Supporting Information

Ultrasensitive photoelectrochemical detection of glutathione based on the multifunctional catalytic properties of phosphotungstic acid

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Reagents and Apparatus

Phosphotungstic acid (PTA), glutathione (GSH), oxidized glutathione (GSSG), L-cysteine (L-cys), ascorbic acid (AA), dopamine (DA) and glucose (Glu) were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Anhydrous sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), copper sulfate ($CuSO_4 \cdot 5H_2O$), sodium citrate ($C_6H_5Na_3O_7 \cdot 3H_2O$), anhydrous ethanol, and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Natural killer cells (NK-92), human acute lymphoblastic leukemia cells (CEM) and special culture medium were purchased from Guangzhou Saiku Biotechnology Co. RIPA lysate was purchased from Dalian Meilun Biotechnology Co. All chemicals were of analytical grade and did not require further purification. All solutions were prepared with Milli-Q ultrapure water.

Transmission electron microscope (TEM) images were recorded by using field emission transmission electron microscope FEI Talos F200S G2 instrument (FEI, USA). X-ray diffraction (XRD) patterns were characterized by a Bruker D8 Advance diffractometer under Cu-Kα radiation (λ = 1.5406 Å). Ultraviolet photoelectron spectroscopy (UPS) analysis was performed using a Thermo Scientific ESCALAB 250 Xi XPS system under He I (hν = 21.2 eV) radiation. UV-Vis absorption spectra were characterized using a Varian Cary 5000 Scan UV-Vis-NIR spectrophotometer with $BaSO_4$ as reference. X-ray photoelectron spectroscopy (XPS) study was performed on an ESCALAB 250 (Thermo Scientific) using an Al Kα monochromated source (1486.6 eV). PEC tests were performed using a homemade PEC system. The photoelectric signal detection was performed on a CHI660C electrochemical workstation (Chenhua

Instruments, Shanghai, China) with a three-electrode system, Cu_2O/ITO as the working electrode, platinum column as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode. The illumination source was a 300W PLS-SXE300 Xe lamp and the shutter controller was a PFS40A shutter controller (Bofeilei Technology Co., Ltd., Beijing, China).

The effect of glutathione and cuprous oxide interaction verified by cyclic voltammetry

When GSH is introduced into the supporting electrolyte solution, it can effectively enrich the surface of electrode by forming Cu-S bonds with copper ions that exist on the surface of Cu_2O since GSH contains thiol groups. By doing so, it can increase the effective concentration of GSH. The redox peak signal intensity of Cu gradually decreases with the increase of GSH concentration, as shown in Figure S1A. This is because the thiol group in GSH can form a stable chemical bond with Cu coordination. On the other hand, as illustrated in Figure S1B, the thiol groups in the GSSG molecule were oxidized to form disulfide bonds and hence could not form chemical bonds with Cu ligands, indicating that GSSG had no effect on the signal intensity of the redox peak of Cu. These experimental outcomes are in agreement with the findings reported in the literature[1-3].

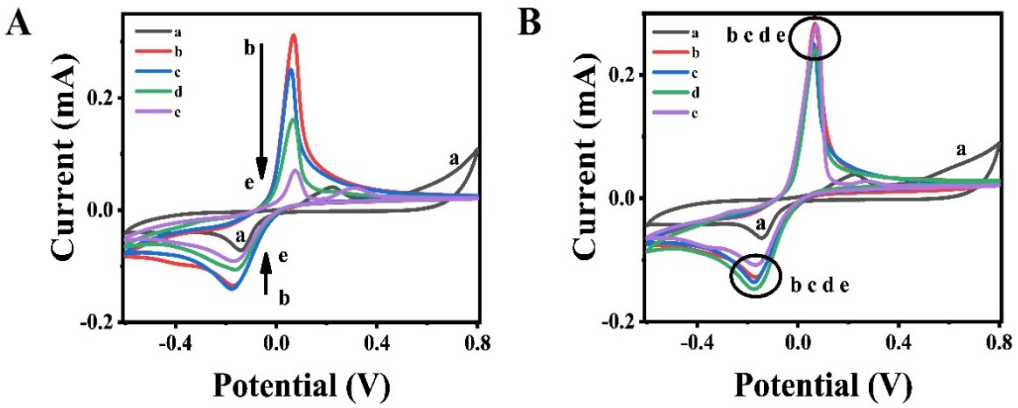

Fig. S1 The effect of (A) GSH and (B) GSSG on the CV response of electroactive Cu_2O nanocubes. Panel (a) represents the response of Cu_2O alone, whereas in panel (b), the response of Cu_2O is shown in combination with 10.0 μmol/L PTA. Panels (c-e) show the response of Cu_2O combining with 10.0 μmol/L PTA and three different concentrations of GSH/GSSG (1.00, 10.0, and 100 μmol/L) in 0.1 mol/L Na_2SO_4 solution (pH = 7.4) with a scan rate of 0.1 V/s and a scan potential range of -0.6-0.8 V.

References

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