# Electronic Supplementary Information 

# Construction of dentate bonded $\mathbf{T i O}_{2}$ - $\mathbf{C d S e}$ heterostructures with enhanced photoelectrochemical property: Versatile labels toward photoelectrochemical and electrochemical biosensing 

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Scheme S1. Schematic illustration for the formation process and mechanism of $\mathrm{TiO}_{2}-\mathrm{CdSe}$ heterostructures.

## Preparation of AuNPs

Typically, $25 \mathrm{~mL} 0.01 \%$ (wt) $\mathrm{HAuCl}_{4}$ aqueous solution was stored in 50 mL round-bottom flaskand heated to boiling, then $0.4 \mathrm{~mL} 1 \%(\mathrm{wt})$ sodium citrate was added into the boiling solution under stirring for 30 min . Gold colloidal solution inwine red color was obtained eventually and was used for the following modification of the immunosensor.


Fig.S1 TEM image (A) and UV-vis spectrum (B) of AuNPs. Inset of A shows size distribution of AuNPs.


Fig. $\mathbf{S} 2$ Optimization of $\mathrm{pH}(\mathrm{A})$ and AA concentration (B).


Fig. S3Time-based photocurrent response of the immunosensorincubated with 5 $\mathrm{ng} \cdot \mathrm{mL}^{-1} \mathrm{HIgG}$. A 30 W white LED light was used as the illumination source and the applied potential is 0 V .


Fig. S4 Reproducibilityof the immunosensor detected by PEC method.

Table S1. Detection results of HIgG in human serum

| Detected concentration of HIgG in serum sample ( $\mathrm{ng} \cdot \mathrm{mL}^{-1}$ ) | $\begin{gathered} \text { Added } \\ \text { HIgG } \\ \left(\mathrm{ng} \cdot \mathrm{~mL}^{-1}\right) \end{gathered}$ | $\begin{gathered} \text { Detected } \\ \text { concentration } \\ \text { of } \mathrm{HIgG} \text { by } \\ \text { PEC } \\ \left(\mathrm{ng} \cdot \mathrm{~mL}^{-1}\right) \end{gathered}$ | $\begin{gathered} \text { RSD } \\ (\%) \end{gathered}$ | Recovery <br> (\%) | $\begin{gathered} \text { Detected } \\ \text { concentration } \\ \text { of } \mathrm{HIgG} \text { by } \\ \mathrm{EC} \\ \left(\mathrm{ng} \cdot \mathrm{~mL}^{-1}\right) \end{gathered}$ | RSD | Recovery |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.65 | 0.30 | $\begin{gathered} \hline 0.98,0.92 \\ 0.90,1.01 \\ 1.02 \end{gathered}$ | 5.64 | 101.7 | $\begin{gathered} 1.05,1.02, \\ 0.92,0.99 \\ 0.98 \end{gathered}$ | 5.12 | 104.4 |
|  | 0.60 | $\begin{gathered} \text { 1.20, } 1.18 \\ \text { 1.26, 1.33, } \\ 1.21 \end{gathered}$ | 4.82 | 98.8 | $\begin{gathered} \text { 1.31, 1.35, } \\ \text { 1.22, 1.28, } \\ 1.19 \end{gathered}$ | 5.21 | 101.6 |
|  | 1.00 | $\begin{gathered} \text { 1.71, 1.68 } \\ \text { 1.75, 1.61 } \\ 1.68 \end{gathered}$ | 3.11 | 102.2 | $\begin{gathered} 1.58,1.62 \\ 1.56,1.69 \\ 1.61 \end{gathered}$ | 3.01 | 97.7 |

