Supporting Information

Fluorescent Immunosensor based on the Catalytic Activity of CuS Nanoparticles for Sensitive Detection of Cancer Biomarker†

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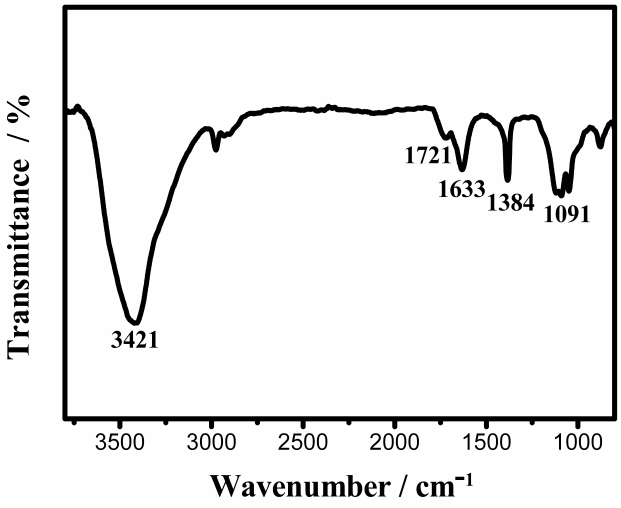

Fig. S1. FTIR spectrum of carboxylated CuS NPs.

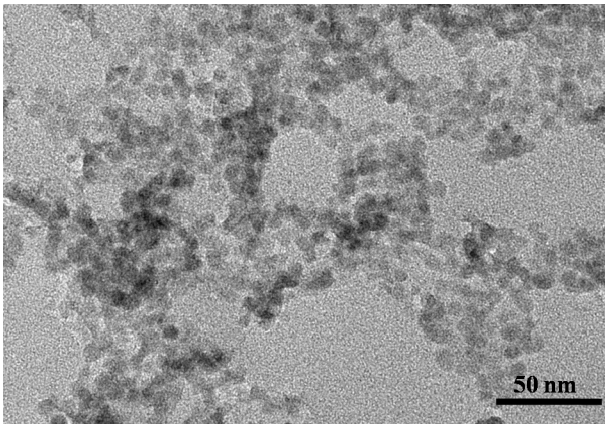

Fig. S2. HRTEM image of CuS NPs.

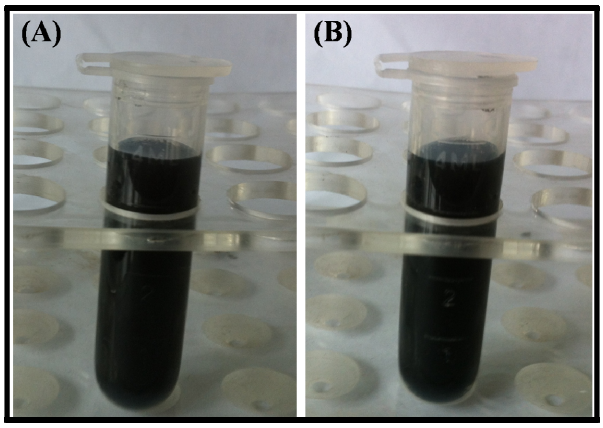

Fig. S3. The photos of prepared CuS suspension in water (A) and after being put aside for 24 hours (B).

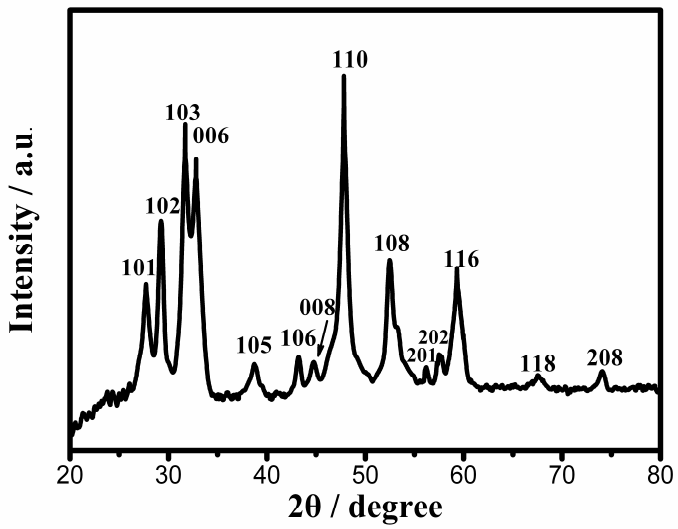

Fig. S4. The XRD pattern of prepared CuS NPs.

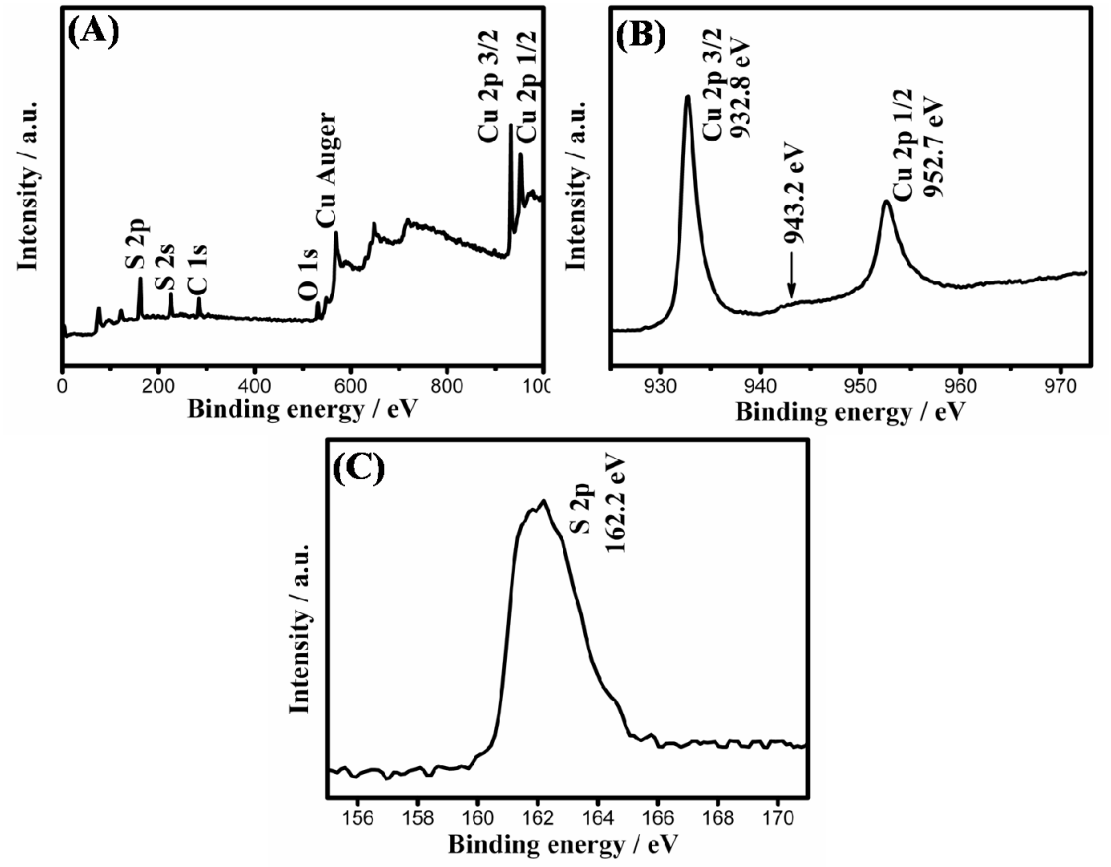

Fig. S5. The XPS spectra of prepared CuS NPs. (A) survey spectrum, (B) Cu 2p region XPS spectrum, and (C) S 2p region XPS spectrum.

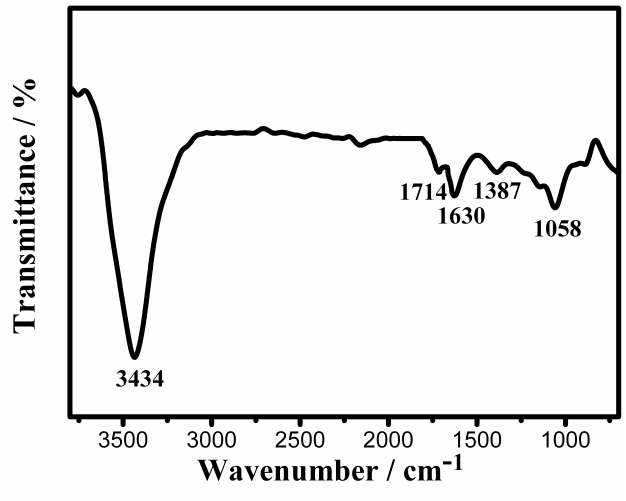

Fig. S6. FTIR spectrum of carboxylated MWCNTs.

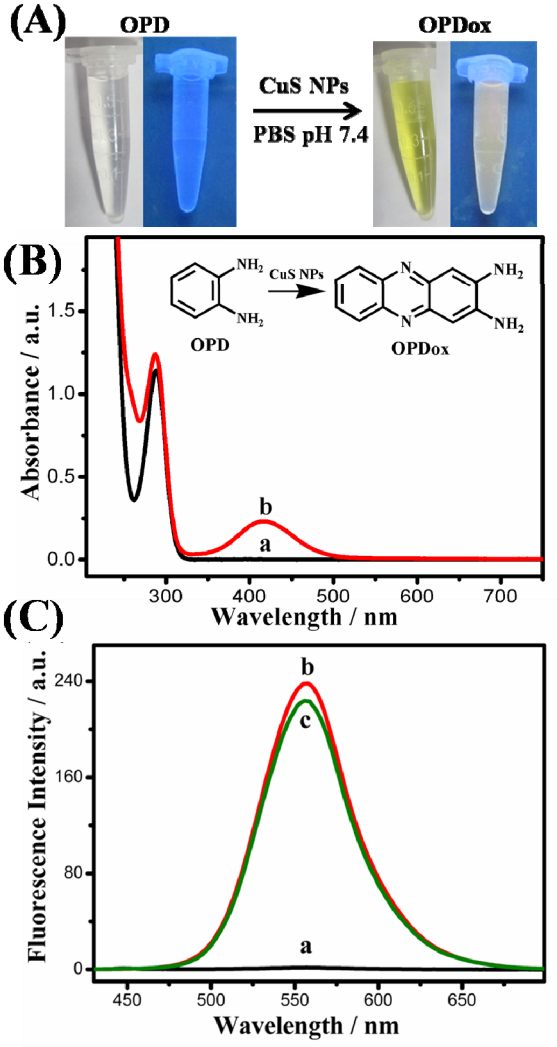

Fig. S7. (A) In the presence of CuS NPs, nonfluorescent substrate OPD could be oxidized into the fluorescent product OPDox at physiological pH. (B) UV-visible absorbance of OPD (curve a) and its oxidation product OPDox (curve b). (C) The fluorescent signals produced by (a) 0 μg mL^{-1} CuS NPs, (b) 4 μg mL^{-1} CuS NPs and (c) 4 μg mL^{-1} CuS-Ab_2 probes with 1.0 mM OPD in 0.1 M phosphate buffer at pH 7.4 with the incubation time of 20 min at 40℃.

In the presence of CuS NPs, nonfluorescent substrate OPD could be oxidized into the fluorescent product OPDox (Fig. S7 A), with a maximum absorbance at 417 nm (Fig. S7 B) and a stable fluorescent emission at 558 nm (Fig. S7 C). And labeling process of CuS to proteins did not lead to a significant loss of its activity (Fig. S7 C).

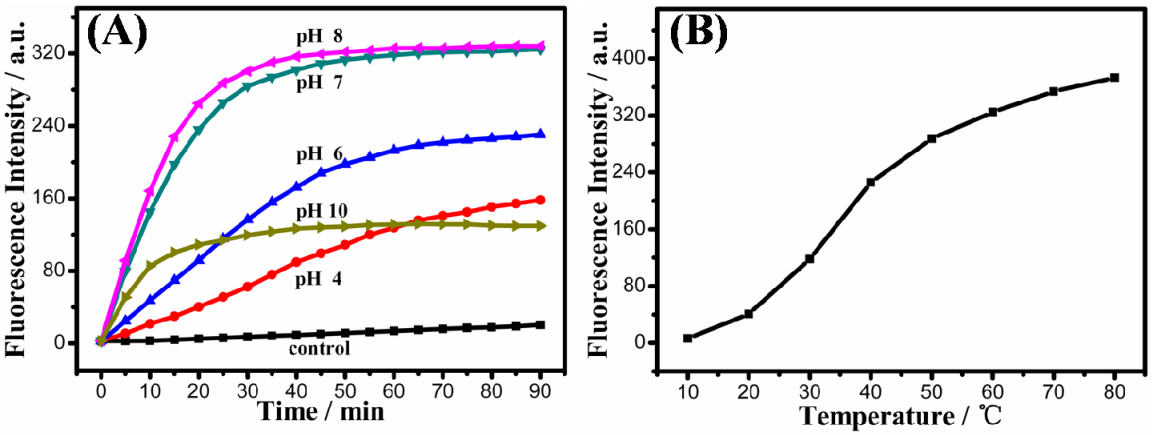

Fig. S8. (A) The pH-dependent fluorescence intensity changes at 558 nm of OPDox at different time points at 40 ℃. (B) The temperature-dependent fluorescence intensity changes at 558 nm of OPDox at pH 7.4 with the incubation time of 20 min. Assay conditions: 0.1 M phosphate buffer containing 4 μg mL^{-1} CuS NPs and 1.0 mM OPD (control in A: 0.1 M phosphate buffer (pH 7) containing 0 μg mL^{-1} CuS NPs and 1.0 mM OPD).

The activity of CuS NPs was dependent on pH and temperature. As pH value of the buffer solution increased from 4 to 10, the activity of CuS NPs to the oxidation of OPD increased first and decreased later with the optimum activity at pH 7-8 (Fig. S8 A). The control experiments in Fig. S8 A conducted at pH 7 in the absence of CuS NPs showed that oxidation of OPD hardly happened without CuS NPs. As temperature increased from 10 to 80 ℃, the activity of CuS NPs increased gradually (Fig. S8 B). The results indicated that CuS NPs maintained its activity over a wide range of temperature and worked efficiently at physiological pH. This novel activity in aqueous media helped to widen the biochemical applications of CuS NPs.

Table S1. Analytical properties of other methods for PSA immunoassays.

Method	Linear range (ng mL^{-1})	Detection limit (ng mL^{-1})	Reference
ELISA	0.003-1	0.003	[46]
Amplified electrochemical immunosensor	0.001-10	0.0004	[47]
Colorimetric immunosensor	0.05-20	0.04	[48]
Electrochemiluminescence immunosensor	0.003-50	0.0007	[49]
CuS- based fluorescent immunosensor	0.0005-50	0.0001	this work