ELECTRONIC SUPPLEMENTARY INFORMATION

Platinum-based nanodendrites as glucose-oxidase mimicking surrogates

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Calculation of nanozyme concentration

Calculation of k_{cat} was performed assuming a nanozyme concentration determined by different methods:

(1) <u>Total mass of catalyst</u>

Using this assumption, nanozyme concentration is equal to the total amount of Pt atoms measured by MP-AES. We added a theoretical concentration of 0.1 mg NZ · mL^{-1} per catalytic reaction. In the case of AuPt-NDs, the amount of Pt is 57% of total mass:

$$0.1\,\frac{mgAuPt\ NDs}{ml}\cdot\frac{0.57\ mg\ Pt}{1\ mg\ AuPt\ NDs}\cdot\frac{1\ mmolPt}{195.084\ mmol\ Pt}\cdot\frac{1000\ mL}{1\ L}=0.292\ mM\ Pt$$

For Pt-NDs, the amount of Pt is close to 100% of total mass:

$$0.1\,\frac{mg\ Pt\ NDs}{ml}\cdot\frac{1\ mg\ Pt}{1\ mg\ Pt\ NDs}\cdot\frac{1\ mmolPt}{195.084\ mmol\ Pt}\cdot\frac{1000\ mL}{1\ L}=0.512\ mM\ Pt$$

(2) <u>Number of nanoparticles</u>

Nanozyme concentration is considered as the total number of nanoparticles in solution, which is measured by NTA using a nanozyme solution of known concentration in weight (0.1 mg·mL^{-1}).

For AuPt-NDs, $5.33\cdot10^{10}$ particles were measured in a 0.1 mg·mL^{-1} solution.

$$5.33\cdot10^{10}\frac{NPs}{mL}\cdot\ \frac{1\ mol}{6.022\cdot10^{23}NPs}\cdot\frac{1000\ mmol\ NPs}{1mol\ NPs}\cdot\ \frac{1000\ mL}{1\ L}=8.80\cdot10^{-8}\ mM$$

For Pt-NDs, $1.31\cdot10^{10}$ particles were measured in a 0.1 mg·mL^{-1} solution.

$$1.31\cdot10^{10}\frac{NPs}{mL}\cdot\ \frac{1\ mol}{6.022\cdot10^{23}NPs}\cdot\frac{1000mmol\ NPs}{1mol\ NPs}\cdot\ \frac{1000\ mL}{1\ L}=2.17\cdot10^{-8}\ mM$$

(3) Number of surface atoms

Concentration of surface atoms per unit volume is considered as the nanozyme concentration, as it is assumed that atoms in the nanoparticle core are not participating in the catalysis. Two different methods can be used to determine the number of surface atoms. First method calculates surface area using nanoparticle radii obtained by direct measurement via TEM or NTA:

- Using TEM-determined radii to calculate surface of each AuPt nanoparticle:

$$4 \cdot \pi \cdot 27^2 = 9156 \frac{nm^2}{NP}$$

$$9156 \frac{nm^2}{NP} \cdot 5.33 \cdot 10^{10} \frac{NPs}{mL} \cdot \frac{1000\ mL}{1\ L} \cdot \frac{1\ unit\ cell}{0.139\ nm^2} \cdot \frac{2\ \ Pt\ at.}{1\ unit\ cell} \cdot \frac{1000\ mol\ Pt}{6.022 \cdot 10^{23}\ Pt\ at.} \cdot = 1.08 \cdot 10^{-2}\ mM$$

- Using NTA-determined radii to calculate surface of each AuPt nanoparticle:

$$4 \cdot \pi \cdot 44^2 = 24316 \frac{nm^2}{NP}$$

$$24316 \frac{nm^2}{NP} \cdot 5.33 \cdot 10^{10} \frac{NPs}{mL} \cdot \frac{1000\ mL}{1\ L} \cdot \frac{1\ unit\ cell}{0.139\ \ nm^2} \cdot \frac{2\ \ Pt\ at.}{1\ unit\ cell} \cdot \frac{1000\ mol\ Pt}{6.022 \cdot 10^{23}\ Pt\ at.} = 2.88 \cdot 10^{-2}\ mM$$

- Using TEM-determined radii to calculate surface of each Pt nanoparticle:

$$4 \cdot \pi \cdot 40^2 = 20096 \frac{nm^2}{NP}$$

$$20096 \frac{nm^2}{NP} \cdot 1.31 \cdot 10^{10} \frac{NPs}{mL} \cdot \frac{1000\ mL}{1\ L} \cdot \frac{1\ unit\ cell}{0.139\ nm^2} \cdot \frac{2\ \ Pt\ at.}{1\ unit\ cell} \cdot \frac{1000\ mmol\ Pt}{6.022 \cdot 10^{23}\ Pt\ at.} \cdot = 6.46 \cdot 10^{-3}\ mM$$

- Using NTA-determined radii to calculate surface of each Pt nanoparticle:

$$4 \cdot \pi \cdot 96^2 = 115753 \, \frac{nm^2}{NP}$$

$$115753 \, \frac{nm^2}{NP} \cdot 1.31 \cdot 10^{10} \, \frac{NPs}{mL} \cdot \frac{1000 \, mL}{1 \, L} \cdot \frac{1 \, unit \, cell}{0.139 \, nm^2} \cdot \frac{2 \, Pt \, at.}{1 \, unit \, cell} \cdot \frac{1000 \, mol \, Pt}{6.022 \cdot 10^{23} \, Pt \, at.} = 3.38 \cdot 10^{-2} \, mM$$

Second approach consists in measuring the area of metal atoms per gram of nanoparticle using BET:

- For AuPt-NDs, 20.5 m^2 of surface was found in 1 g of catalyst.

$$\frac{0.1 \, mg \, AuPt \, NDs}{ml} \cdot \frac{1000 \, mL}{1 \, L} \cdot \frac{1g \, Pt}{1000 \, mg \, Pt} \cdot \frac{20.5 \, m^2 \, Pt}{g \, Pt} \cdot \frac{1 \, unit \, cell}{1.39 \cdot 10^{-19} \, m^2} \cdot \frac{2 \, Pt \, at}{1 \, unit \, cell} \cdot \frac{1000 \, mmol \, Pt}{6.022 \cdot 10^{23} \, at. \, Pt} = 4.56 \cdot 10^{-2} \, mM$$

- For Pt-NDs, 2.57 m^2 of surface was found in 1 g of catalyst.

$$\frac{0.1 \, mg \, Pt \, NDs}{ml} \cdot \frac{1000 \, mL}{1 \, L} \cdot \frac{1g \, Pt}{1000 \, mg \, Pt} \cdot \frac{2.57 \, m^2 \, Pt}{g \, Pt} \cdot \frac{1 \, unit \, cell}{1.39 \cdot 10^{-19} \, m^2} \cdot \frac{2 \, Pt \, at}{1 \, unit \, cell} \cdot \frac{1000 \, mmol \, Pt}{6.022 \cdot 10^{23} \, at. \, Pt} = 5.72 \cdot 10^{-3} \, mM$$

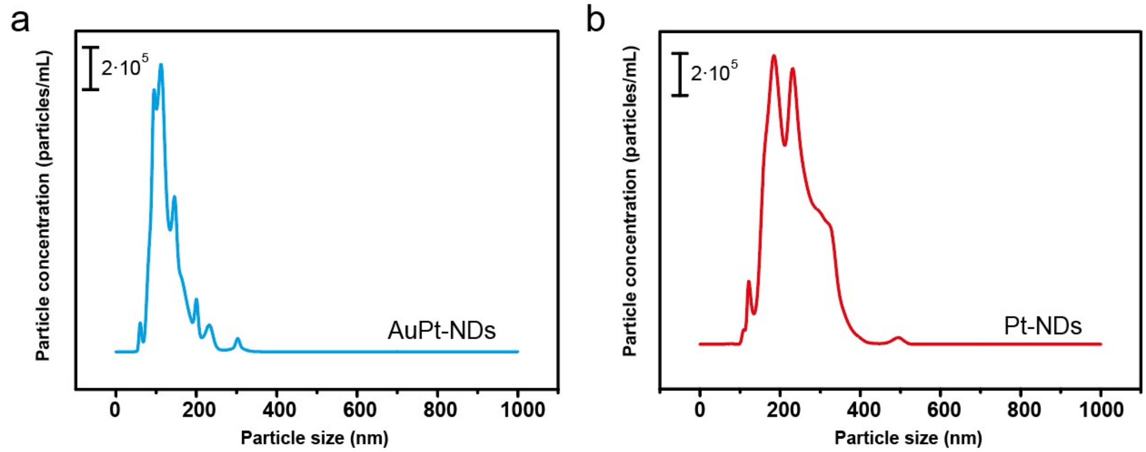

Figure ESI-1: *Size distribution determined by NTA: (a) Particle size distribution histograms corresponding to AuPt NDs; (b) Particle size distribution histograms corresponding to Pt NDs.*

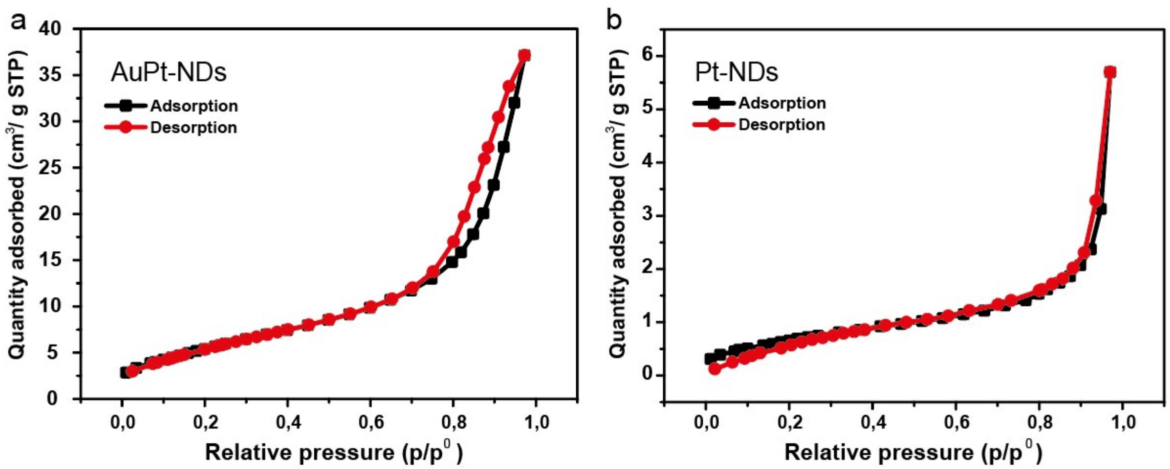

Figure ESI-2: *(a) N_2 adsorption isotherm at 77 K of AuPt ND with a specific surface area of 20.5 m^2/g; (b) N_2 adsorption isotherm at 77 K of Pt ND with a specific surface area of 2.57 m^2/g.*

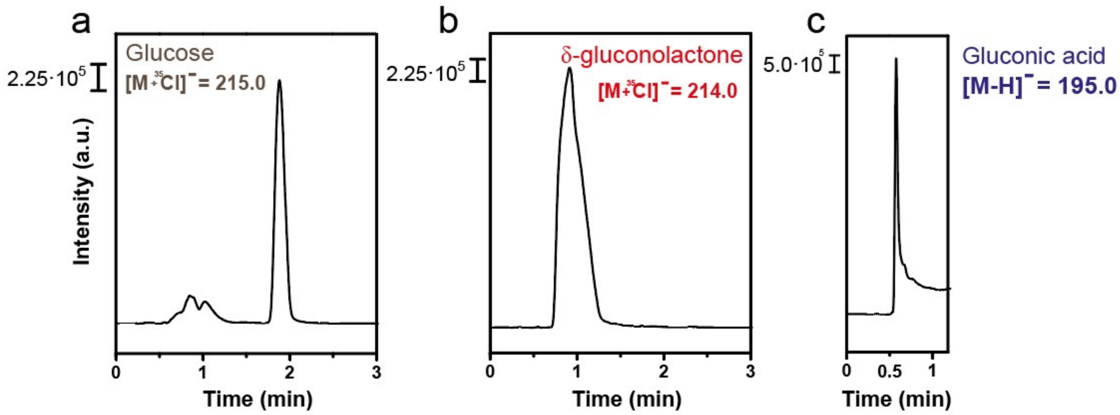

Figure ESI-3: *MS analysis of reaction and by-product adducts: (a) Glucose standard characterization. [Glu-Cl] adduct was detected by the coupled ACQUITY QDa mass detector with an m/z = 215.0; (b) δ-gluconolactone standard characterization. [δ-glu-Cl] adduct was detected by the coupled ACQUITY QDa mass detector with an m/z = 214.0; (c) gluconic acid standard characterization. [G.A-H] detected by the coupled ACQUITY QDa mass detector with an m/z = 195.0. Analysis were performed by UPLC-MS and separated with the aid of a BEH AMIDE® UPLC column at 85 ºC.*

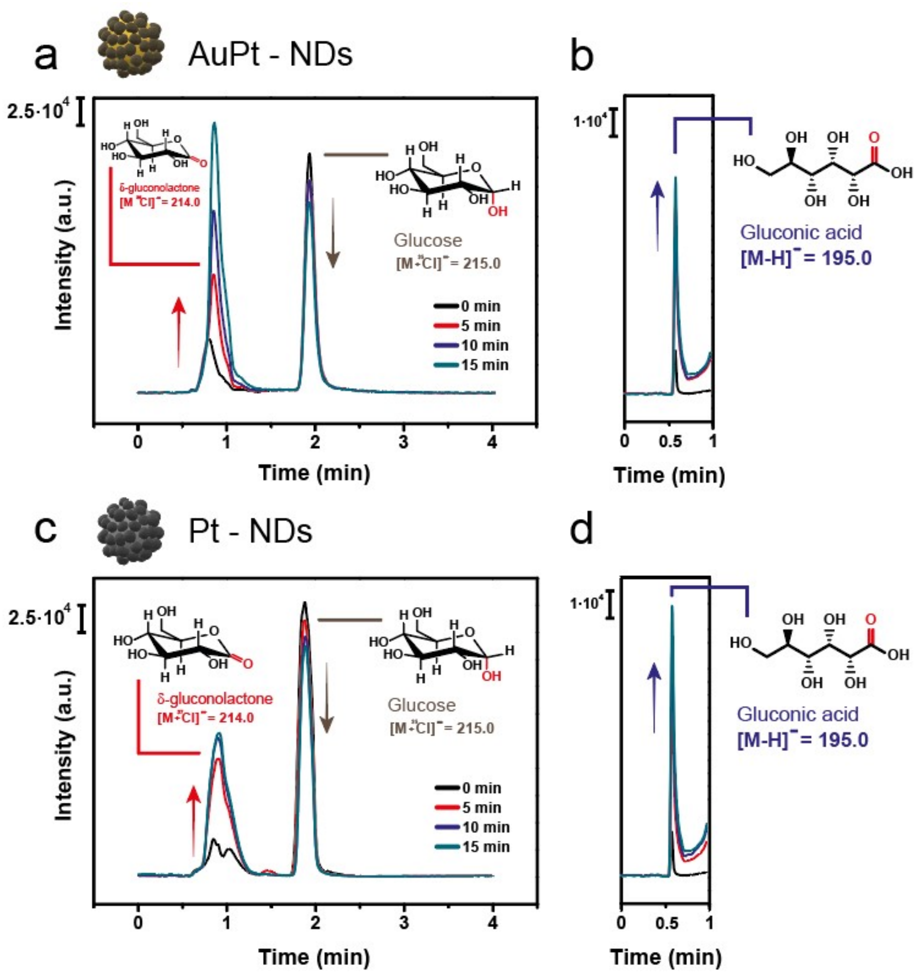

Figure ESI-4: *(a) Catalytic reaction of AuPt NDs monitored by UPLC-MS after 0, 5, 10 and 15 minutes reaction. Glucose depletion with a retention time of 1.92 minutes and a [Glu-Cl] adduct with an m/z = 215.0, δ-gluconolactone formation appeared with a retention time of 0.98 minutes and a [δ-glu-Cl] adduct with an m/z = 214.0, gluconic acid formation appeared with a retention time of 0.55 minutes and a [G.A.-H] with an m/z = 195.0; (b) Catalytic reaction of Pt NDs monitored by UPLC-MS after 0, 5, 10 and 15 minutes reaction. Glucose depletion with a retention time of 1.92 minutes and a [Glu-Cl] adduct with an m/z = 215.0, δ-gluconolactone formation appeared with a retention time of 0.98 minutes and a [δ-glu-Cl] adduct with an m/z = 214.0, gluconic acid formation appeared with a retention time of 0.55 minutes and a [G.A.-H] with an m/z = 195.0.*

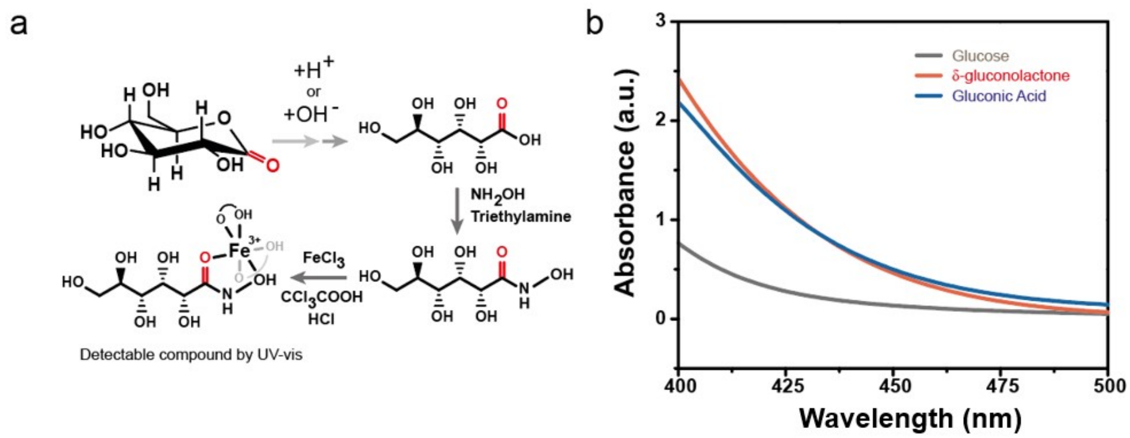

Figure ESI-5: *(a) Schematic illustration of the conversion of δ-gluconolactone into gluconic acid during the reaction with hydroxylamine and trivalent Fe salt to form a red colored Fe-hydroxamate complex; (b) absorption spectra of glucose, δ-gluconolactone and gluconic acid treated with hydroxylamine and trivalent Fe salt to perform colored characterization.*

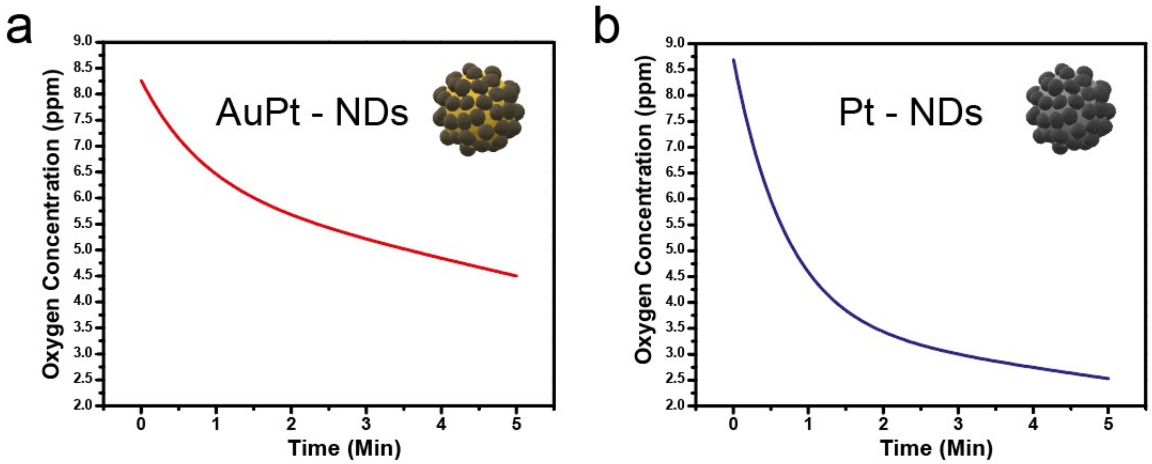

Figure ESI-6: *(a) Oxygen consumption in glucose oxidation reaction with AuPt NDs, (b) oxygen consumption in glucose oxidation reaction with Pt NDs. Reaction conditions; pH: 7.4; [Cat]: 0.1mg·ml^{-1}; [Glu]: 5.5 mM; Room Temperature.*