

Supporting Information for

**Molybdenum carbide nanotubes: a novel multifunctional  
material for label-free electrochemical immunosensing**

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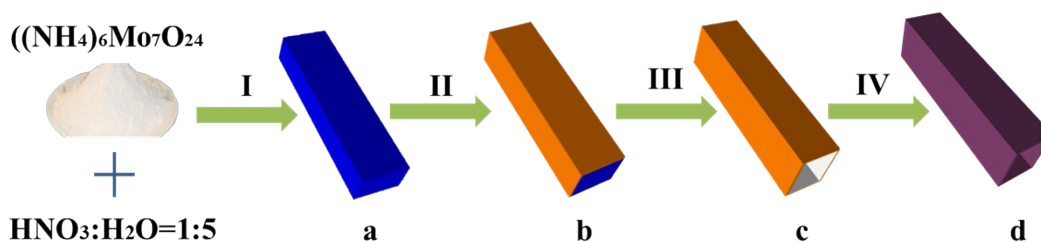
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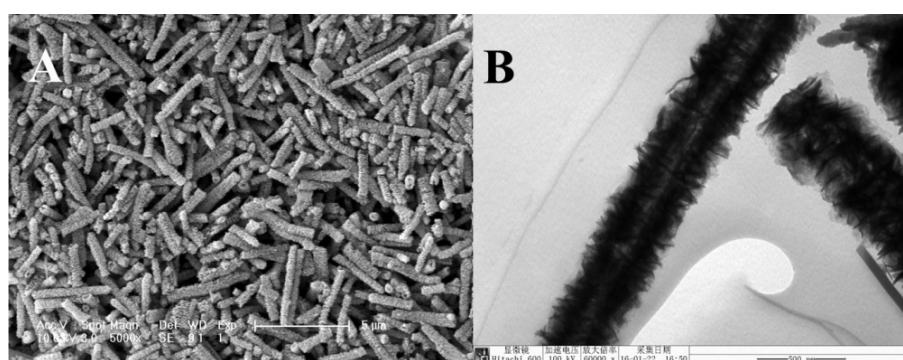
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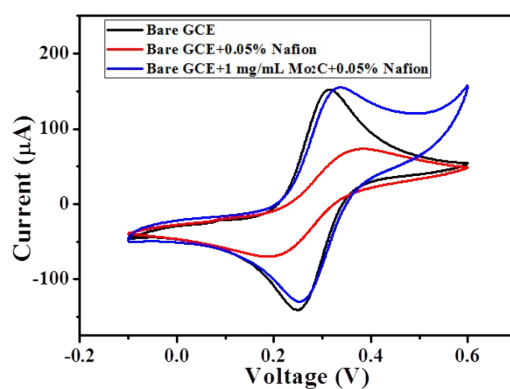
**Scheme S1.** Schematic illustration of the preparation process of Mo<sub>2</sub>C nanotubes. (I) Hydrothermal method for preparation of MoO<sub>3</sub> nanorods. (II) Dopamine was added to form MoO<sub>3</sub>-polydopamine hybrid nanosheets. (III) NH<sub>3</sub>·H<sub>2</sub>O was introduced to etch MoO<sub>3</sub> and form Mo-polydopamine tube. (IV) high-temperature calcination to produce well-crystalline Mo<sub>2</sub>C nanotubes.

**Preparation of Mo<sub>2</sub>C nanotubes.** According to the reported literature, Mo<sub>2</sub>C nanotubes were synthesized through two steps (Scheme S1). MoO<sub>3</sub> nanorods template were firstly prepared through hydrothermal method. Briefly, 1.4 g of ammonium heptamolybdate tetrahydrate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was dissolved in 40 mL of mixed solution of 65% HNO<sub>3</sub> and deionized H<sub>2</sub>O with a volume ratio of 1:5. Then, the above solution was transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for 20 h. After cooling, the white product was collected by centrifugation and washed with water and ethanol for several times, dried at 70 °C for next step. In the second step, the obtained MoO<sub>3</sub> nanorods were used as template to synthesize Mo<sub>2</sub>C nanotube. In brief, 100 mg of the MoO<sub>3</sub> nanorods was added into 20 mL of deionized H<sub>2</sub>O in a glass bottle and ultrasonic 15 min, then 200 mg of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and 50 mg of dopamine hydrochloride were dissolved into the above solution completely. Then ethanol (40 mL) was poured into the above solution.

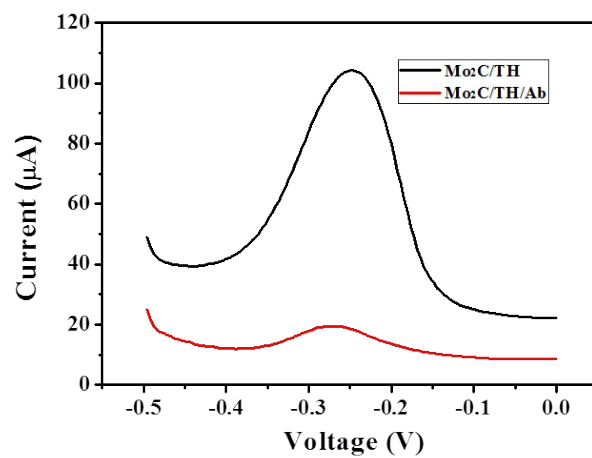
After stirring for another 5 min, 28~30 %  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (0.3 mL) was quickly injected into the above reaction solution and the mixed solution reacted for 120 min with gentle stirring. Finally, the orange-red precipitate was obtained by centrifugation, washed several times with ethanol and dried. In order to obtain the well-crystalline  $\text{Mo}_2\text{C}$  nanotubes, the above obtained orange-red precipitate was then annealed at 750 °C under Ar flow.



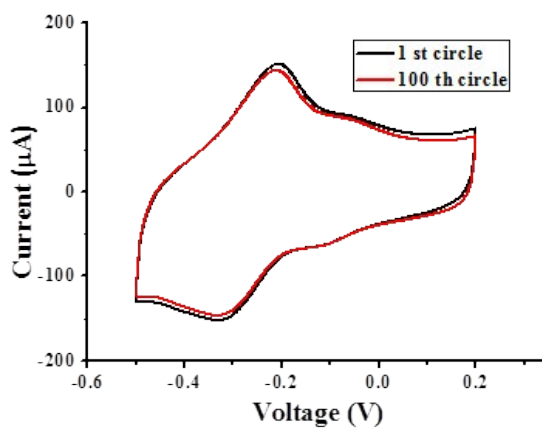
**Figure S1.** (A) SEM and (B) TEM characterizations of the prepared  $\text{Mo}_2\text{C}$  nanotubes.



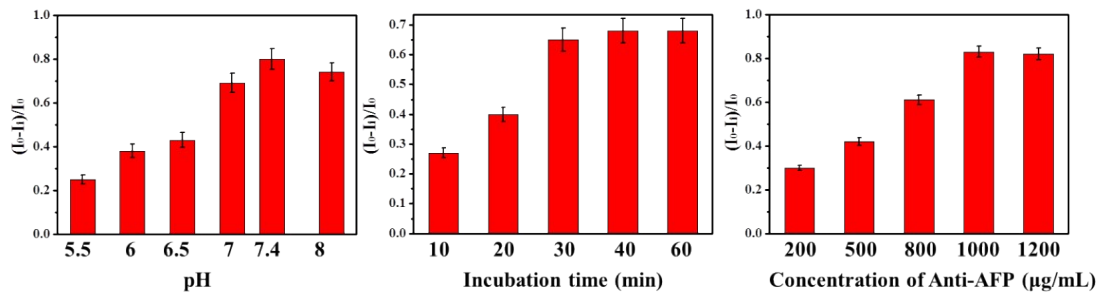
**Figure S2.** CV curve of the bare GCE, 0.05% Nafion modified GCE and 1 mg/mL  $\text{Mo}_2\text{C}$  nanotube + 0.05% Nafion modified GCE in 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ .



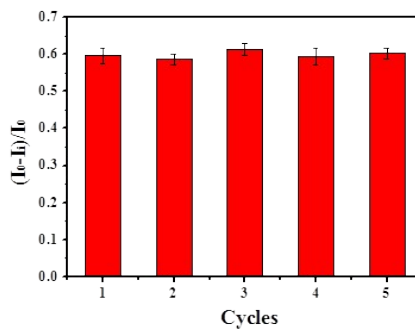
**Figure S3.** DPV curves of GCE modified with Mo<sub>2</sub>C/TH and Mo<sub>2</sub>C/TH/Ab composites.



**Figure S4.** The CV curves of Mo<sub>2</sub>C/thionin modified GCE that scan at the first cycle and scan after 100 cycles with the scan rate of 0.8 V/s in 0.1 M PBS buffer (pH=7.4).



**Figure S5.** Effects of (A) pH of detection solution, (B) the amount of anti-AFP, (C) incubation time on the immunosensor.



**Figure S6.** The reproducibility of the immunosensor for AFP (1 ng/mL) detection with five electrodes.

**Table S1.** Comparison of different electrochemical immunosensors for detection of AFP.

Modified materials	Linear range (ng/mL)	Detection limit (ng/mL)	Ref.
graphene/SnO <sub>2</sub> /Au	0.02-50	0.01	1
Au/PAMAM/ethyleneamine–viologen	0.001-45	0.00013	2
Au–Pd/N-graphene	0.05-30	0.005	3
GoldMag nanocomposite/graphene	0.01–200	0.001	4
TiO <sub>2</sub> /CdS	0.05-50	0.04	5
gold nanorods	0.1-200	0.04	6
carbon nanotubes/ mesoporous silica and graphene	0.1-100	0.06	7
palladium–graphene	0.01-12	0.005	8
Mo <sub>2</sub> C nanotubes/thionin	0.01-10	0.003	This work

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