# Supporting Information

## Competitive coordination-based immobilization-free electrochemical biosensor for highly sensitive detection of arsenic(V) using $CeO_2$–DNA nanoprobe

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## Experimental Section

### Materials

Cerium (III) nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.99%), sodium arsenite, and cesium dihydrogen As(V) ($H_2AsCsO_4$, 99.99% were purchased from J&K Scientific Co., Ltd. (Beijing, China). Sodium chloride (NaCl), sodium hydroxide (NaOH), and other anion salts were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents are of analytical grade. All aqueous solutions were prepared using ultrapure water obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA, USA). The MB modified ssDNA (MB-ssDNA) with a sequence 5'-MB-AAAAA-3' was purchased Sangon Biotechnology Co., Ltd. (Shanghai, China).

### Instrumentations

Transmission electron microscopy was performed on JEM-1400 (JEOL, Japan). Fluorescence spectroscopy was applied by Edinburgh FLS 920 (Edinburgh, England). UV-Vis spectroscopy was achieved by UV-1700 (Shimadzu, Japan). MTT experiment was done on the microplate reader from Synergy 2 Biotek (U. S.). Laser scanning confocal microscopy (Leica, Germany) was used to acquire the cell images. pH-3C meter (Leici, China) was used throughout the experiment.

### Apparatus and instrumentation

Electrochemical experiments were performed on an Autolab electrochemical workstation (Metrohm, Netherlands) based on a three-electrode system: ITO electrode was used as a working electrode, Ag/AgCl electrode and a platinum wire were used as the reference and counter electrode, respectively. Transmission electron microscopy (TEM) was taken on an HT7700 microscope (Hitachi, Japan). Absorption spectra were taken using a NanoDropOneC (Thermo, America). X-ray diffraction (XRD) analysis was obtained through D8 ADVANCE (Bruker AXS) X-ray diffractometer. Zeta

potential was performed on dynamic light scattering on the Zetasizer Nano ZEN3690 (Malvern Instruments Ltd., Malvern, UK). The scanning electron microscopy (SEM) and elemental analysis conducted by using S-4800 (Hitachi, Japan).

**Preparation of ITO electrode**

The ITO electrodes were pretreated according to the previously reported procedures. Briefly, the ITO glass slides were sequentially cleaned by ultrasonication in ethanol, and ultrapure water, respectively. Subsequently, the ITO electrodes were treated with 1 mM NaOH for 5 h. Finally, the ITO electrodes were washed with ultrapure water and the negatively charged ITO electrode surface was obtained.

**Preparation of $CeO_2$ NPs**

The $CeO_2$ NPs were synthesized according to the previously reported method. Typically, 0.868g $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in 5 mL ultrapure water was added dropwise to the 35 mL of NaOH solution (0.016 g). The mixture was stirred vigorously for 30 min. Then, the obtained solution was sealed in an autoclave and heated to 180 °C. After 24 h, the solution was cool to room temperature. The obtained precipitate was washed by ethanol and deionized water to afford $CeO_2$ NPs.

**Procedures for As(V) detection**

The differential pulse voltammetry (DPV) was applied to examine the performance of electrochemical sensing. For the preparation of the nanoprobe, 0.5 μM MB-ssDNA was suspended in 100 μL of 90 μg/mL $CeO_2$ solution (10 mM HEPES, 200 mM NaCl, pH 7.6) for 10 min. Afterward, As(V) with different concentrations was added to the nanoprobe solution. After incubation for 10 min, the electrochemical measurements were carried out. To further estimate the selectivity of the as-proposed platform for As(V), other possible interfering substances, including As(III), $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$,

$Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $CO_3^{2-}$, $SO_3^{2-}$, $SO_4^{2-}$, $CN^-$, $NO_3^{2-}$, $F^-$, $Ac^-$, $I^-$, $Br^-$ and $CrO_4^{2-}$ were tested under the same operation conditions. The concentration of As(V) and other interfering substances are 10 μM and 100 μM, respectively.

**Supplementary Figures**

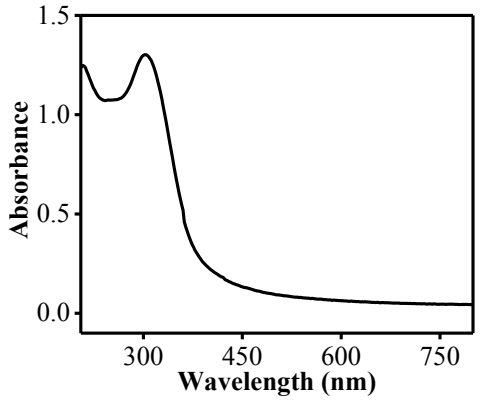


**Fig. S1** UV−vis absorption spectra of $CeO_2$ NPs.

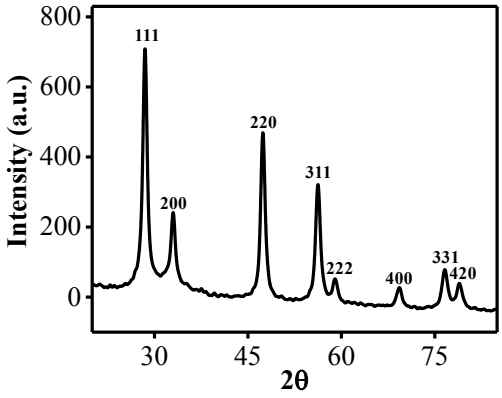


**Fig. S2** XRD pattern of $CeO_2$ NPs.

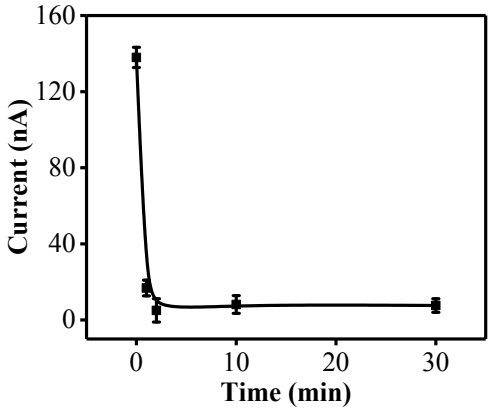


**Fig. S3** DPV peak currents of MB-ssDNA with $CeO_2$ NPs at different times.

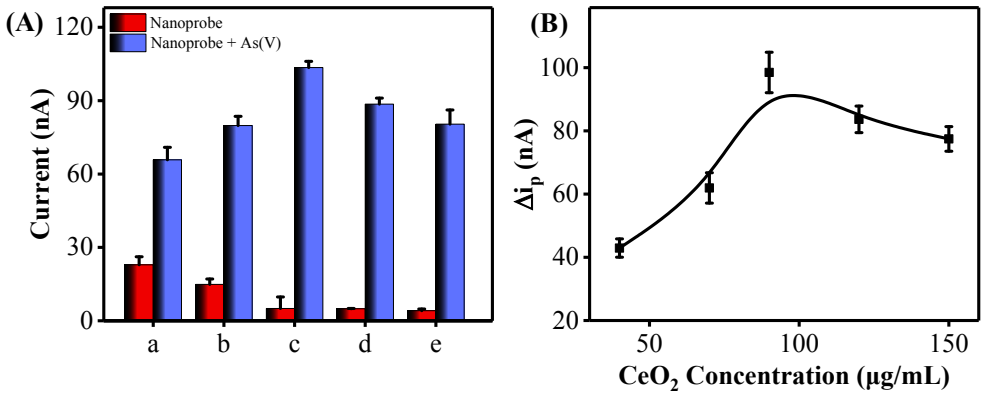


**Fig. S4** (A) DPV peak currents of the nanoprobe with (blue bars) and without (red bars) 100 μM As(V) versus various $CeO_2$ concentrations. (a) 40, (b) 70, (c) 90, (d) 120, (e) 150 μg/mL. (B) The DPV peak current change $\Delta i_p$ versus the different $CeO_2$ concentration ($\Delta i_p = i_p - i_{p,0}$, in which $i_{p,0}$ and $i_p$ are the DPV peak currents in the absence and presence of As(V) under various $CeO_2$ concentrations, respectively).

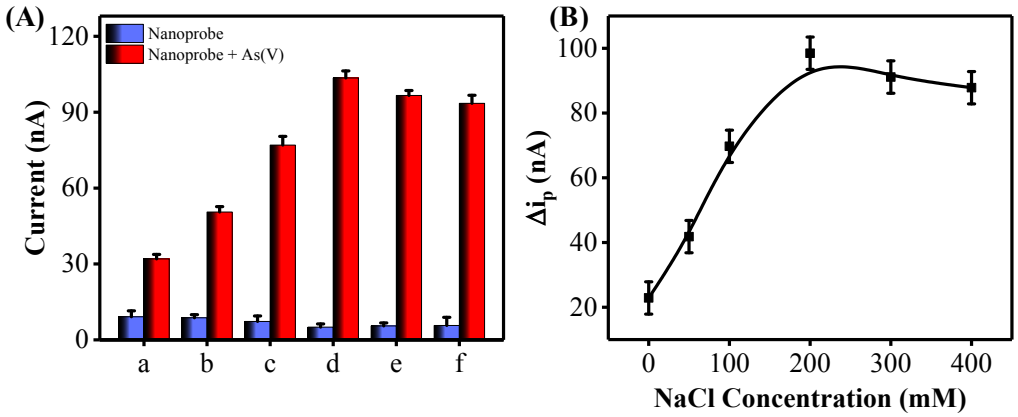


**Fig. S5** (A) DPV peak currents of the nanoprobe with (red bars) and without (blue bars) 10 μM As(V) versus various salt concentration. (a) 0, (b) 50, (c) 100, (d) 200, (e) 300, (f) 400 mM NaCl. (B) The DPV peak current change $\Delta i_p$ versus the different salt concentration ($\Delta i_p = i_p - i_{p,0}$, in which $i_{p,0}$ and $i_p$ are the DPV peak currents in the absence and presence of As(V) under various NaCl concentration, respectively.)

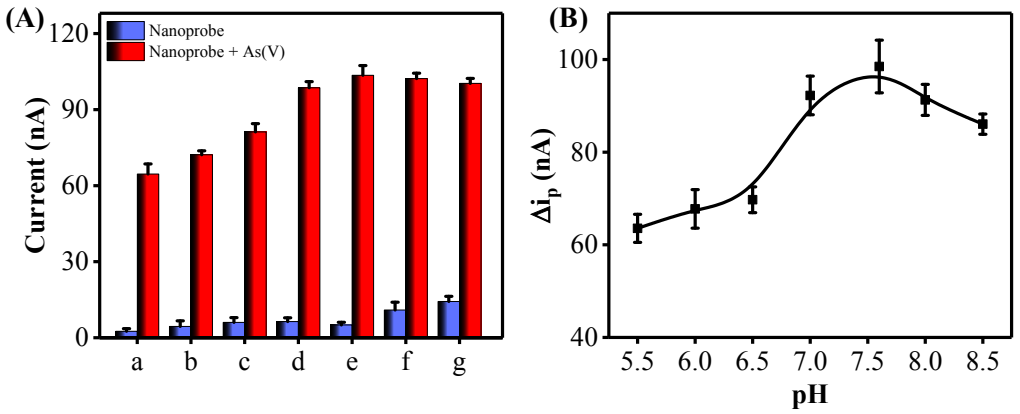


**Fig. S6** (A) DPV peak currents of the nanoprobe with (red bars) and without (blue bars) 100 μM As(V) versus various pH. (a) 5.5, (b) 6.0, (c) 6.5, (d) 7.0, (e) 7.6, (f) 8.0. (g) 8.5. (B) The $\Delta i_p$ versus the pH ($\Delta i_p = i_p - i_{p,0}$, in which $i_{p,0}$ and $i_p$ are the DPV peak currents in the absence and presence of As(V) under various pH, respectively.)

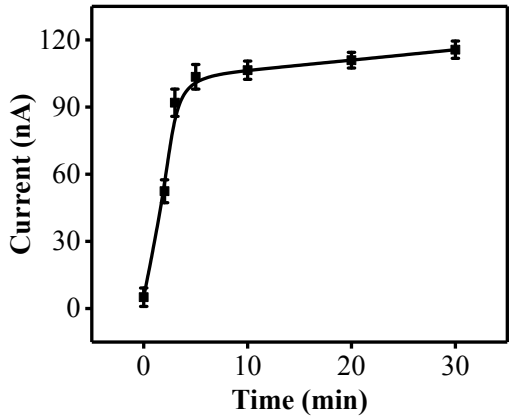


**Fig. S7** DPV peak currents of the nanoprobe versus As(V) at different times. The concentrations of $CeO_2$, MB-ssDNA and As(V) were 90 μg/mL, 0.5 μM and 100 μM, respectively.

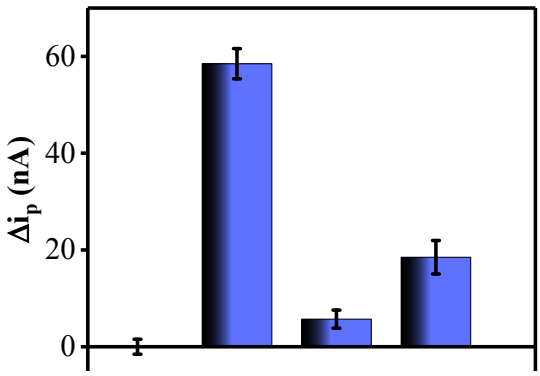


**Fig. S8** DPV peak currents of the nanoprobe under different conditions. (a) blank, (b) 10 μM As(V), (c) 10 μM $PO_4^{3-}$, (d) 100 μM $PO_4^{3-}$. (a and b: $\Delta i_p = i_p - i_{p,0}$, in which $i_{p,0}$ and $i_p$ are the DPV peak currents in the absence and presence of As(V), c and d: $\Delta i_p = i_p - i_{p,0}$, in which $i_{p,0}$ and $i_p$ are the DPV peak currents in the absence and presence of $PO_4^{3-}$ .

**Table 1** Determinaiton of As(V) in water samples by this method and ICP-MS method.

| Samples | Added (μM) | Found (μM) | Recovery (%) | RSD (%, n=3) | ICP-MS | Related error (%) |
|---|---|---|---|---|---|---|
| Tap water | 0 | - | - | - | - | - |
| | 1 | 1.05 | 105 | 3.2 | 1.02 | 2.9 |
| | 2 | 1.96 | 98 | 3.9 | 1.91 | 2.6 |
| Lake water | 0 | - | - | - | - | - |
| | 1 | 0.96 | 96 | 2.7 | 0.99 | -3.0 |
| | 2 | 1.98 | 99 | 4.1 | 2.1 | -5.7 |