Electronic Supplementary Information (ESI)

Carboxylated graphene nanodisks/glucose oxidase nanotags and Mn:CdS/TiO_2 matrix based dual signal amplification strategy for ultrasensitive photoelectrochemical detection of tumor markers

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Section 1: Experimental section

Preparation of CdS:Mn/TiO_2/FTO electrode

Before modification, the FTO slices were sequentially cleaned by acetone, 1 M NaOH of water/ethanol mixture (1:1, v/v) and 30% of H_2O_2. Then, they were treated with $TiCl_4$ to form a homogeneous and stable TiO_2 nano-seed layer on their surface. A 4 μL of the TiO_2 gel (prepared by adding 75 mg of the TiO_2 nanoparticles into 4.26 mL of terpineol solution dissolved with 81 mg of ethyl cellulose) was dropped onto the surface of the $TiCl_4$ treated FTO, and sintered at 450 ^oC for 1 h. After cooling down to room temperature, the CdS:Mn QD multiple films were deposited according to a successive ionic layer adsorption and reaction (SILAR) method with some modifications[1], using $Na_2S{\cdot}9H_2O$ (0.1 M) methanol/water solution and the mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.1 M) and $Mn(Ac)_2{\cdot}4H_2O$ (0.08 M) as reaction solutions. This SILAR cycle was repeated 6 times and the CdS:Mn/TiO_2/FTO was acquired.

Section 2: Figures and Tables

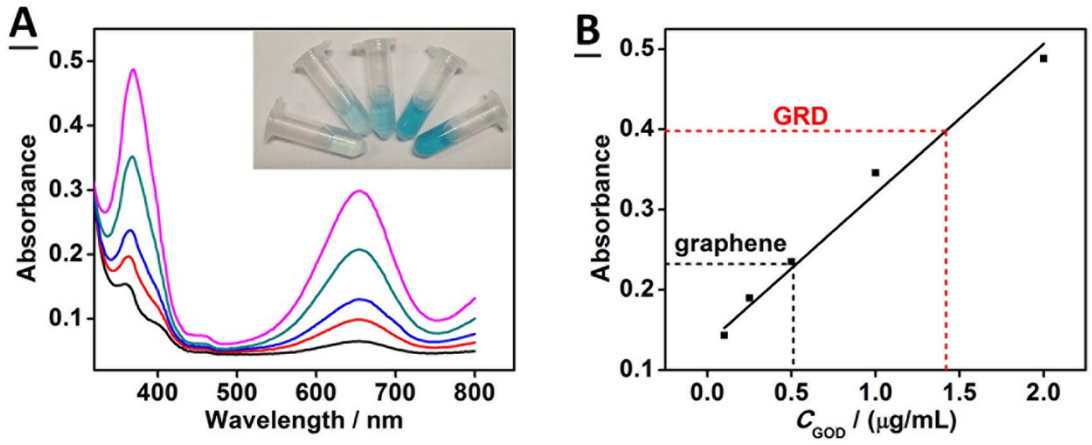

Fig. S1. (A) From down to top: UV-vis absorption spectra of 0.1, 0.25, 0.5, 1.0, and 2.0 μg/mL GOD mixed with 35 μM glucose, and then reacted with 1 μM TMB and 60 μg/mL HRP, respectively. (B) the calibration plots of the colorimetric assay toward different-concentration GOD standards (Insets: the corresponding photographs.)

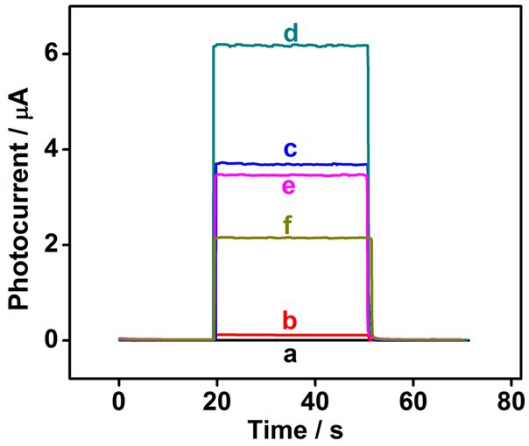

Fig. S2. The photocurrent responses of the bare (a) FTO, (b) TiO_2/FTO, (c) CdS/TiO_2/FTO, (d) CdS:Mn/TiO_2/FTO, (e) Ab/CdS:Mn/TiO_2/FTO, and (f) BSA/Ab/CdS:Mn/TiO_2/FTO, respectively.

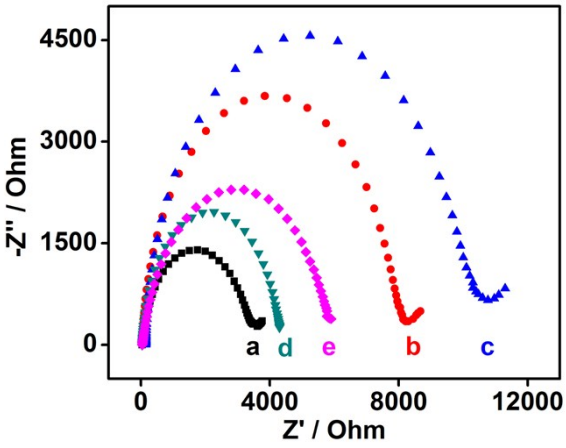

Fig. S3. The EIS plots of (a) CdS:Mn/TiO_2/FTO, (b) Ab/CdS:Mn/TiO_2/FTO, (c) BSA/Ab/CdS:Mn/TiO_2/FTO, (d) GRD-CEA/BSA/Ab/CdS:Mn/TiO_2/FTO, and (e) GRD-GOD-CEA/BSA/Ab/CdS:Mn/TiO_2/FTO respectively.

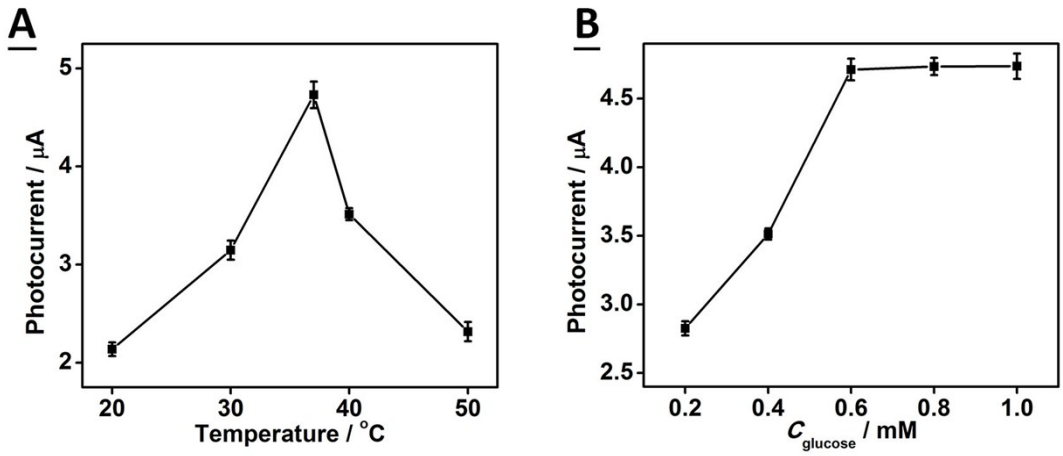

Fig. S4. The influence of (A) incubation time and (B) glucose concentration on the photocurrent of the immunosensor.

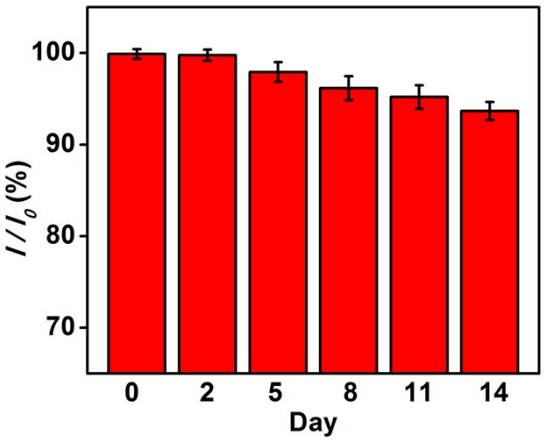

Fig. S5. The photocurrent of the PEC immunosensors after they were stored at 4 °C for different time.

Table S1. Comparison of the analytical performances of our PEC sensor with the previously reported method.

Method	Linear Range	Detection Limit	Reference
Enzymatic biocatalytic precipitation	0.5 pg-5 ng/mL	0.5 pg/mL	2
Dual-signal amplification strategy	0.5 pg-10 μg/mL	0.13 pg/mL	3
Co-sensitization strategy	1.0 pg-100 ng/mL	0.38 pg/mL	4
Sandwich type using SnO_2 -graphene as labels	0.005-10 ng/mL	0.036 pg/mL	5
Cathode PEC immunoassay	1 pg-100 ng/mL	0.32 pg/mL	6
Sandwich type based on Ab_2-CuS	0.5 pg-100 ng/mL	0.16 pg/mL	7
Semiautomated support immunoassay	10 pg-100 ng/mL	4.0 pg/mL	8
Label-free type based on CdTe/Au-TiO_2 matrix	50 pM-50 μM	50 pM	9
Dual-signal amplification coupling dual inhibition effect	0.001-1μg/mL	0.3ng/mL	10
Label-free immunoassay based on Energy transfer effect	5.0 pg-20 ng/mL	1.756 pg/mL	11
GOD-GRD based dual-signal amplification strategy	10 fg-1 ng/mL	5.65 fg/mL	This work

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