Supporting Information

Facile Surface Functionalization of MXene by Pillar[5]arene for Enhanced Electrochemical Performance

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1. Experimental Section

1.1 Materials

All the reagents were commercially available analytical reagents (AR) and used as supplied without any further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Ti_3C_2Tx MXene was purchased from the Jilin 11 Technology Co., Ltd (Jinlin, China). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 98%), N-Hydroxysuccinimide (NHS, 98%), dimethyl sulfoxide (DMSO) were purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Methyl orange (MO), Isatin (IS), Calcein (CA) and Fluorescein sodium (FS) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

1.2 Synthesis of the P5

P5 was synthesized according to the previous literature.¹ Compound **1** (0.8 g, 1.1 mmol) and potassium carbonate (0.6 g, 4.4 mmol) were added in acetonitrile (100 mL). Then 4-bromobutyric acid (0.38 g, 2.2 mmol) was added and the reaction mixture was stirred at 80°C for 12 h under nitrogen atmosphere. The solvent was removed to give a crude product which was purified by column chromatography to give P5 as a white solid powder (86%).

1.3 Synthesized procedures of MXene-P5

The hybrid MXene-P5 nanocomposites were prepared by condensation reaction. Stirring a mixture of EDC·HCl (90 mg), NHS (60 mg), and P5 (60 mg) in solvents (H2O 7 mL and DMSO 3 mL) at room temperature for 1 h. MXene solution (5 mg/mL, 8 mL) was added in above solution for reacting 36 h at room temperature. The MXene-P5 composite material can be obtained by wash and centrifugation (4000 rpm, 10 min). Finally, the resultant MXene-P5 was redispersed in the deionized water.

1.4 Preparation of the MXene-P5/GCE

The glassy carbon electrode (GCE) was cleaned. The MXene-P5 nanocomposite (5.0 mg) was added into ultrapure water (5.0 mL), and the mixed solution was treated with ultrasound for 20 minutes to obtain a homogeneous nanocomposite suspension liquid. The fabrication of the MXene-P5/GCE was prepared by drop-coating an MXene-P5 aqueous suspension (generally, 14 μ L) onto the pretreated GCE surface. The prepared electrodes were dried for 1.5 h with N₂. As a comparison, the GCE and MXene/GCE were also prepared by the same processes as the MXene-P5/GCE.

1.5 Structural Characterizations

Infrared spectroscopy was obtained on a Fourier transform infrared spectrometer (Thermofisher is5, USA). X-ray photoelectron spectroscopy were carried out using a XPS spectrometer (Escalab 250Xi, Thermo Scientific), and the XPS spectra were corrected based on the C 1s at 284.6 eV. Morphology and elemental composition were studied using scanning electron microscope (SEM, Hitachi SU-8010; TEM, Talos F200X). The thermal stability was measured by a thermogravimetric analyzer (TGA 209 F1, Germany) at a flowing nitrogen atmosphere under a 10K/min heating rate. AFM images were obtained using a Shimadzu SPM-9700HT with the samples on cleaved mica. XRD measurements were conducted on a Bruker D8 Advanced Xray diffractometer. Images of the contact angle were taken by Dataphysics-OCA20 (Germany). Electrochemical data were tested on an electrochemical workstation (CHI750E, China). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were tested by the three-electrode system, the modified GCE as working electrode, platinum wire as counter electrode, saturated calomel electrode (SCE) as reference electrode, respectively ¹H spectra was recorded on a Bruker Avance DMX 400 spectrophotometer (Germany).

2. Supplementary Figures



Fig. S1. The synthesis route of P5.



Fig. S2. ¹H NMR spectra of the P5.



Fig. S3. ¹³C NMR spectra of the P5.



Fig. S4. XRD patterns of the MXene.



Fig. S5. XPS of MXene and MXene-P5.



Fig. S6. Tyndall effect in MXene solution.



Fig. S7 (a) SEM images of MXene-P5 on a porous anodic aluminium oxide support. (b-f) TEM image and EDXS images of the MXene-P5.



Fig. S8. The deconvolution of Ti 2p spectra of MXene (a) and MXene-P5 (b).



Fig. S9. TGA of MXene, P5 and MXene-P5 from room temperature to 700°C.



Fig. S10. Zeta potential of MXene and MXene-P5.



Fig. S11. Photographs of MXene-P5.



Fig. S12. The shape of a water droplet on the surface of MXene-P5@MO (a), MXene-P5@FS (b), MXene-P5@CA (c) and MXene-P5@IS (d) respectively.

3. References

(a) T. Ogoshi, K. Demachi, K. Kitajima and T. Yamagishi, *Chem. Commun.*, 2011,
47, 7164-7166; (b) L. Ma, S. Wang, C. Li, D. Cao, T. Li and X. Ma, *Chem. Commun.*,
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