Supplementary Materials: Revealing the Active Site of the Peroxidase-Like Activity on Gold Nanoparticles: The Determination of Surface Accessibility

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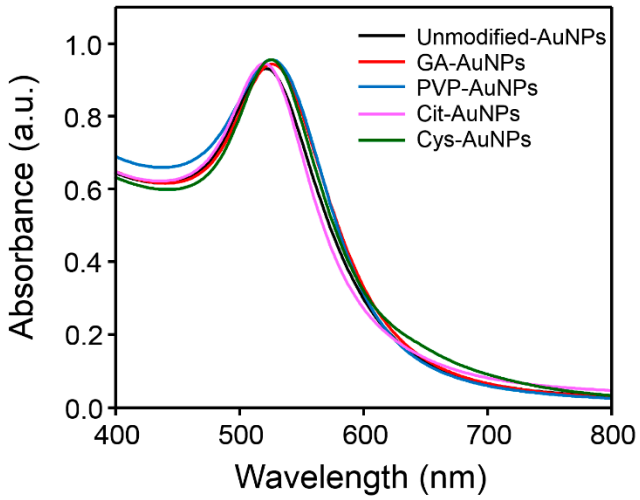

Figure S1. UV-Vis absorption spectra of unmodified AuNPs, GA-AuNPs, PVP-AuNPs, Cit-AuNPs, and Cys-AuNPs, respectively.

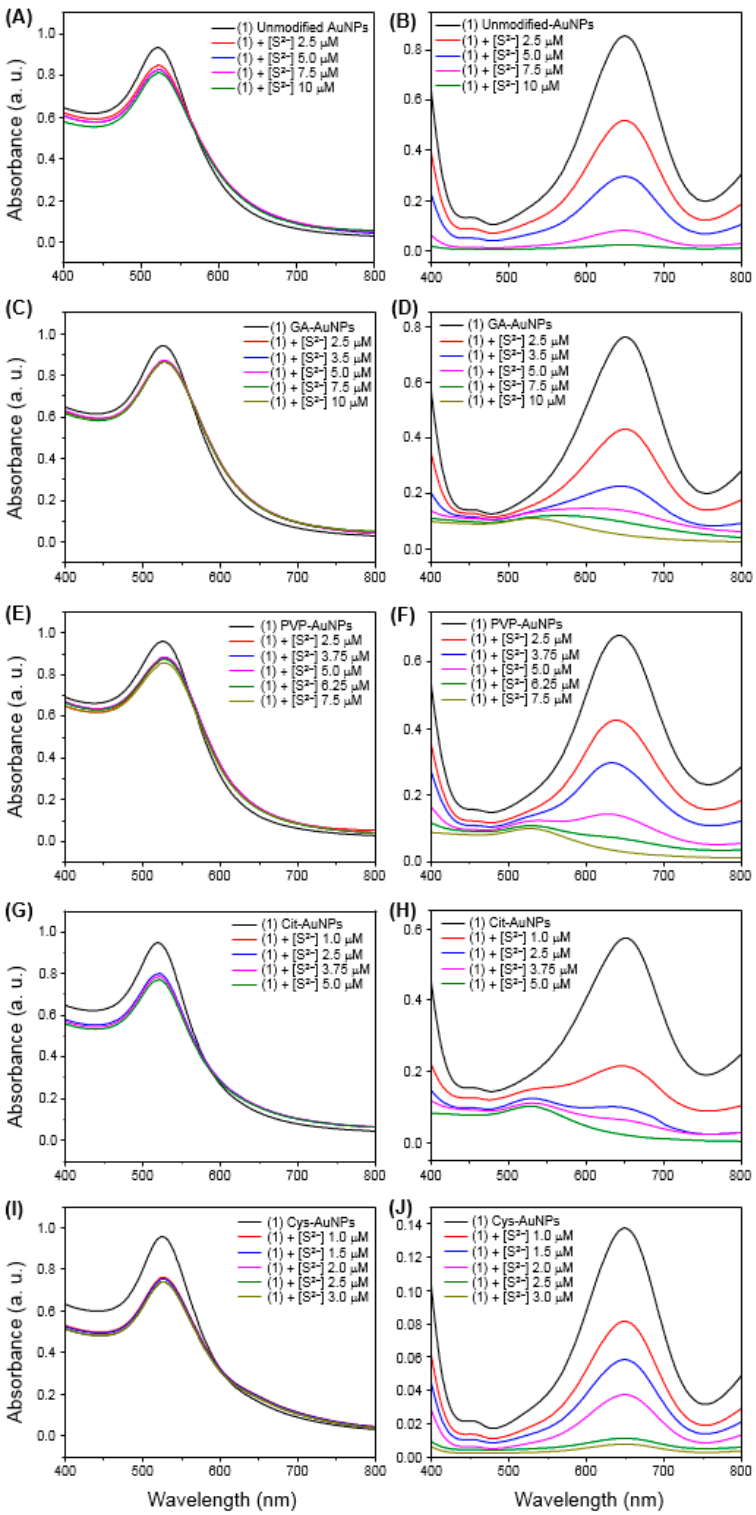

Figure S2. Absorption spectra to examine the SPR band and the corresponding inhibition extent of the peroxidase-like activity for (A), (B) unmodified AuNPs; (C), (D) GA-AuNPs; (E), (F) PVP-AuNPs; (G), (H) Cit-AuNPs; (I), (J) Cys-AuNPs in the H_2O_2 and TMB mixture as increasing the added concentrations of S^{2-}, respectively. Experiments were carried out using different AuNPs in acetate buffer (10 mM, pH 4) and H_2O_2 (0.2 M) with TMB (0.5 mM).

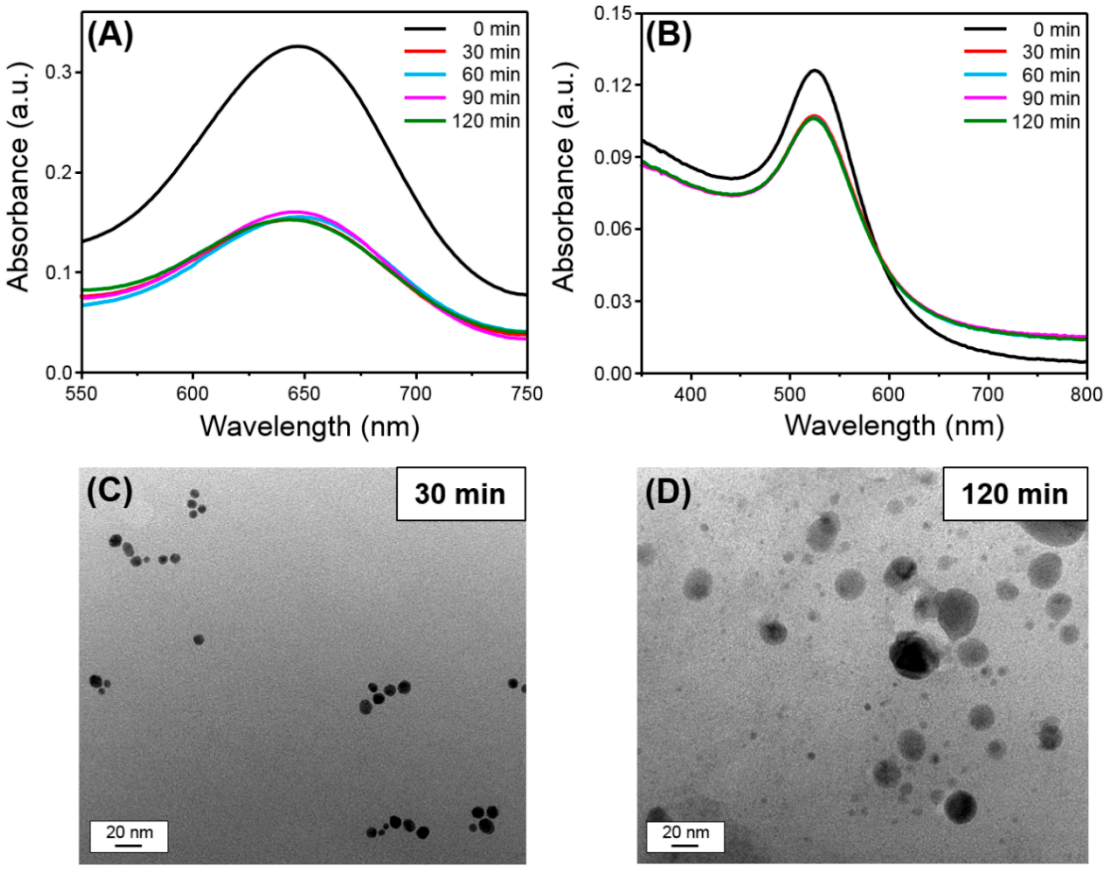

Figure S3. Absorption spectra of (A) GA-AuNPs in the H_2O_2 (0.2 M) and TMB (0.5 mM) mixture and (B) GA-AuNPs before and after the addition 10 μM S^{2-} for different incubation time, respectively. TEM images of GA-AuNPs with the addition of S^{2-} for (C) 30 min and (D) 120 min. TEM images showed GA-AuNPs significantly became large as time increased, but the inhibition extent of the peroxidase-like activity of GA-AuNPs did not change. This indicated that the inhibition of the peroxidase-like activity by S^{2-} was due to blockage of the active sites on the surface rather than aggregation of AuNPs.

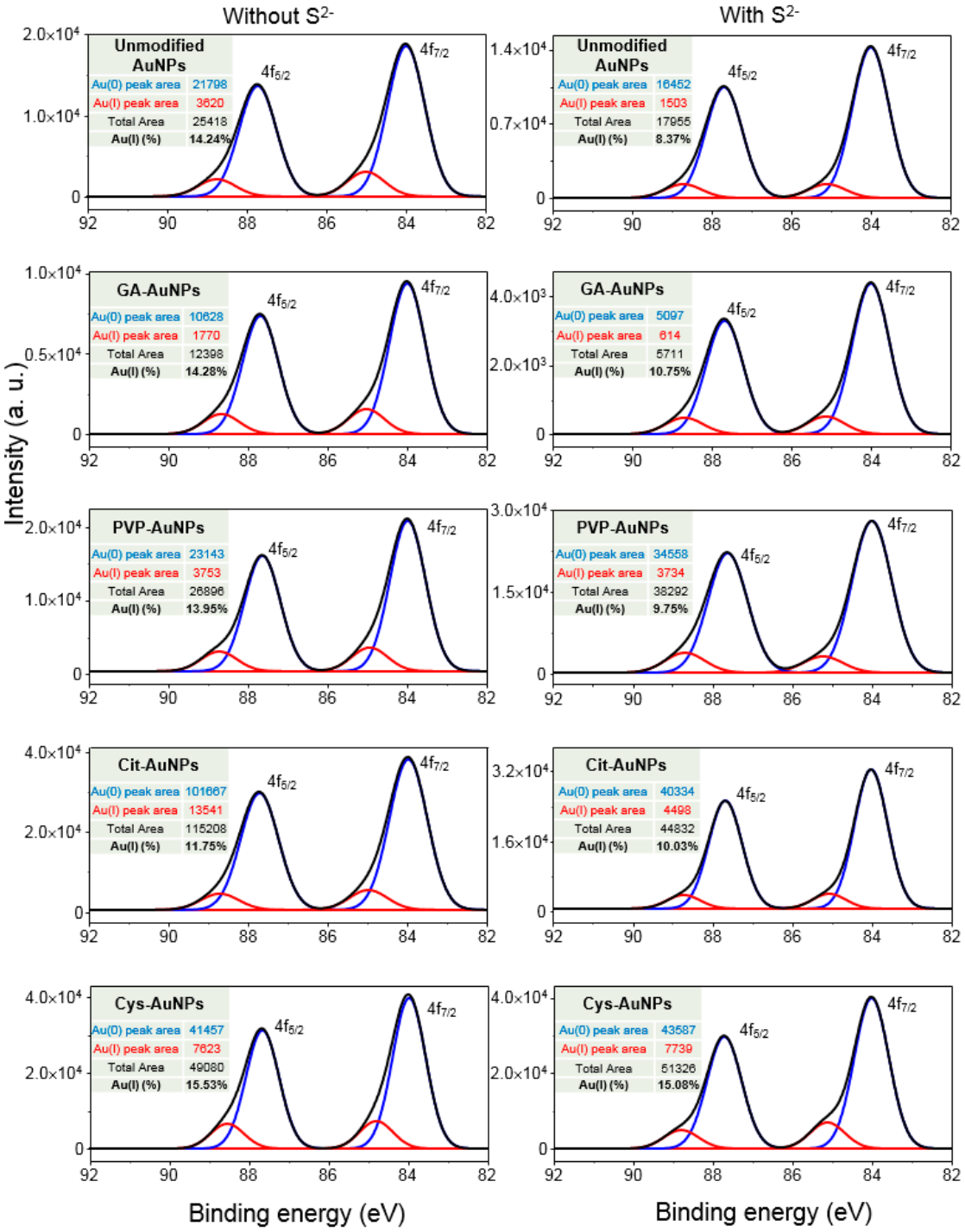

Figure S4. XPS spectra of Au 4f for unmodified AuNPs, GA-AuNPs, PVP-AuNPs, Cit-AuNPs, and Cys-AuNPs without S^{2-} (left side) and with S^{2-} (right side), respectively. The inset table showed peak area for the deconvoluted Au(I) as red trace and Au(0) as blue trace, respectively.

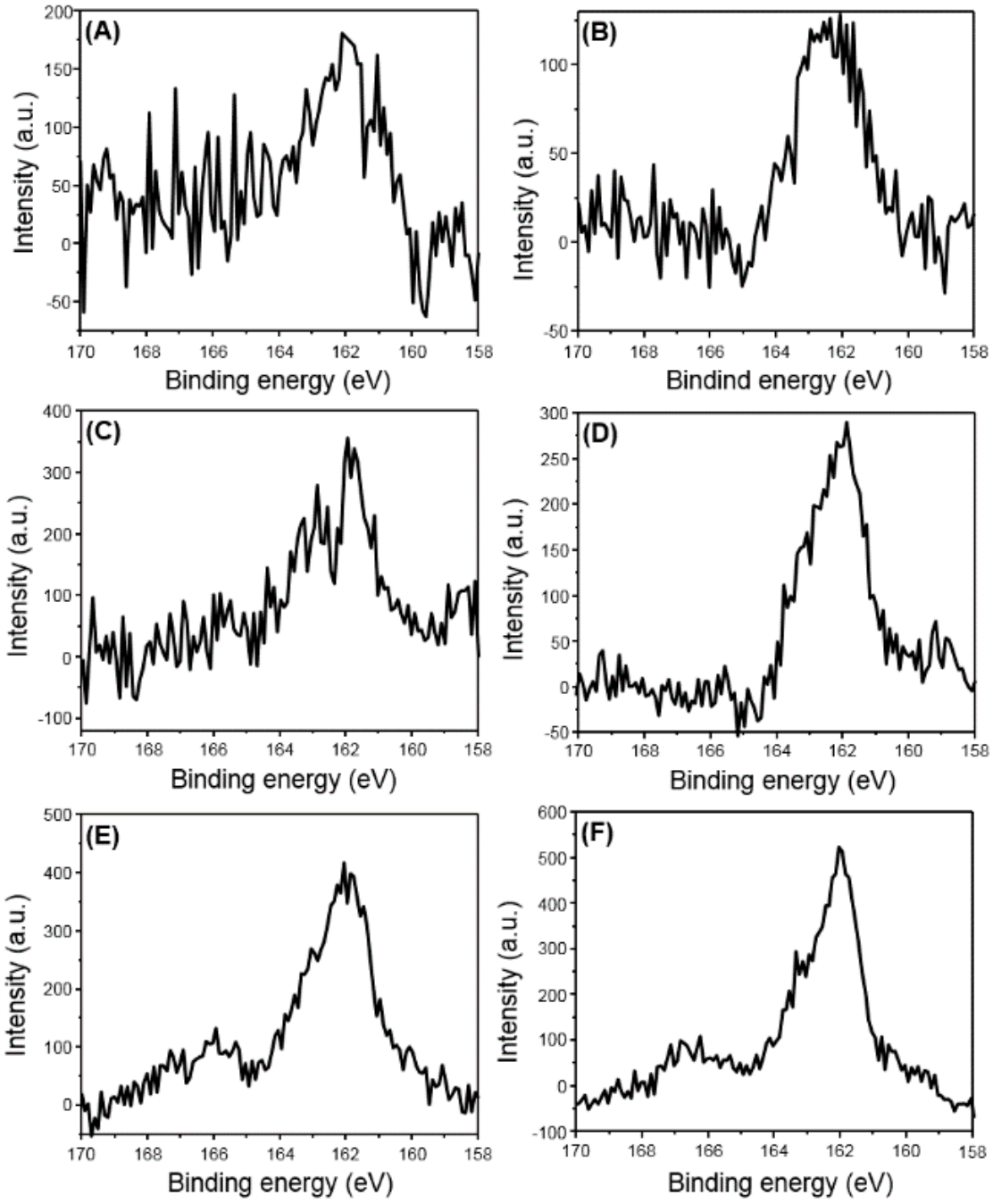

Figure S5. XPS spectra of S2p for (A) unmodified AuNPs, (B) GA-AuNPs, (C) PVP-AuNPs, and (D) Cit-AuNPs upon the addition of S^{2-}, respectively. XPS spectra of S2p for (E) Cys-AuNPs without and (F) Cys-AuNPs with the addition of S^{2-}.

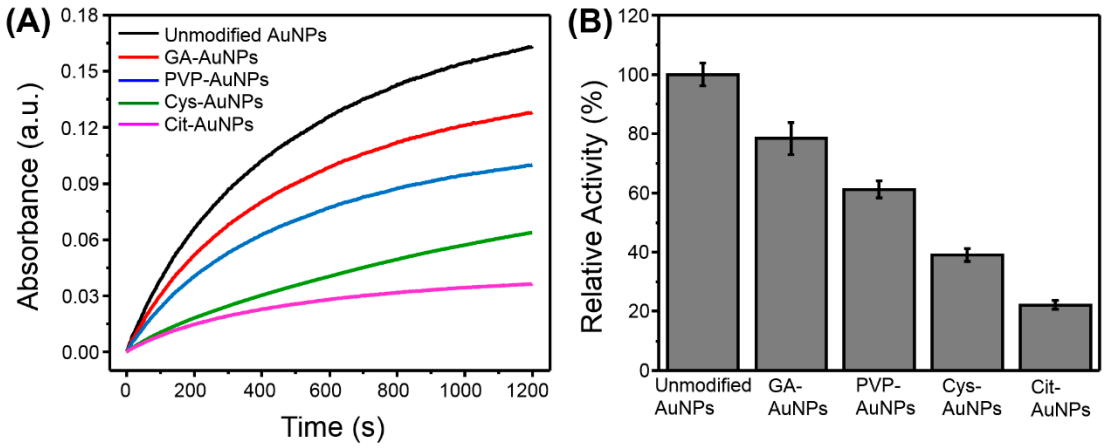

Figure S6. Comparison of the peroxidase-like activities of different surface modified AuNPs (with equivalent content of AuNPs). (A) The time dependent absorbance at 410 nm of oxidized ABTS. (B) The absorbance at 410 nm after the catalytic reaction with five kinds of AuNPs for 10 min. Experiments were carried out using different kinds of AuNPs in acetate buffer (10 mM, pH 4) and H_2O_2 (0.2 M) with ABTS (0.5 mM).

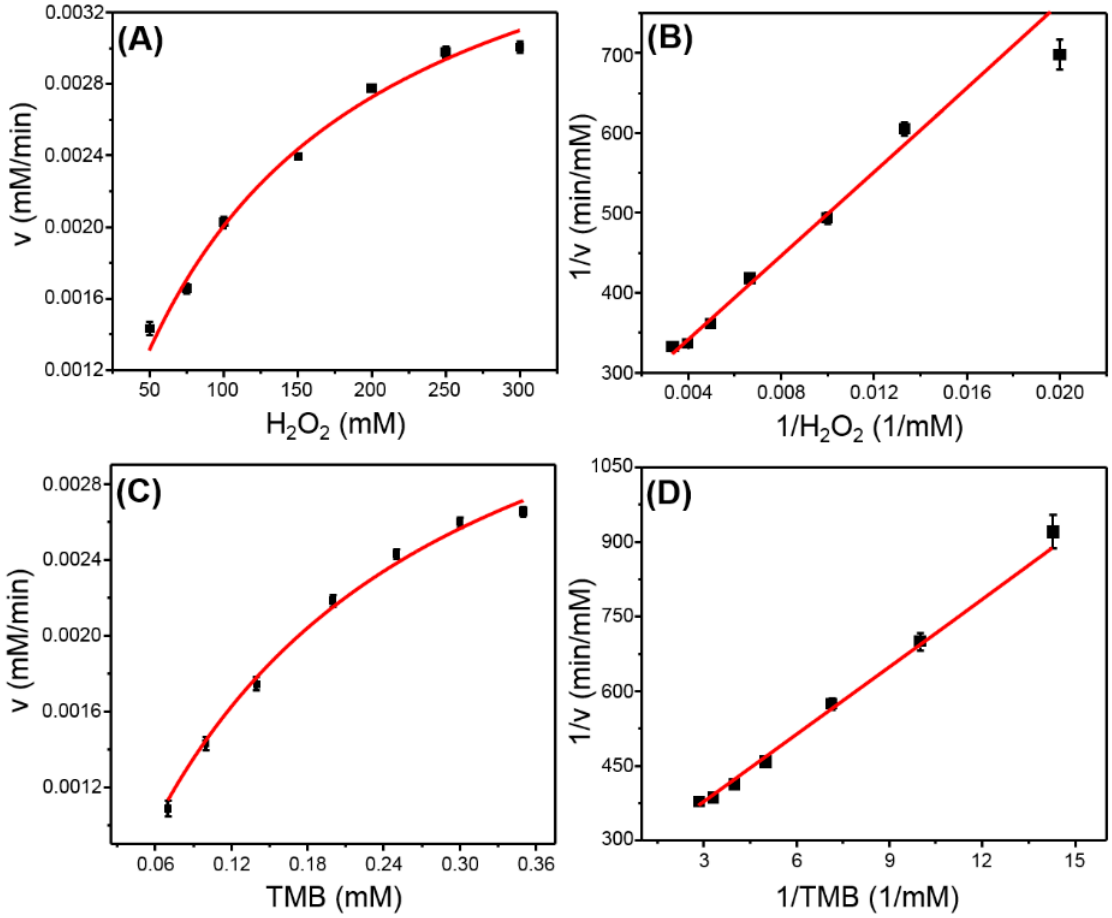

Figure S7. The steady-state kinetics of unmodified AuNPs in acetate buffer (10 mM, pH 4) with (A) H_2O_2 and (C) TMB as the substrate, respectively, which showed the peroxidase-like activity of unmodified AuNPs followed the Michaelis-Menten curve in a certain range of concentrations of substrates. (B) and

(D) are the corresponding double-reciprocal plots derived from Lineweaver-Burk linearization with substrate H_2O_2 and TMB, respectively.

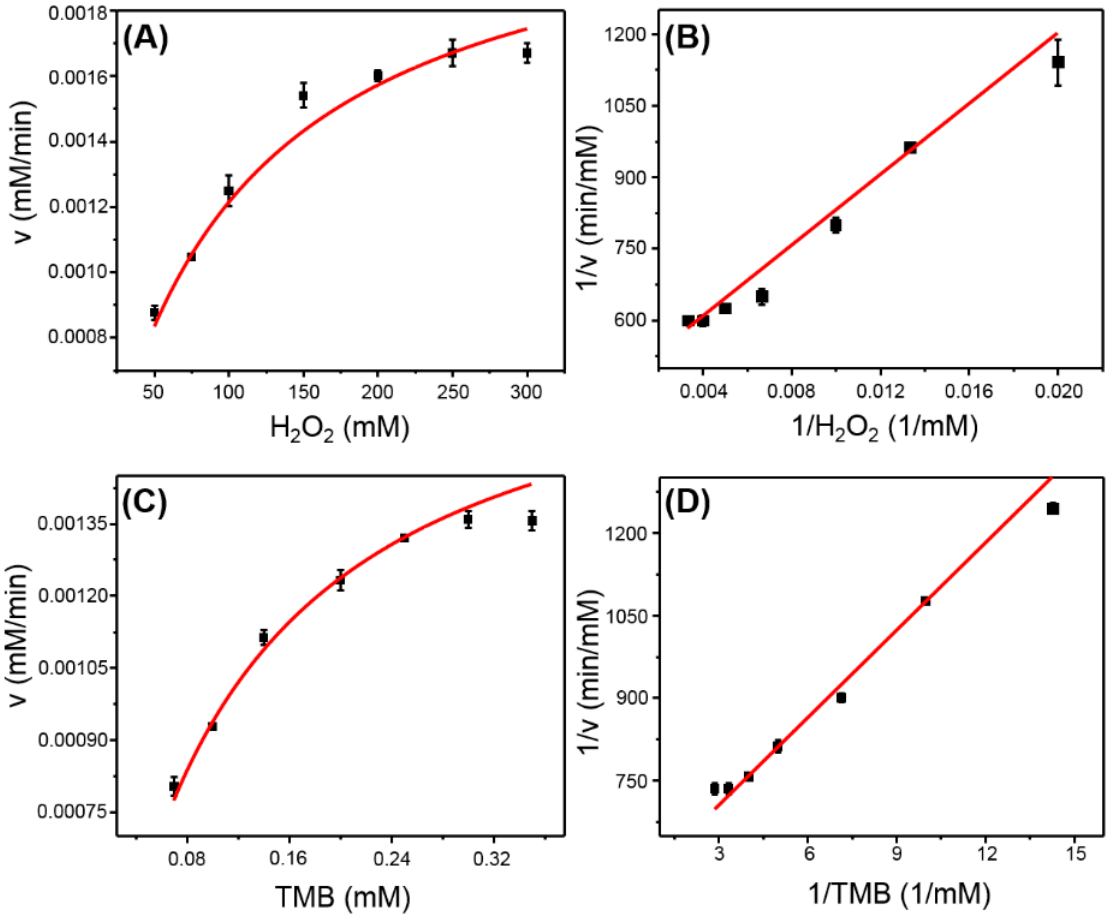

Figure S8. The steady-state kinetics of GA-AuNPs in acetate buffer (10 mM, pH 4) with (A) H_2O_2 and (C) TMB as the substrate, respectively, which showed the peroxidase-like activity of GA-AuNPs followed the Michaelis-Menten curve in a certain range of concentrations of substrates. (B) and (D) are the corresponding double-reciprocal plots derived from Lineweaver-Burk linearization with substrate H_2O_2 and TMB, respectively.

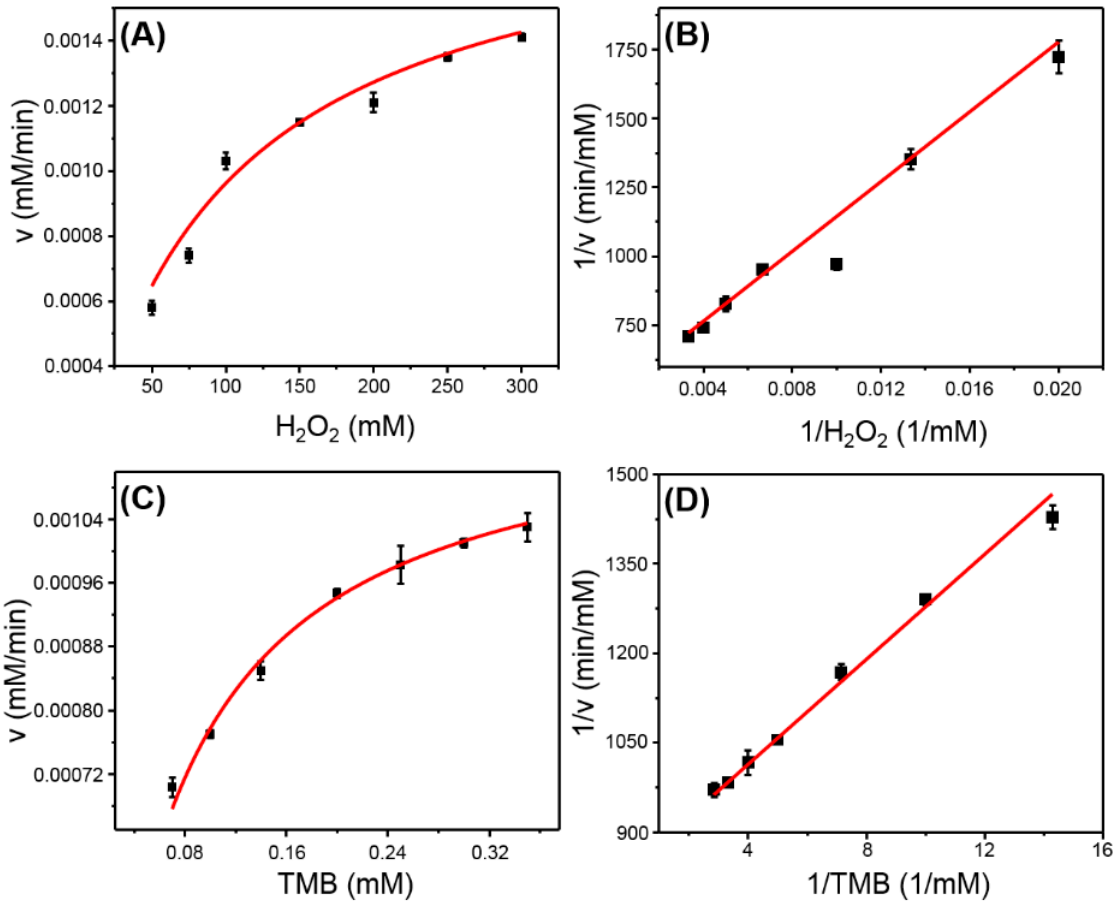

Figure S9. The steady-state kinetics of PVP-AuNPs in acetate buffer (10 mM, pH 4) with (A) H_2O_2 and (C) TMB as the substrate, respectively, which showed the peroxidase-like activity of PVP-AuNPs followed the Michaelis-Menten curve in a certain range of concentrations of substrates. (B) and (D) are the corresponding double-reciprocal plots derived from Lineweaver-Burk linearization with substrate H_2O_2 and TMB, respectively.

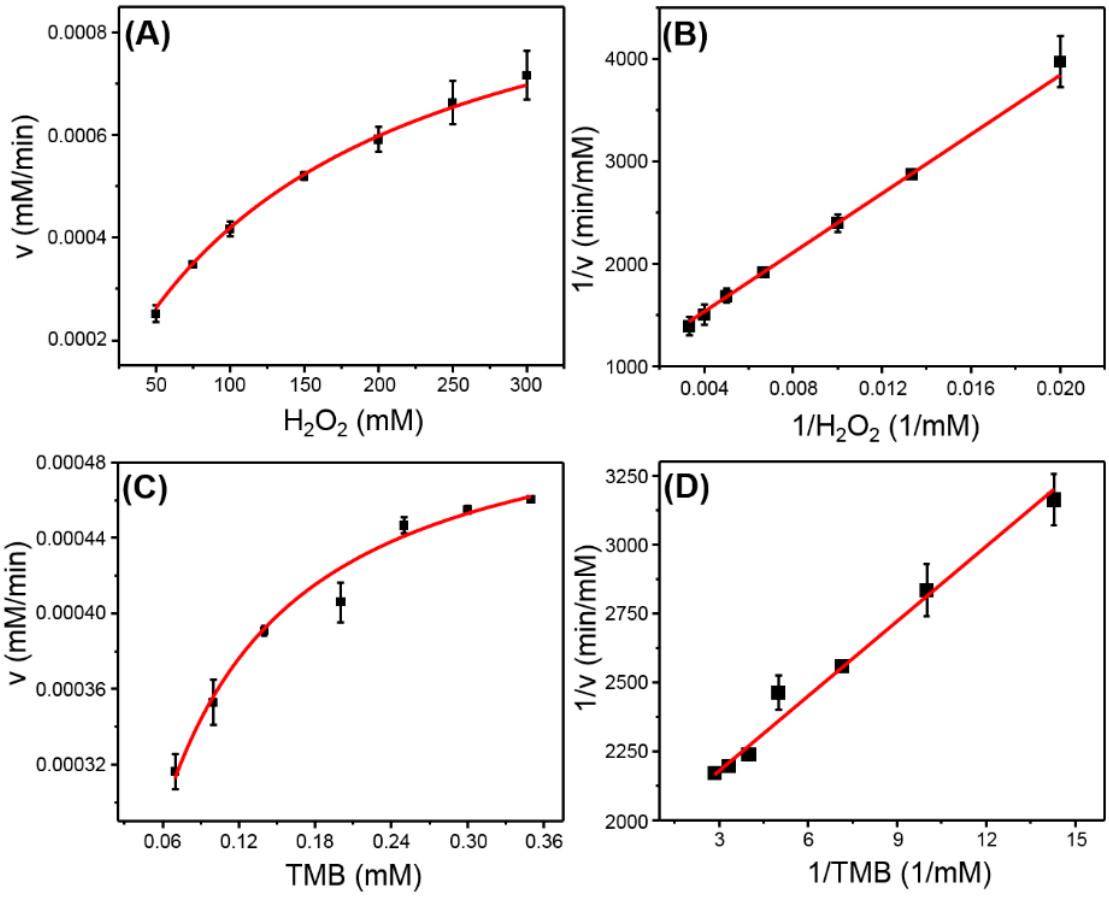

Figure S10. The steady-state kinetics of Cit-AuNPs in acetate buffer (10 mM, pH 4) with (A) H_2O_2 and (C) TMB as the substrate, respectively, which showed the peroxidase-like activity of Cit-AuNPs followed the Michaelis-Menten curve in a certain range of concentrations of substrates. (B) and (D) are the corresponding double-reciprocal plots derived from Lineweaver-Burk linearization with substrate H_2O_2 and TMB, respectively.

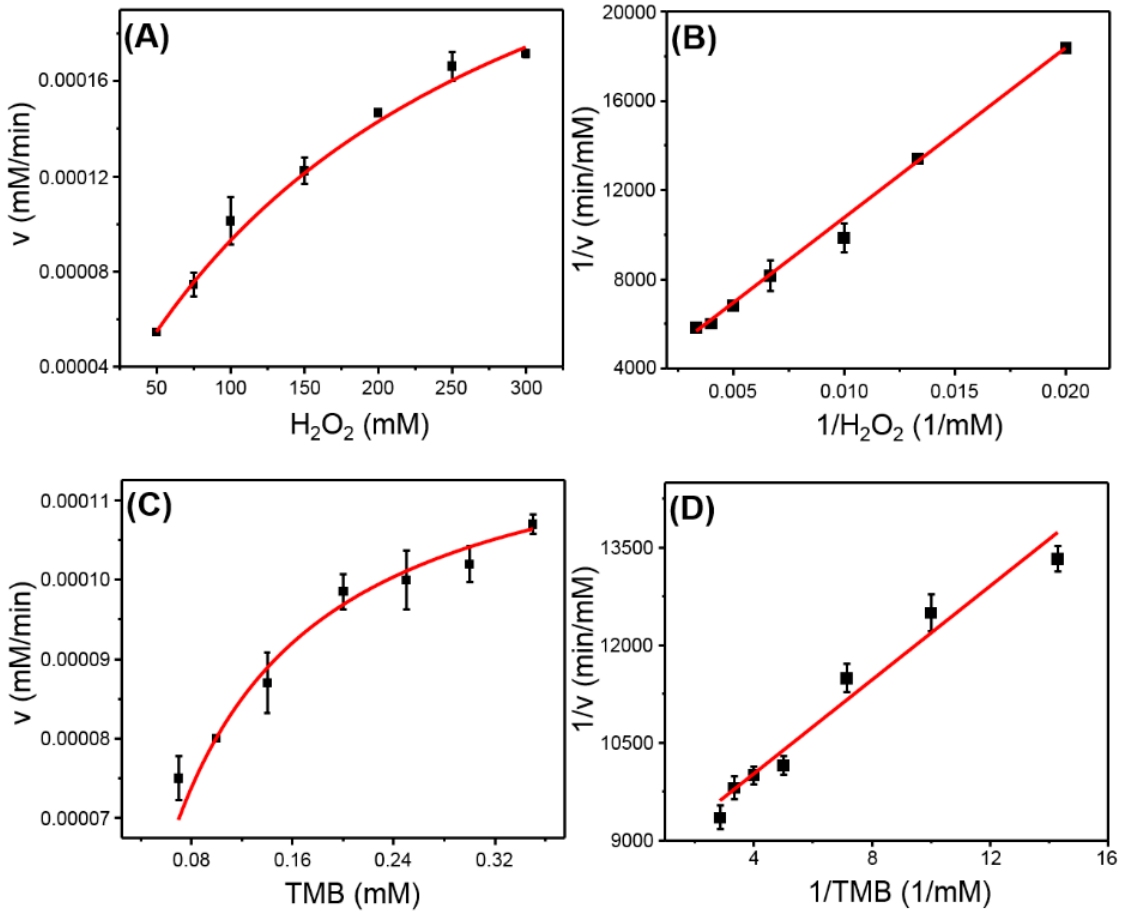

Figure S11. The steady-state kinetics of Cys-AuNPs in acetate buffer (10 mM, pH 4) with (A) H_2O_2 and (C) TMB as the substrate, respectively, which showed the peroxidase-like activity of Cys-AuNPs followed the Michaelis-Menten curve in a certain range of concentrations of substrates. (B) and (D) are the corresponding double-reciprocal plots derived from Lineweaver-Burk linearization with substrate H_2O_2 and TMB, respectively.

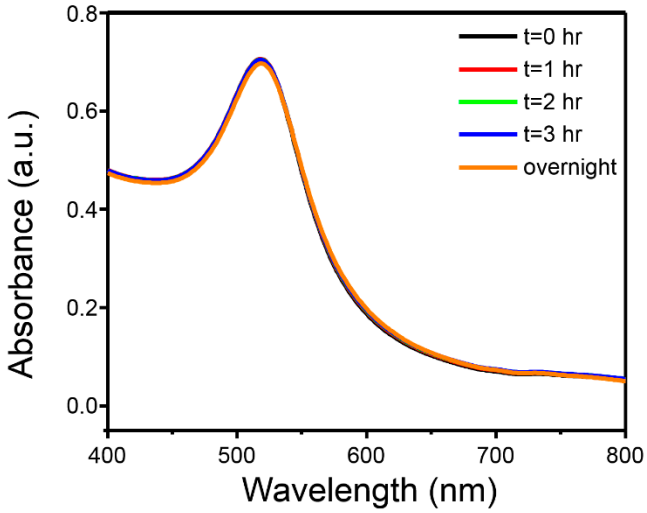

Figure S12. Absorption spectra of Cit-AuNPs (0.1 mg mL^{-1}) with H_2O_2 (10 mM) in acetate buffer solution (10 mM, pH 4.2) for different incubation time.