

Supporting Information

Supersensitive Photoelectrochemical Aptasensor Based on Br,N-Codoped TiO₂ Sensitized by Quantum Dots

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Materials and Reagents

Cadmium chloride hemi(pentahydrate) ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) was acquired from Hengxing Chemical Reagent Co., Ltd. (Tianjin, China). Terrabutyltitanate (TBOT), hexadecyl trimethyl ammonium bromide (CTAB), ethanol, hydrogen peroxide (H_2O_2), sodium borohydride (NaBH_4), melamine ($\text{C}_3\text{H}_6\text{N}_6$), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), L-ascorbic acid (AA), sodium chloride (NaCl), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were obtained from Kelong Chemical Company (Chengdu, China). Dithiothreitol (DTT), gold chloride (HAuCl_4), hexanethiol (HT) were purchased from Sigma Chemical Co. (St. Louis, MO, USA.). Phosphate buffered saline (PBS, pH = 7.0) was prepared using 0.1 M KH_2PO_4 , 0.1 M KCl and 0.1 M Na_2HPO_4 . Ferricyanide/ferrocyanide mixed solution ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) was obtained by dissolving potassium ferricyanide and potassium ferrocyanide with PBS (pH = 7.4) solution. All aqueous solutions were prepared with deionized water (DI water, 18.2 M Ω /cm). Carcinoembryonic antigen (CEA) was obtained from Biocell Biotech Co., Ltd. (Zhengzhou, China). Exonuclease III (Exo III) was purchased from Dingguo Biological Technology Co., Ltd. (Beijing, China). Capture DNA, HP1, HP2 were obtained from Shanghai Sangon Biotechnology Inc. (Shanghai, China). The DNA sequences were listed in the following table:

Table S1. Sequences Used in the Experiment.

Name	Sequence (5'→3')
Capture DNA	CTTCGTATAGTCCATCACGAAAAAATGGACTATACGAAGTCCAGC-SH

HP1	GAATAAGCTGGACTTCGAACCTTATACCAGCTTATTCAATT
HP2	HS-GCTGGACTTCGTATAGTCCATTTTCCGAAGTCCAGCTTATTC

Apparatus

The measurement of photocurrent was performed by the PEC workstation (Ivium, Netherlands). Gel Doc XR+ System (Bio-Rad, California, USA) was used to take images of gels. The characterization of elements was carried out by X-ray photoelectron spectrometer microprobe (XPS, Thermo Scientific Escalab 250Xi, USA). Cyclic voltammetry was performed at the CHI 760e electrochemical workstation (Shanghai Chenhua Instrument, Shanghai China). The morphologies of materials were obtained by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and highresolution transmission electron microscopy (HRTEM, Tecnai G² F20 S-TWIN, FEI, USA). A three-electrode system was used for photocurrent measurement, in which a bare/modified glassy carbon electrode (GCE) with 4 mm diameter as the working electrode, a Pt wire as the counter electrode and a Ag/AgCl (saturated KCl) electrode as the reference electrode.

Preparation of Br, N-codoped TiO₂

Br, N-codoped TiO₂ was synthesized by reference to the previously reported method¹ with some modifications. Initially, 2 mL of TBOT, 0.5 mL of ultrapure water and 40 mL of ethanol were mixed to form a homogeneous solution under vigorous stirring. After reaction for 6 h, a large amount of TiO₂ was separated by centrifugation and dried at 60 °C. Subsequently, the acquired bulk TiO₂ (0.3 g) was dispersed in the

mixture solution containing $\text{C}_3\text{H}_6\text{N}_6$ (3 mL, 0.1 g/mL), CTAB (3 mL, 0.2 g/mL) and ultrapure water (50 mL). 10 mL of ammonia solution was poured into the prepared mixture solution followed by sealing in a 100 mL autoclave for hydrothermal reaction at 150 °C for 24 h. Finally, the obtained precipitate was separated by centrifugation and dried at 80 °C under vacuum to obtain Br, N-codoped TiO_2 for later use.

Preparation of CdS QDs

Firstly, 0.1623 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was mixed with 30 mL of ultrapure water and heated to 70 °C. Next, a freshly prepared Na_2S (30 mL, 0.0627 g/mL) solution was slowly injected into the mixture solution and kept at 70 °C for 3 h with continuous reflux. The color of the reaction solution immediately turned to orange-yellow. The collected precipitate was centrifuged and washed twice with absolute ethanol and ultrapure water, respectively. Finally, the CdS QDs were re-dispersed in ultrapure water and stored at 4 °C in the dark for further use.

Exo III-Assisted Recycling Assay

Briefly, 1.5 μL of DTT was added to HP2 (2.0 μM , 50 μL) for 1 h at 4 °C for reduction of disulfide bonds. Then the mixture solution containing HP1 (2.0 μM , 50 μL), different concentrations of target (50 μL , CEA), pretreatment of HP2 (2.0 μM , 50 μL), and Exo III (2.5 U/ μL , 10 μL) was incubated at 37 °C for 1.5 h. The solution was heated to 80 °C for 10 min to inactivate for Exo III and prevented the digestion reaction. The obtained solution was stored at -20 °C when not in use.

Characterization of Assembled CdS QDs After Target Detection

The morphology of the CdS QDs after target detection was characterized by HRTEM. As illustrated in Figure S1, numerous CdS QDs with the average diameter approximately 10 nm were incubated on T-DNA strand *via* S-Cd bond. The prepared CdS QDs demonstrated not clear lattice fringes, which was ascribed to the successful modification of capture DNA and T-DNA.

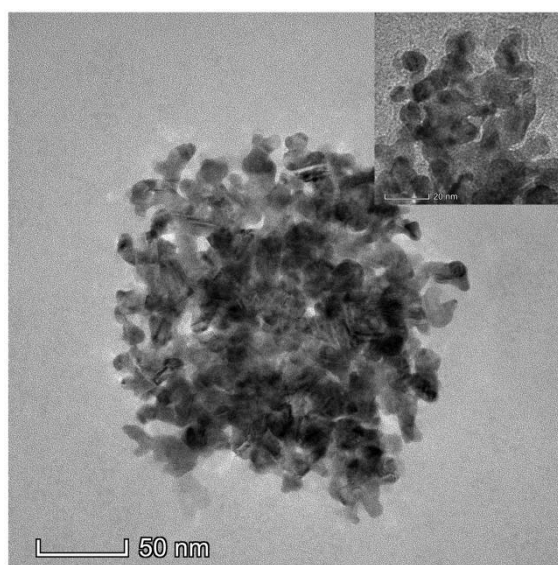


Figure S1. The HRTEM image of assembled CdS QDs after target detection.

Characterization of Br, N-codoped TiO₂ and CdS QDs

The original TiO₂ only allowed it to absorb ultraviolet light (< 387 nm).² In contrast, the visible light absorption in 400-700 nm range enhanced weakly due to the doping of Br and N elements in TiO₂ (Figure S2A). This might led to the further improvement of the visible light absorption ability of Br, N-codoped TiO₂. In addition, the energy band gap of 2.86 ± 0.2 eV can be calculated from the absorption edge at 434 nm by following the relationship of $E_g = 1240/\lambda_g$ (E_g is the energy band gap, λ_g is the threshold of absorption wavelength), which is in agreement with the reported

value.¹ The ultraviolet absorption spectrum of CdS was shown in Figure S2B. An energy band gap of 2.4 eV could be obtained based on the absorption edge of 515 nm, which is in accord with the literature.³

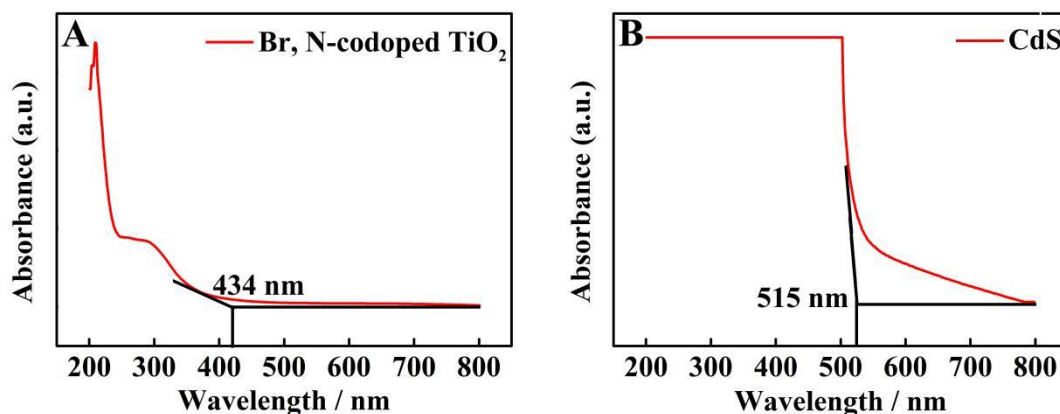


Figure S2. Ultraviolet-visible absorption spectra of Br, N-codoped TiO₂ and CdS QDs.

Experimental Optimization

The photocurrent signal of the constructed PEC aptasensor was associated with the volume of Br, N-codoped TiO₂ and incubation time of the CdS QDs. As seen from Figure S3A, the photocurrent increased with the increase of the volume of Br, N-codoped TiO₂ and the maximum photocurrent intensity occurred when the volume was 5 μ L. Therefore, 5 μ L of Br, N-codoped TiO₂ was selected as the optimized volume. As increasing the incubation time of the CdS QDs, the photocurrent of the modified electrode showed the maximum value at 30 min (Figure S3B), while it decreased with the further increased incubation time of CdS QDs. Hence, the incubation time was chosen as 30 min.

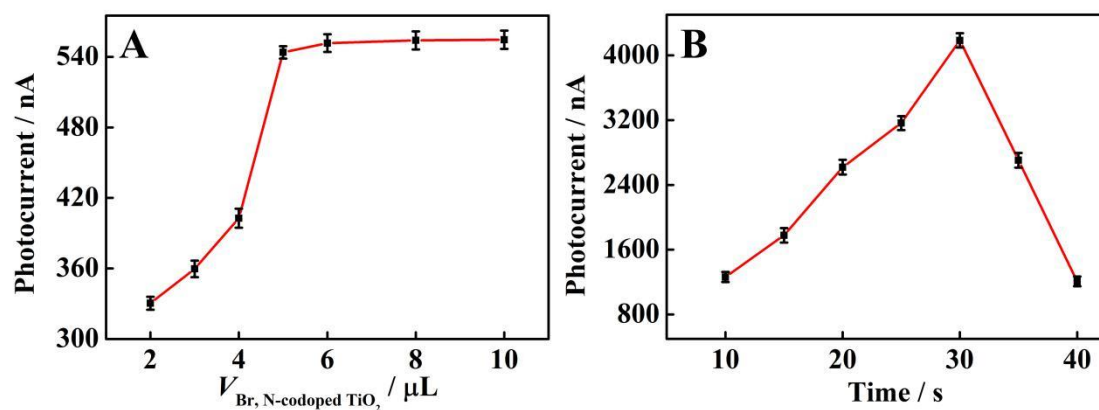


Figure S3. Optimization of (A) the volume of Br, N-codoped TiO_2 and (B) the incubation time of CdS QDs.

References

- (1) Zhang, C.; Zhou, Y. M.; Bao, J. H.; Sheng, X. L.; Fang, J. S.; Zhao, S.; Zhang, Y. W.; Chen, W. X. *ACS Appl. Mater. Interfaces* **2018**, *10*, 18796-18804.
- (2) Fan, G. C.; Han, L.; Zhang, J. R.; Zhu, J. J. *Anal. Chem.* **2014**, *86*, 10877-10884.
- (3) Zhao, M.; Fan, G. C.; Chen, J. J.; Shi, J. J.; Zhu, J. J. *Anal. Chem.* **2015**, *87*, 12340-12347.