Electronic Supplementary Information (ESI)

Mussel-Inspired Green Synthesis of Silver Nanoparticles on Graphene Oxide Nanosheets for Enhanced Catalytic Applications

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Experimental

Preparation of acetonide protected dopamine (Dopa*) Acetonide protected dopamine was prepared following a literature procedure (Zhongqiang Liu, Bi-Huang Hu, and Phillip B. Messersmith, *Tetrahedron Letters*, **2010**, 51, 2403).

Phth-dopamine. 5.5 g *N*-carbethoxyphthalimide (25 mmol) and 4.5 g dopamine hydrochloride (25 mmol) were added in 150 mL methanol and stirring. The mixture was degassed with nitrogen for 30 min, followed by addition of 14 mL triethylamine (100 mmol). The mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation and then the residue was treated with 30 mL of 1 M HCl. After the mixture was extracted with ethyl acetate, the organic layer was washed with 1 M HCl and water. The solution was dried over $MgSO_4$, and evaporated to give a yellow solid, which was

recrystallized in EtOAc/hexane to give pale yellow crystals, 3.79 g (53.4%).

¹H NMR (600 MHz, DMSO-d_6): δ (ppm) = 8.86 - 8.57 (catecholic protons), 7.84 (m, 4H), 6.57 (m, 2H), 6.39 (m, 1H), 3.71 (t, 2H, J = 7.4 Hz), 3.30 (water), 2.72 (t, 2H, J = 7.4 Hz).
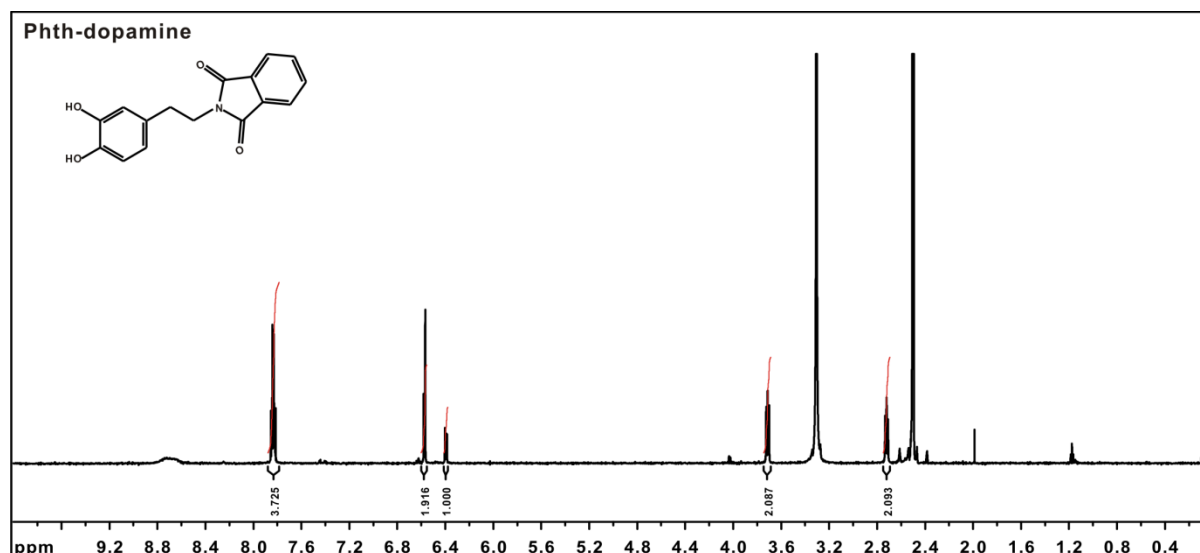

Phth-dopamine(acetonide). 2.5 g Phth-dopamine (10 mmol) and 4.45 mL DMP (2 equiv) were added in anhydrous benzene (100 mL). One neck of the flask was fitted with a Soxhlet extractor, the thimble of which was filled with 14 g of anhydrous CaCl₂; the other neck of the flask was sealed with a septum for sampling purpose. After the system was degassed with a nitrogen for 5 min, 67 mg p-toluenesulfonic acid monohydrate (2.0 mol%) was added. The reflux was stopped after 2 h. The mixture was cooled down, and filtered through a short silica-gel column, which was washed with DCM. The combined filtrate and washings were evaporated to produce a light yellow solid, which was recrystallized in DCM/hexane to give white crystals, 1.62 g (57%).

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.83 (m, 2H), 7.70 (m, 2H), 6.67-6.61 (m, 3H), 3.86 (t, 2H, J = 7.8 Hz), 2.88 (t, 2H, J = 7.8 Hz), 1.65 (s, 6H).

Phth-dopamine(acetonide)
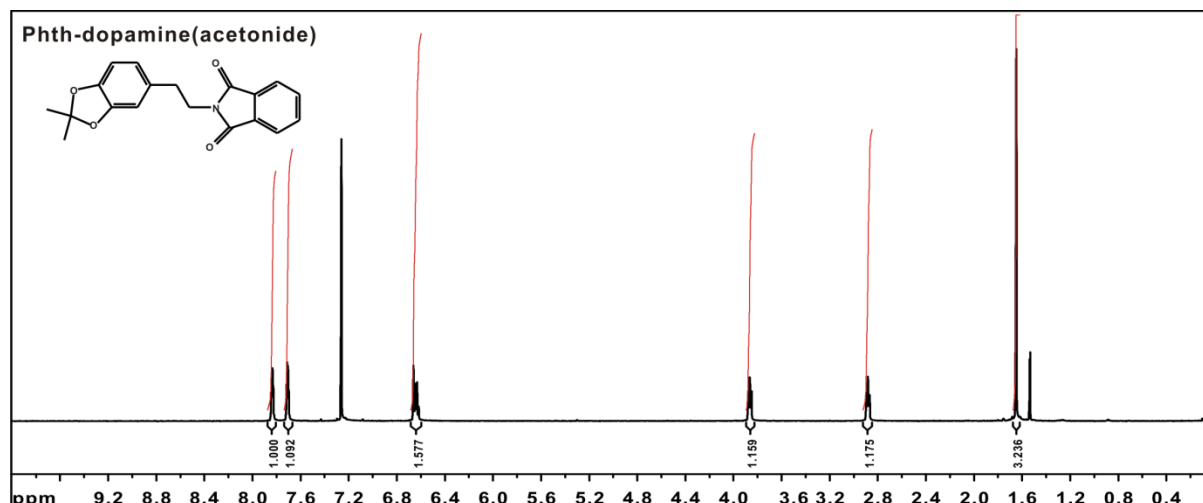
Dopamine(acetonide). 1.20 g Phth-dopamine(acetonide) and 2.5 mL hydrazine monohydrate (10 equiv) were added to a solution mixture of 50 mL methanol and 50 mL DCM. The mixture was stirred at room temperature for 3 days. The white precipitate was removed by filtration and washed with DCM. The combined filtrate was concentrated by rotary evaporation. After addition of 50 mL DCM, the mixture was stirred for another day. The filtrate was concentrated and dried under vacuum to produce light yellow oil, 0.57 g (81.3%) ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) = 6.67-6.58 (m, 3H), 2.92 (t, 2H), 2.66 (t, 2H), 1.67 (s, 6H), 1.34 (br, 2H).

Dopamine(acetonide)
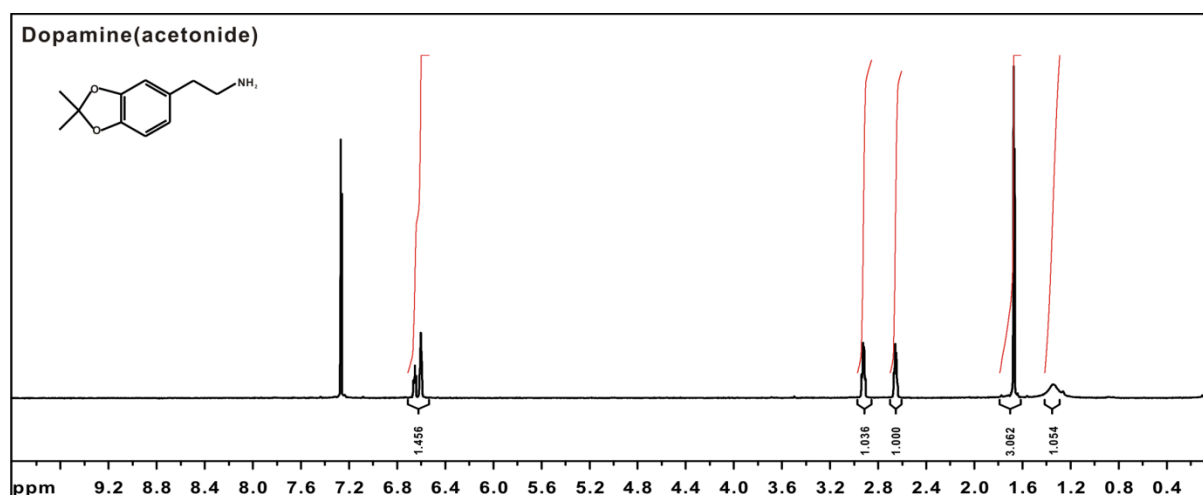
Preparation of GO and GO-Dopa. Graphite oxide was synthesized from graphite powder (Aldrich) by the modified Hummers method and exfoliated to give a brown dispersion of graphene oxide (GO) under ultrasonication. The GO powder dissolved in a known volume of

water is subjected to ultrasonication for 40 min to give a stable suspension of GO (conc. 0.50 mg mL^{-1}) and then centrifuged at 4000 rpm for 10 min to remove any aggregates remaining in the suspension. The synthesized 100 mg of Dopa* was added in 100 mL GO suspension with 125 mg EDC (Aldrich) and stirred for 12 h. The resulting suspension was dialyzed (MWCO 12000-14000, Spectra/Por) for 3 days to remove any residues and byproduct. For the hydrolysis of acetonide protecting group, 0.6 mL of TFA was added to 40 mL of GO-Dopa* solution and stirred for 3 h with a subsequent dialysis for an additional day. The self-polymerization of dopamine was strictly controlled under controlled pH conditions (pH 3.3 – 3.5) and N_2 purging.

Preparation of hybrid Ag/GO-Dopa. To a 5 mL solution of GO-Dopa (pH 3.4), 464 μL of aqueous AgNO$_3$ solution (58.9 mM) was added in order to afford the 5 mM GO-Dopa solution (concentration based on Ag). The mixture was stirred for 3 h at room temperature. Then the mixture was dialyzed for 12 h to remove any unreacted salts and residues.

Catalytic reduction of 4-nitrophenol by hybrid Ag/GO-Dopa catalyst. To a 2 mL (5×10^{-5} M) of aqueous 4-nitrophenol (>99%, Aldrich) solution was mixed with 0.8 mL (0.1 M) of fresh NaBH$_4$ (800 equiv. to the substrate, Aldrich) solution. 9 μL of Ag/GO-Dopa aqueous solution (0.05 wt %, 0.5 mol % with respect to the Ag concentration) was added. The mixture was transferred into a quartz cuvette immediately for measurement with UV/vis spectroscopy. The concentration of 4-nitrophenol was determined at a wavelength of 400 nm.

Characterizations. The structure analysis was studied using Fourier-transform infrared (FT-IR) spectrophotometer (Varian, Cray 660) and UV/vis absorption spectra (Varian, Cary 5000). The morphology, size, and size distributions of the Ag nanoparticles were investigated using transmission electron microscopy (TEM, JEOL JEM-2100, accelerating voltage of 200 kV, Gatan CCD camera). X-ray diffraction (XRD) measurements were carried out with a high-resolution X-ray diffractometer (Bruker Co.) from 10 to 80. The surface morphology of the sample was examined using an atomic force microscope (AFM, Dimension D3100, Veeco). The concentration of Ag nanoparticles in Ag/GO-Dopa aqueous solution was analyzed using inductively coupled plasma-mass spectrometer (ICP/MS, Perkin Elmer Co.).
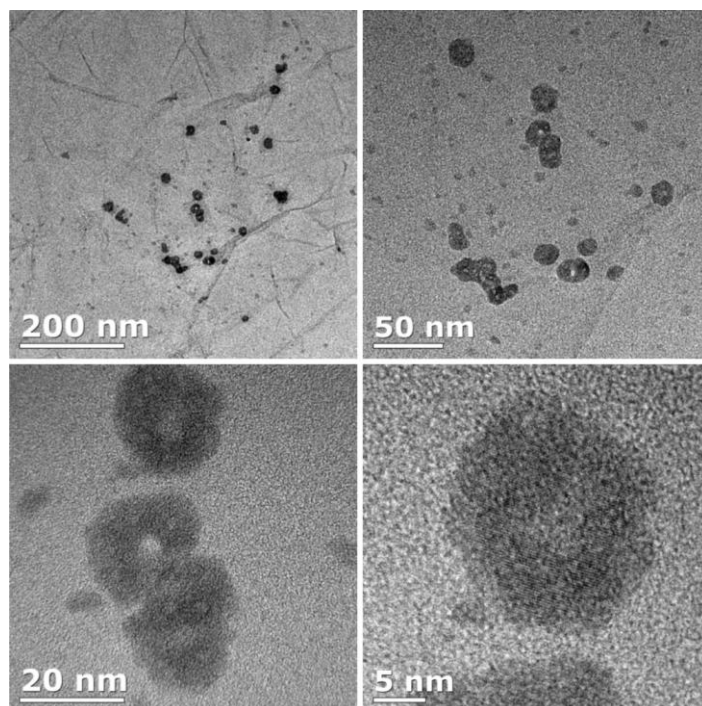
Fig. S1 Representative TEM images of Ag/GO prepared without the dopamine functionalization.
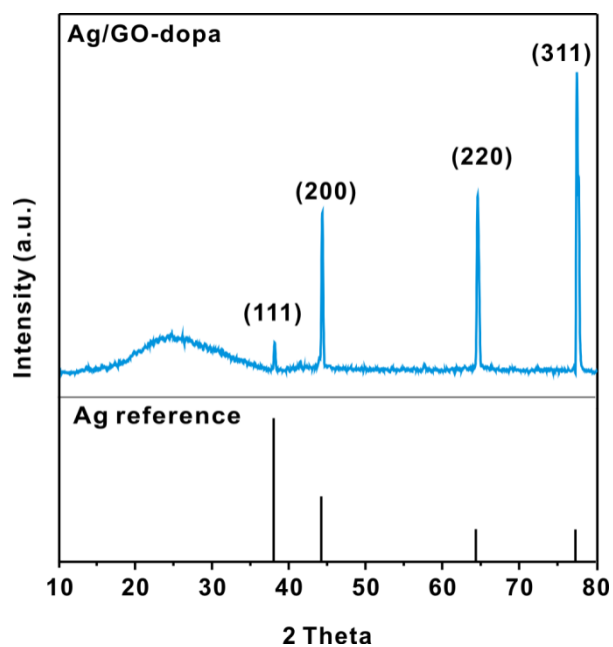

Fig. S2 XRD of Ag/GO-Dopa with a reference. It is of note that the unconventional (311) orientation is noticeably higher than the major (111) peak from standard Ag reference, thus reflecting the different crystal growth direction of Ag NPs over the surface of GO-Dopa.
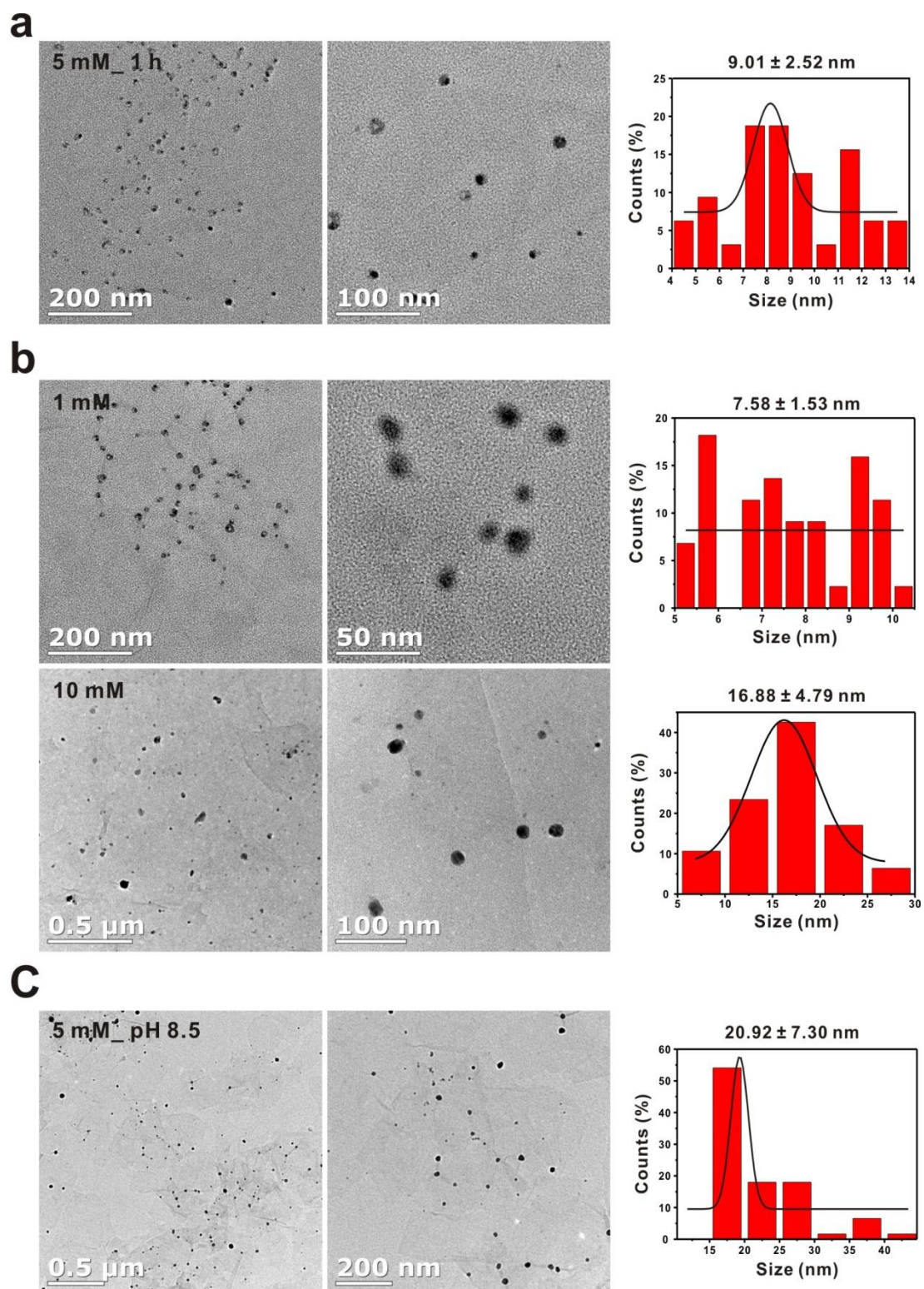
S5

Fig. S3 Representative TEM images of the Ag/GO-Dopa under various reaction conditions. (a) controlled reaction time, (b) different concentration of $AgNO_3$ precursor, and (c) the solution pH.
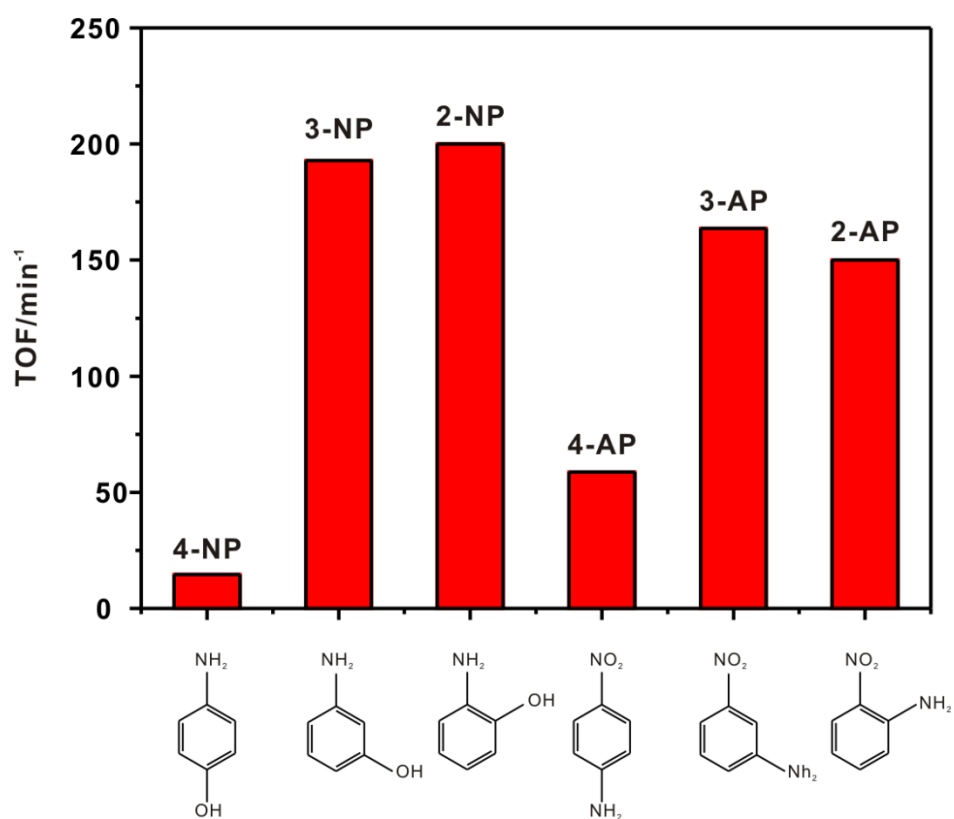
Fig. S4 The catalytic reduction of various nitroarenes by the hybrid Ag/GO-Dopa catalyst.
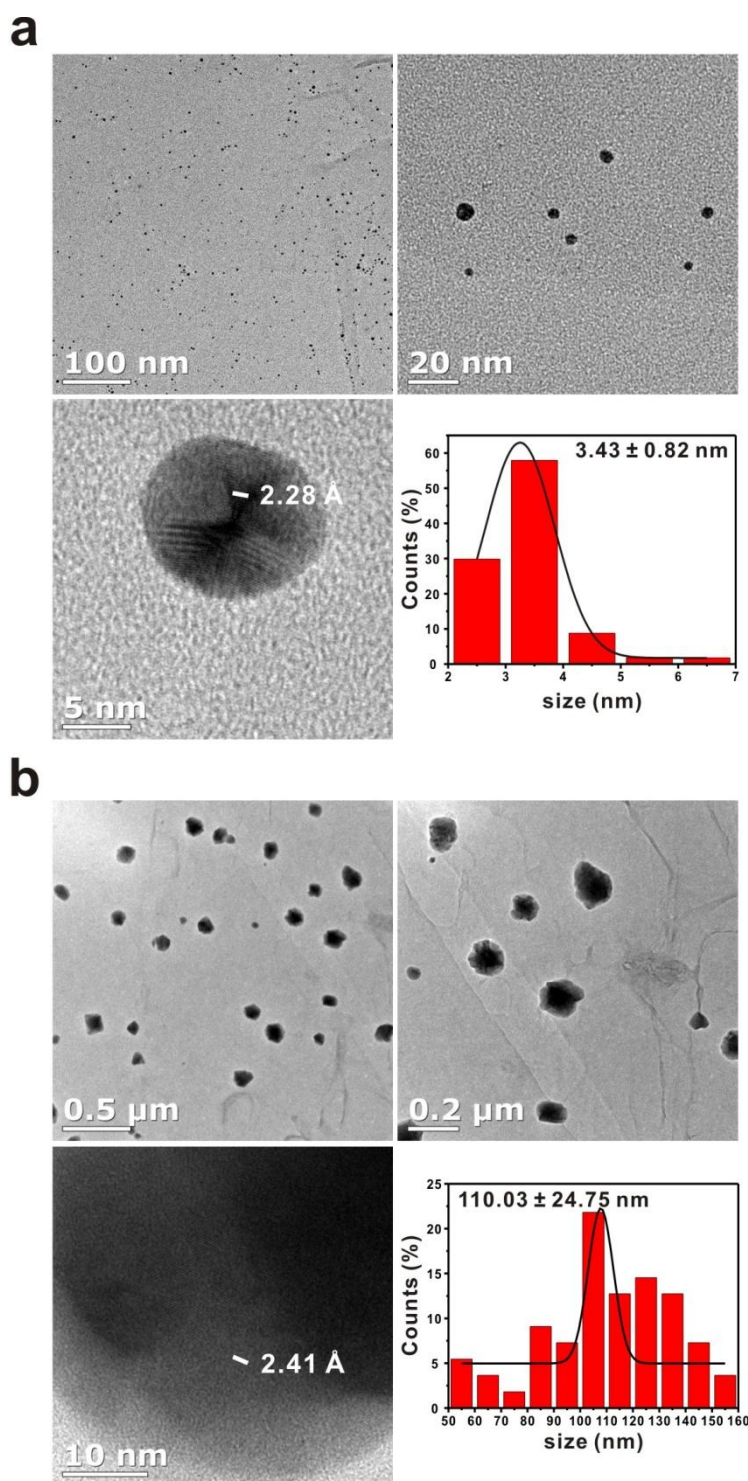
Fig. S5 Representative TEM images of (a) Au/GO-Dopa and (b) Cu/GO-Dopa with a corresponding size distribution histogram of nanoparticles.