Electronic Supplementary Material

for

Regulating peroxidase-like activity of Pd nanocubes through surface inactivation and its application for sulfide detection

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Chemicals and Materials

Sodium tetrachloropalladate (II) (Na_2PdCl_4, 99.998%), poly(vinyl pyrrolidone) (PVP, Mw ≈ 55 000), ascorbic acid (AA), and sodium hydrosulfide hydrate ($NaHS•xH_2O$) were obtained from Sigma-Aldrich (St. Louis, USA). Potassium bromide (KBr) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB) was purchased from Aladdin Industrial Corporation (Shanghai, China). Hydrogen peroxide (H_2O_2, 30wt%) and formaldehyde was obtained from Chuandong Chemical Co., Ltd (Chongqing, China). All reagents were of analytical grade and used as received without further purification. Milli-Q purified water (18.2 MΩ·cm) was used throughout the experiments.

Instrumentations

Absorption spectra were measured using a UV-2550 UV-vis spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and high-angle annular dark-field scanning TEM (HAADF-STEM) images were taken using a Tecnai G2 F30 transmission electron microscopy (FEI, USA). An OXFORD MAX-80 energy dispersive X-ray (EDX) detector integrated in TEM was used to conduct elemental analyses. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA). Dynamic light scattering (DLS) measurement was carried out on an Omni particle size analyzer (Brookhaven, USA).

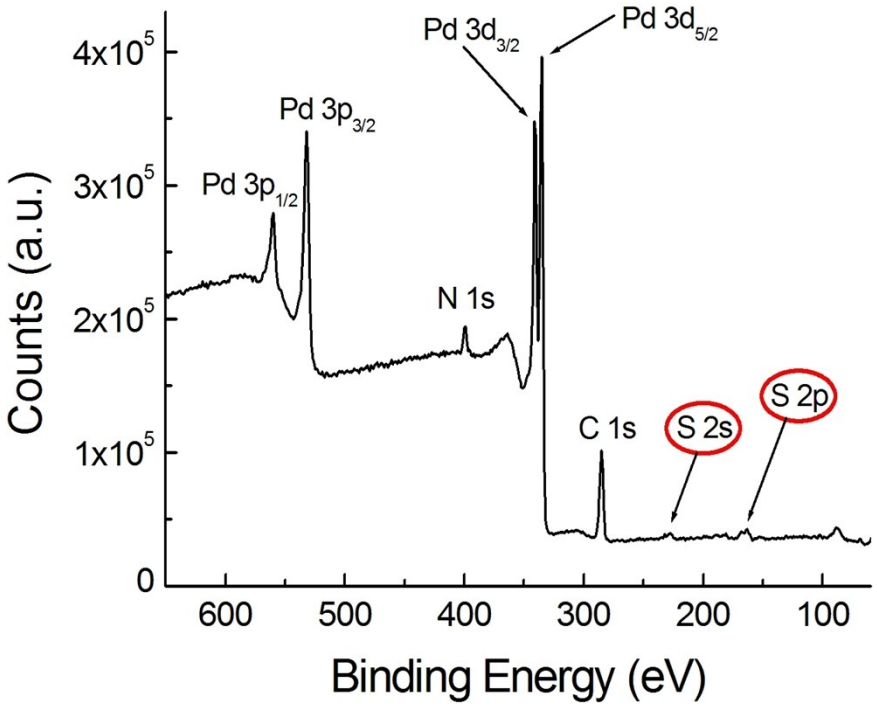

Fig. S1 XPS spectrum of the sample that obtained by the reaction of PdNCs and NaHS.

In order to acquire the sample information as a whole, XPS measurement was further carried out. As shown in Fig. S1, strong peaks assigned to Pd $3d_{5/2}$, Pd $3d_{3/2}$, Pd $3p_{3/2}$ and Pd $3p_{1/2}$ indicated that Pd was the dominating element in the sample after the reaction between PdNCs and NaHS. Obviously, the peaks assigned to S 2p (160.4 eV) and S 2s (225.6 eV) were also found in the spectrum. These results confirmed the formation of PdS after the spectrum. These results confirmed the formation of PdS after the reaction.

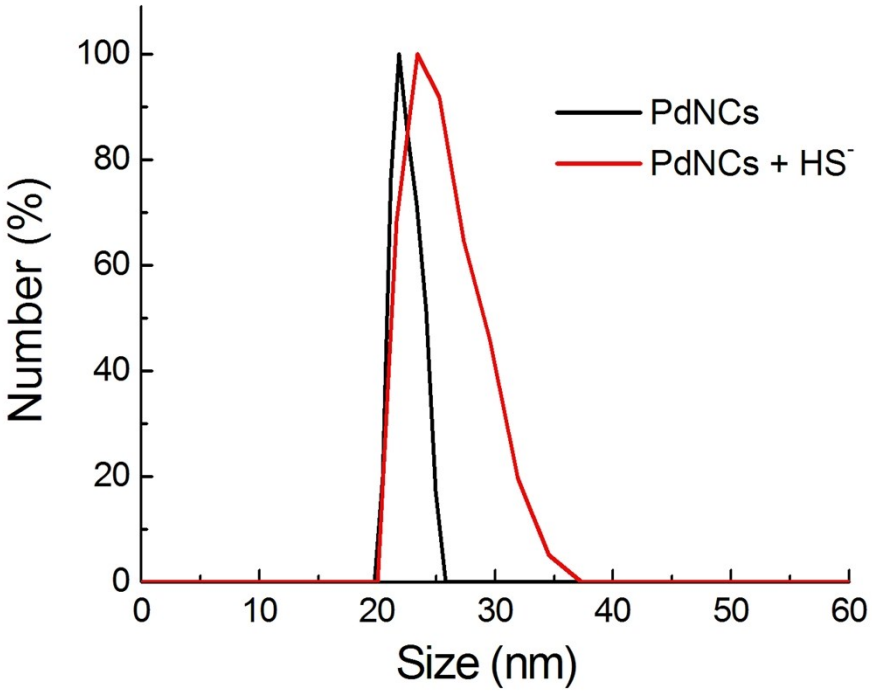

Fig. S2 The hydrodynamic size distribution of PdNCs before and after the addition of NaHS.

DLS measurement showed that the average hydrodynamic size of PdNCs slightly increased from 21.8 nm to 23.4 nm after their reaction with HS^-, accompanying by the broadening of their size distributions (Fig. S2). This evidence also suggested the formation of thin layers of PdS on the surfaces of PdNCs, leading to the increase of their size distribution.

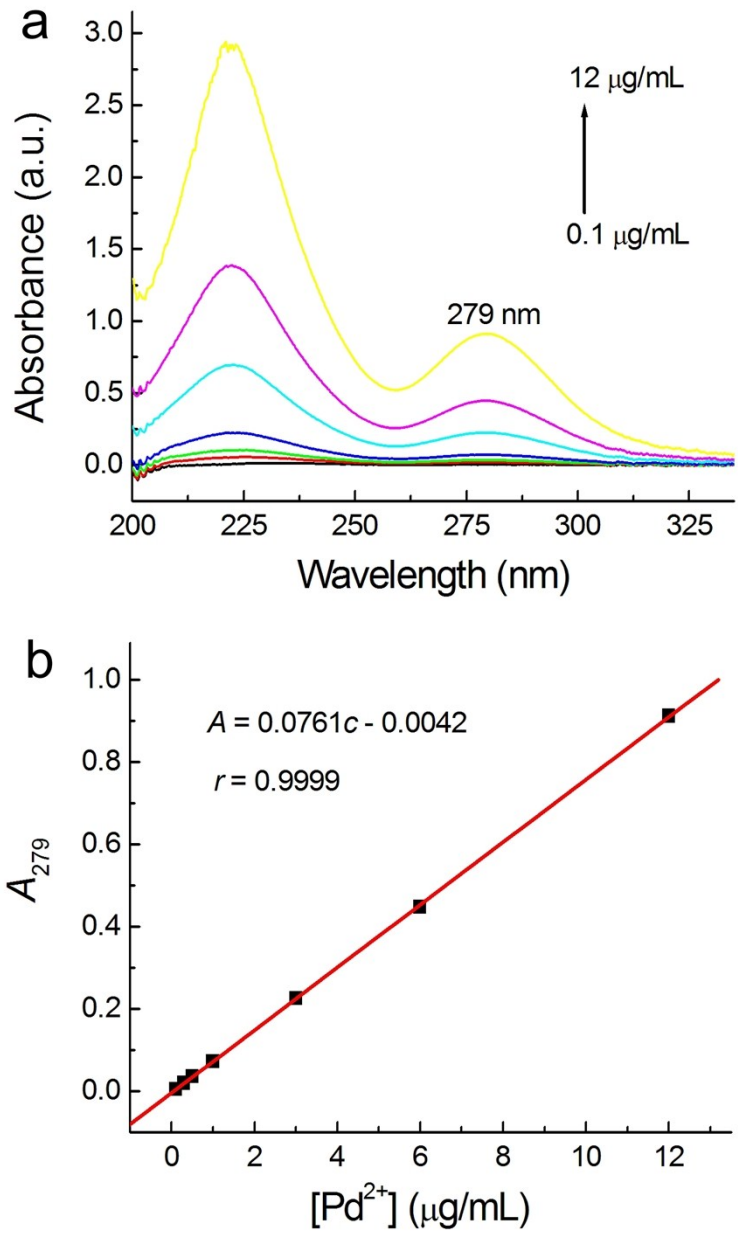

Fig. S3 (a) UV-vis spectra of standard Na_2PdCl_4 solution at different concentrations (0–12 μg/mL). (b) Plot showing the absorbance at 279 nm in the UV-vis spectra as a function of the concentration of $PdCl_4^{2-}$. This fitting curve can be used to calculate the concentration of $PdCl_4^{2-}$ and thus the Pd nanocrystals by measuring the UV-vis spectrum of the sample which was pretreated with aqua regia.

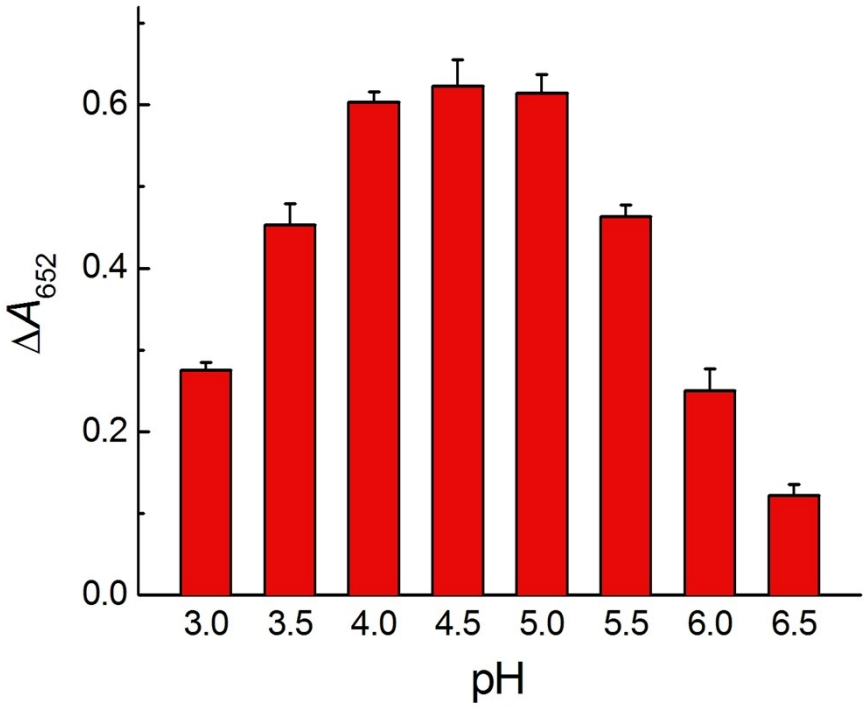

Fig. S4 Study on the pH for sulfide assay. Error bars were obtained from three parallel experiments. The maximal value of the relative absorbance at 652 nm was obtained at pH 4.5.

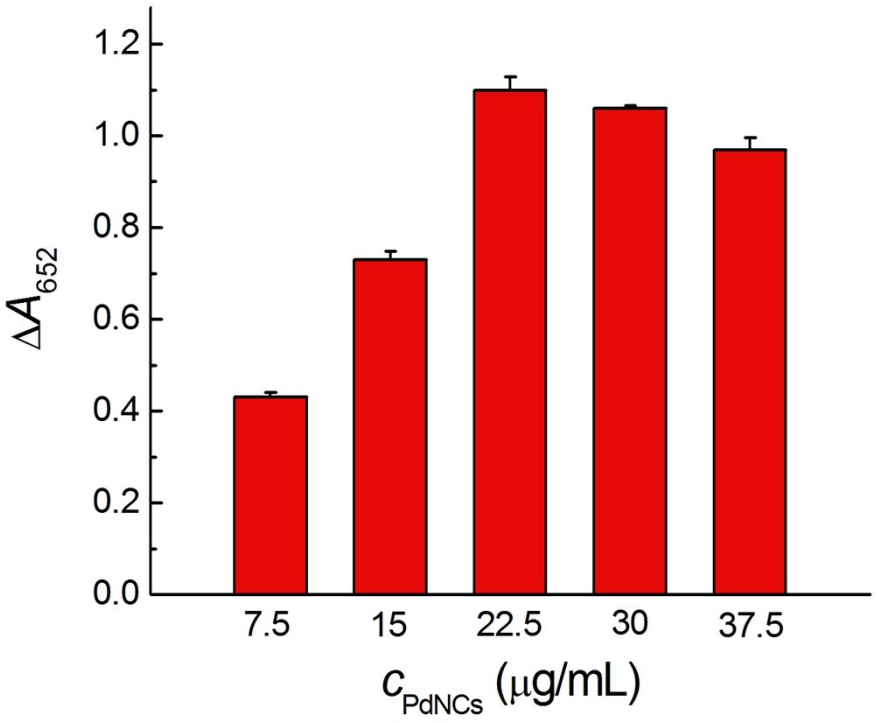

Fig. S5 Study on the concentration of PdNCs for sulfide assay. Error bars were obtained from three parallel experiments. The maximal value of the relative absorbance at 652 nm was obtained when 22.5 μg/mL of PdNCs were added.

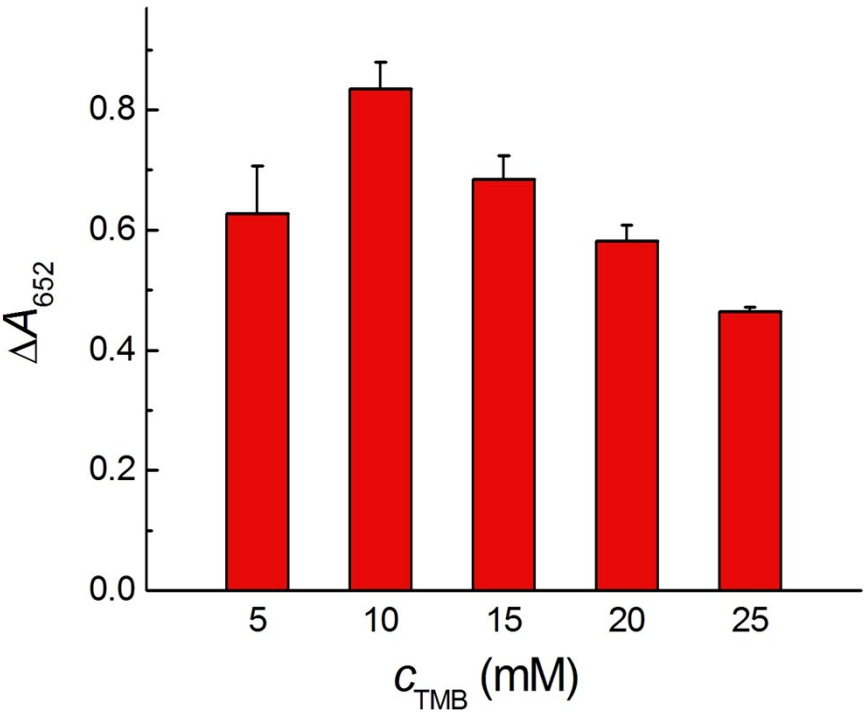

Fig. S6 Study on the concentration of TMB for sulfide assay. Error bars were obtained from three parallel experiments. The maximal value of the relative absorbance at 652 nm was obtained in the presence of 10 mM TMB.

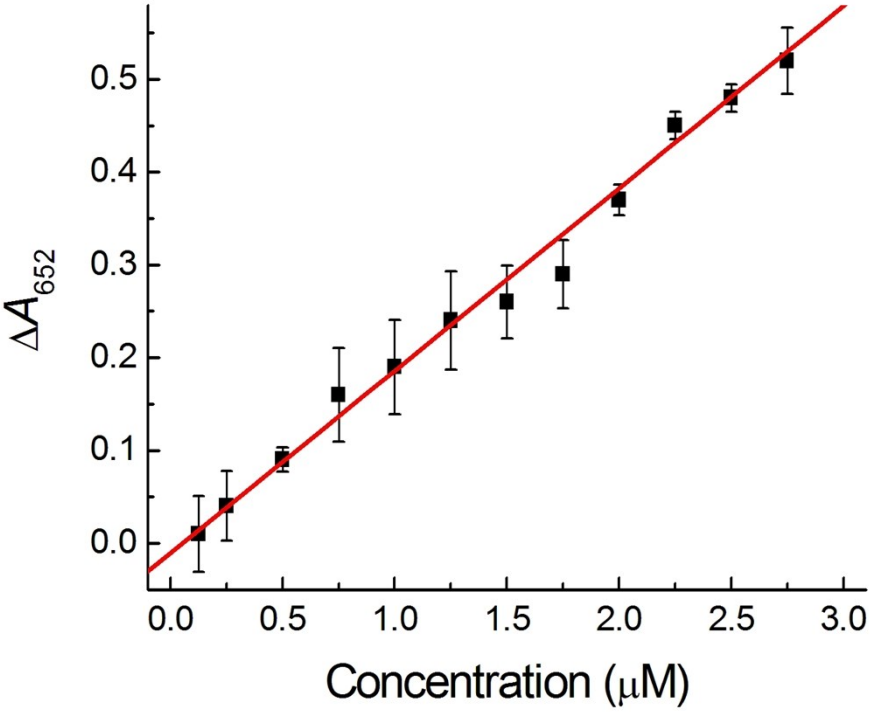

Fig. S7 Plot of the absorbance decrease at 652 nm versus the concentration of added HS^- in a linear range of 0.125–2.75 μM when Pd octahedrons were used as the nanozyme. Error bars represent the standard deviations of three replicate determinations.

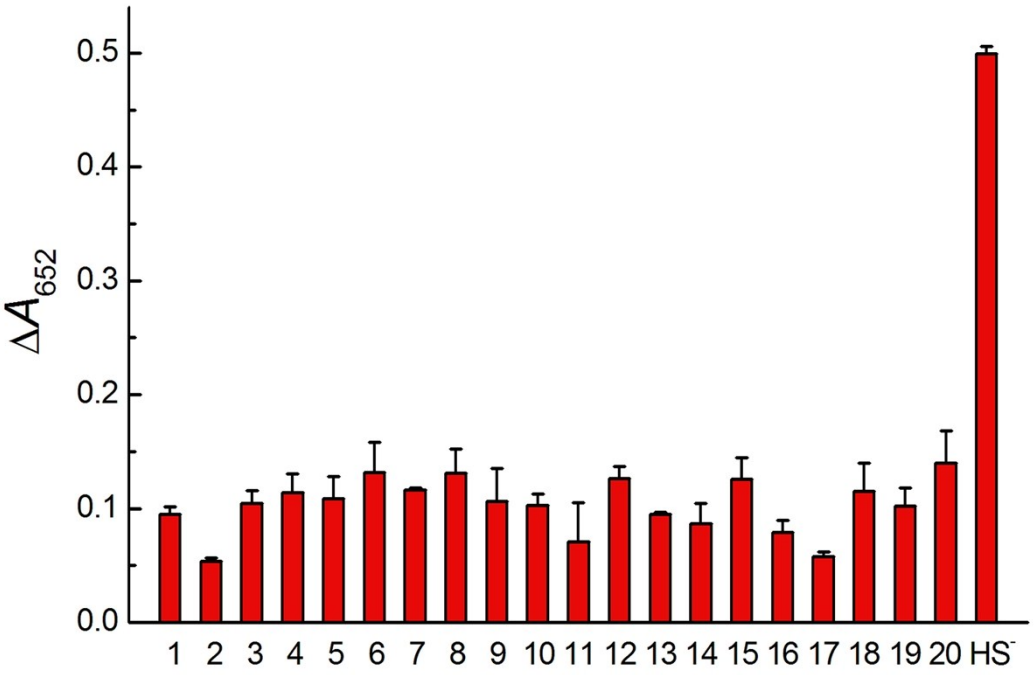

Fig. S8 Selectivity of this analytical method for sulfide assay when Pd octahedrons were used as the nanozyme. Absorbance decrease at 652 nm (ΔA_{652}) in the absence and presence of various ions were recorded using the standard procedure for sulfide detection (1-20: F^-, Cl^-, SO_4^{2-}, NO_3^-, CH_3COO^-, HCO_3^-, SO_3^{2-}, I^-, CO_3^{2-}, Br^-, SiO_3^{2-}, $S_2O_3^{2-}$, HPO_4^{2-}, $H_2PO_4^-$, $S_2O_8^{2-}$, Fe^{3+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}). The concentration of HS^- is 2.5 μM, and the concentrations of other ions are 25 μM. Error bars represent the standard deviations of three replicate measurements.