

Supporting Information

Nanodiamond-Gold Nanocomposites with the Peroxidase-like Oxidative Catalytic Activity

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1. Size distribution of gold nanoparticles generated on ND surface

The size distribution of gold nanoparticles was measured based on 10 TEM images ($n = 258$).

Gold nanoparticles had diameters between 3–55 nm.

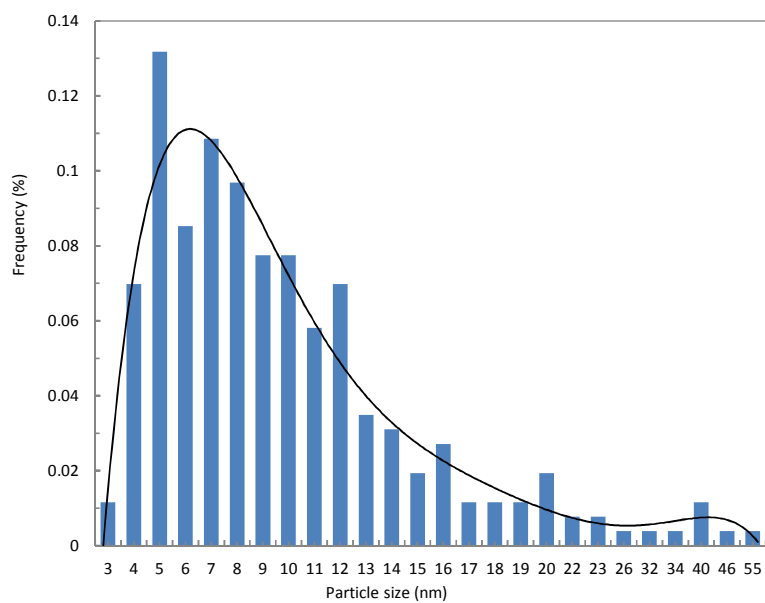


Figure S1. Size distribution of gold nanoparticles generated on the nanodiamond surface.

2. EDX analysis of NDAus

Energy dispersive X-ray spectra of NDAus exhibited a peak due to gold, supporting the presence of gold nanoparticles on the ND surface.

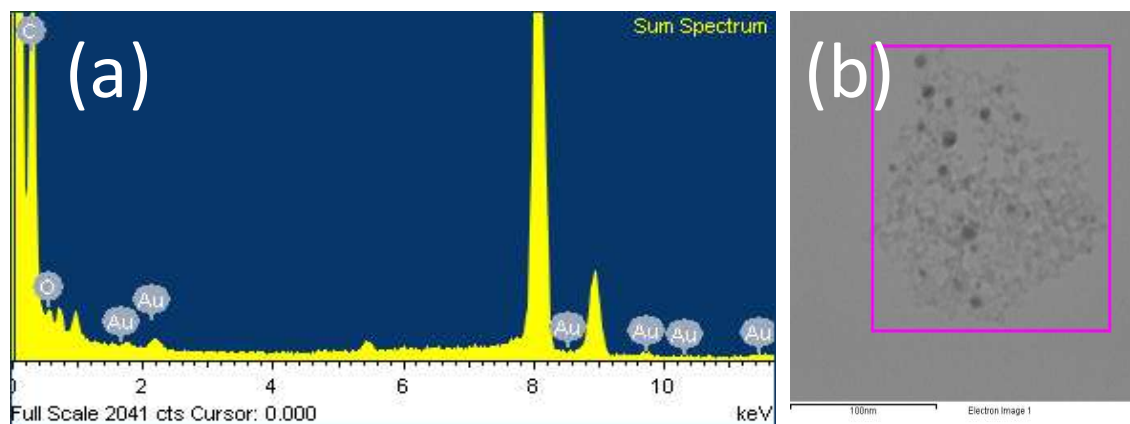


Figure S2. (a) EDX spectrum and (b) corresponding TEM image of NDAus. The pink box indicates the sample area where EDX signals were collected.

3. Size and apparent zeta potential of ND and NDAus

The characteristics of aqueous NDAus dispersions were examined using the zeta potential and dynamic light scattering. The sizes of NDAus were significantly increased to 109 ± 6.9 nm compared to those of bare ND particles (66 ± 9.5 nm). The apparent zeta potential of NDAus was slightly increased to -39 mV compared to -36 mV for bare ND-COOH.

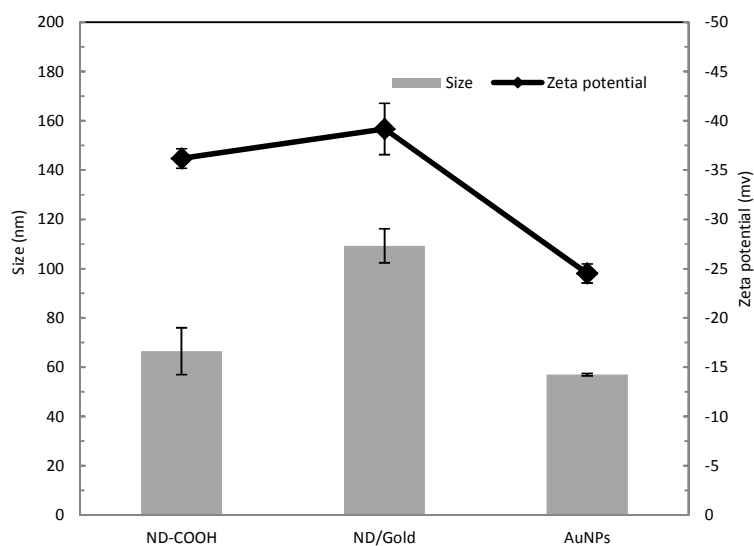


Figure S3. Hydrodynamic diameter and zeta potential of intact ND, NDAus, and gold nanoparticles. All data are average \pm standard deviation ($n = 5$).

4. HPLC-Mass spectrometry of 2,3-diaminophenazine produced by the OPD oxidation

2,3-Diaminophenazine was produced by the catalytic oxidation of *o*-phenylenediamine (OPD). After the catalytic oxidative reaction of OPD (10 mM), the solution was analyzed using HPLC-mass spectrometry (TSQ Quantiva, Thermo Scientific, Thermo Hypersil gold C18 column). The mass spectrum shows production of 2,3-diaminophenazine (Mw: 210.23) without other by product. Absence of OPD (Mw: 109.56) trace implies almost complete conversion of the OPD substrate by the catalytic oxidative reaction.

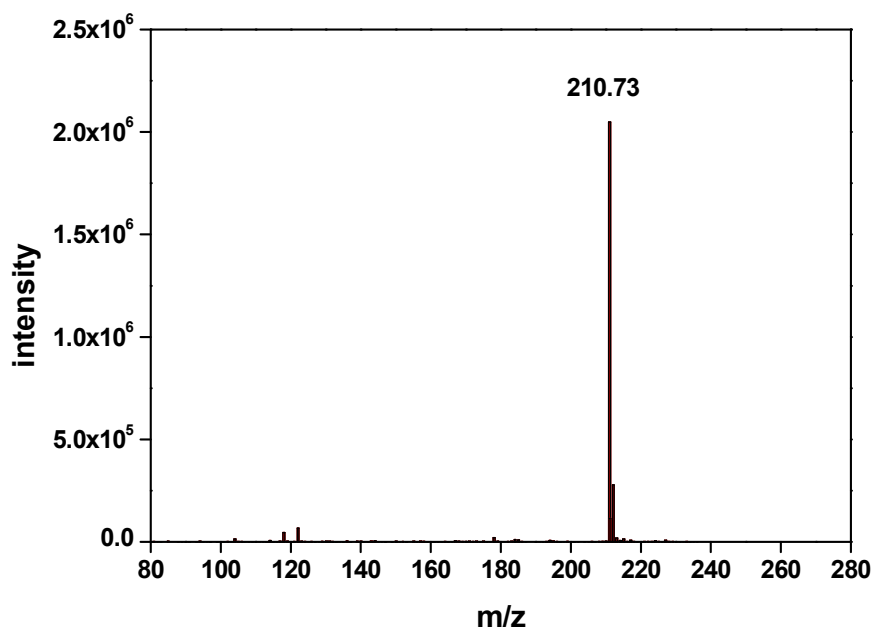


Figure S4. HPLC-mass spectrum of 2,3-diaminophenazine produced by the catalytic oxidation of *o*-phenylenediamine.

5. Comparison of K_M with other carbon-metal composite catalysts

Michaelis constant (K_M) of NDAu was compared with those of other carbon-metal catalyst reported in literatures. All carbon-metal catalysts cited here used TMB (3,3',5,5'-tetramethylbenzidine) as an organic substrate, not OPD (*o*-phenylenediamine). Therefore, direct comparison of kinetic parameter is improper.

Table S1. Comparison of Michaelis constants of various carbon-metal composite catalysts

Catalyst	K_M (mM)		Ref. [†]
	TMB	H ₂ O ₂	
GO-AuNCs	0.16	142.4	1
Graphene-Au NPs	0.14	140.5	2
Fe-doped GO	0.76	0.36	3
SWCNT-AuNPs	n/a	0.21	4
Silica-coated graphene-AuNPs	0.005	5.98	5
SWCNT-AuNPs	0.48	0.65	6
Graphene-Fe ₃ O ₄ -AuNPs	0.20	0.20	7
Graphene-AuNPs	0.38	26.4	8
Graphene-Pt nanoflowers	0.52	25.31	9
ND-AuNPs (this work)*	6.4-48.7	89.7-208.7	

* OPD was used as an organic substrate, while other K_M values were obtained from the experiments using TMB as a substrate.

[†] References are given at the end of this Supporting Information.

6. Change of gold nanoparticles after reuse

Re-used NDAus had larger gold nanoparticles than fresh ones. TEM imaging of re-used NDAu was conducted after five reuse cycles (see below). Every catalytic reuse experiment was carried out at pH 7.2 using OPD (5 mM) and H₂O₂ (20 mM) substrates in the presence of 0.12 mg mL⁻¹ NDAus for 400 seconds.

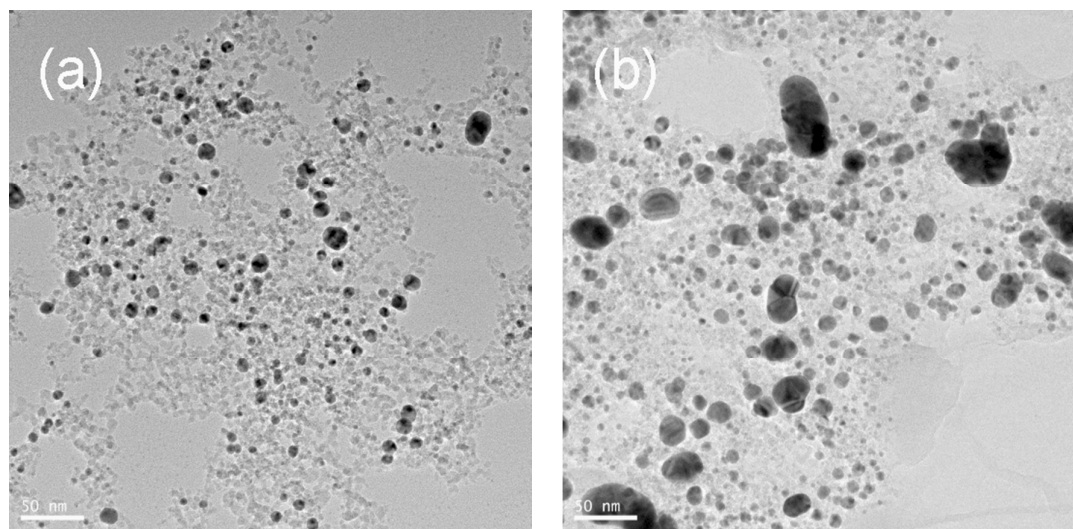


Figure S5. TEM images of NDAus. (a) Fresh NDAus, (b) NDAus after five reuse cycles (scale bar: 50 nm).

7. Combinational catalysis of XOD and NDAus for the detection of xanthine

The solution color changed only when both XOD and NDAus were present. In absence of one of these components, the solution remained transparent, indicating no oxidation of OPD.

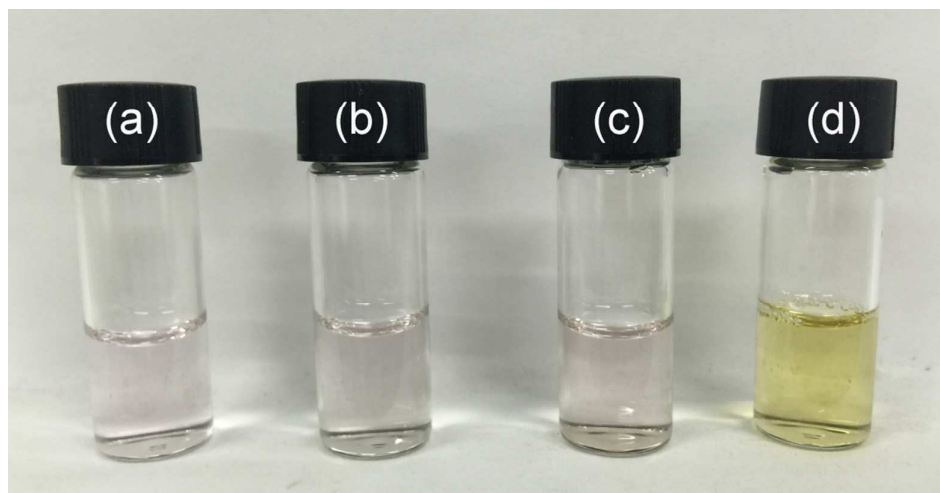


Figure S6. Oxidation of OPD in the presence of both XOD and NDAus. The solutions are (a) NDAus + OPD, (b) NDAus + OPD + xanthine, (c) NDAus + OPD + XOD, and (d) NDAus + OPD + xanthine + XOD. The concentrations of each component were 0.04 mg mL^{-1} NDAus, 10 mM OPD, 1 mM xanthine, and 1.83 units of XOD, respectively.

8. UV-vis spectra of the OPD oxidation reaction mixture

The progress of OPD oxidation utilizing the combinational catalysis of XOD and NDAus was monitored using the intensity change of the UV-vis absorbance peak at 430 nm.

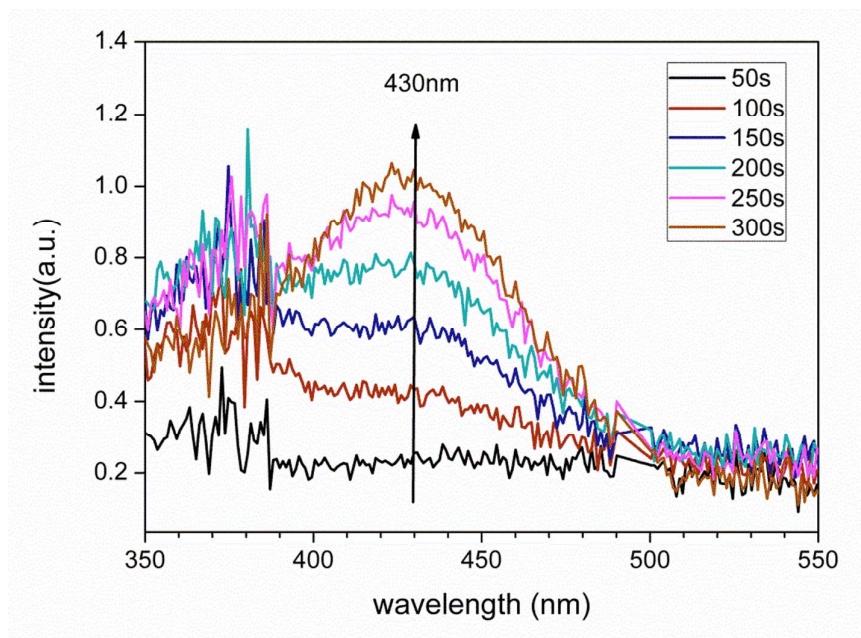


Figure S7. UV-vis spectra representing the progress of OPD oxidation with time. The sample system shown here is composed of 0.04 mg mL^{-1} NDAus, 10 mM OPD, 1 mM xanthine, and 1.83 units of XOD.

References of Supporting Information

1. Tao, Y.; Lin, Y.; Huang, Z.; Ren, J.; Qu, X. Incorporating Graphene Oxide and Gold Nanoclusters: A Synergistic Catalyst with Surprisingly High Peroxidase-Like Activity over a Broad pH Range and its Application for Cancer Cell Research. *Adv. Mater.*, **2013**, *25*, 2594-2599.
2. Liu, M.; Zhao, H.; Chen, S.; Yu, H. Quan, X. Stimuli-Responsive Peroxidase Mimicking at a Smart Graphene Interface, *Chem. Commun.*, **2012**, *48*, 7055-7057.
3. Dong, Y.; Li, J.; Shi, L.; Guo, Z. Iron Impurities as the Active Sites for Peroxidase-like Catalytic Reaction on Graphene and its Derivatives. *ACS Appl. Mater. Interface*, **2015**, *7*, 15403-15413.
4. Zhang, Y.; Xu, C.; Li, B.; Li, Y. InSitu Growth of Positively-Charged Gold Nanoparticles on Single-Walled Carbon Nanotubes as a Highly Active Peroxidase Mimetic and its Application in Biosensing. *Biosens. Bioelec.*, **2013**, *43*, 205-210.
5. Maji, S. K.; Mandal, A. K.; Nguyen, K. T.; Brah, P.; Zhao, Y. Cancer Cell Detection and Therapeutics Using Peroxidase-Active Nanohybrid of Gold Nanoparticle-Loaded Mesoporous Silica-Coated Graphene. *ACS Appl. Mater. Interface* , **2015**, *7*, 9807-9816.
6. Haider, W.; Hayat, A.; Raza, Y.; Chaudhry, A. A.; Rehman, I. U.; Marty J. L. Gold Nanoparticle Decorated Single Walled Carbon Nanotube Nanocomposite with Synergistic Peroxidase Like Activity for D-Alanine Detection, *RSC Adv.*, **2015**, *5*, 24853-24858.
7. Yuan, F.; Zhao, H.; Zang, H.; Ye, F. Quan, X. Three-Dimensional Graphene Supported Bimetallic Nanocomposites with DNA Regulated-Flexibly Switchable Peroxidase-Like Activity. *ACS Appl. Mater. Interface*, **2016**, *8*, 9855-9864.

8. Chen, X.; Tian, X.; Su, B.; Huang, Z.; Chen, X.; Oyama, M. Au nanoparticles on Citrate-Functionalized Graphene Nanosheets with a High Peroxidase-like Performance. *Dalton Trans.*, **2014**, *43*, 7449-7454.
9. Chen, X.; Su, B.; Cai, Z.; Chen, X.; Oyama, M. PtPd Nanodendrites Supported on Graphene Nanosheets: A Peroxidase-like Catalyst for Colorimetric Detection of H₂O₂. *Sens. Actuator B*, **2014**, *201*, 286-292.