S. Q.; Yu, S. S. C. *New J. Chem.* 2006, **30**, 1283-1288.