Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Controlled synthesis and synergistic effect of graphene-supported PdAu bimetallic nanoparticles with tunable catalytic properties

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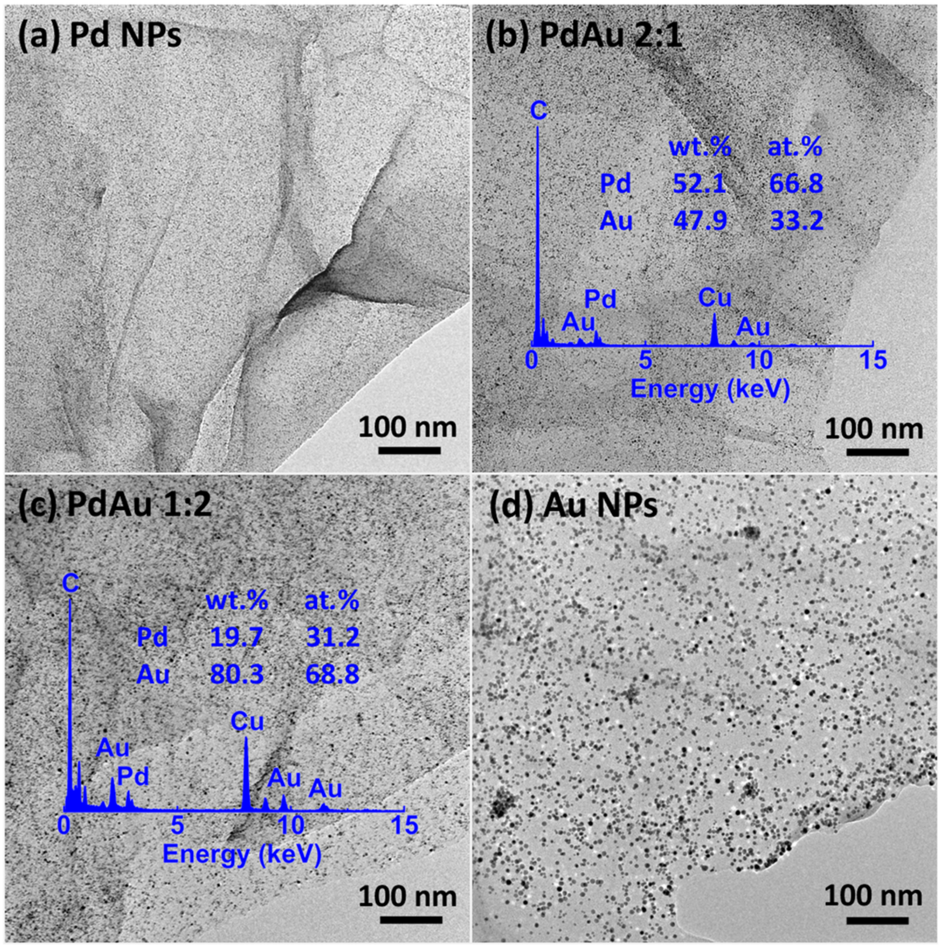


Fig. S1 TEM images of (a) monometallic Pd-NP-graphene hybrid, (b) PdAu-NP-graphene hybrid at Pd-to-Au ratio of 2:1, (c) PdAu-NP-graphene hybrid at Pd-to-Au ratio of 1:2, and (d) monometallic Au-NP-graphene hybrid. Insets in (b) and (c) are corresponding EDS data showing experimental Pd-to-Au ratios, where Cu signal is from TEM grid. All the NPs are decorated on graphene with good uniformity and high coverage, and the experimental Pd-to-Au ratios are close to the designed ones.

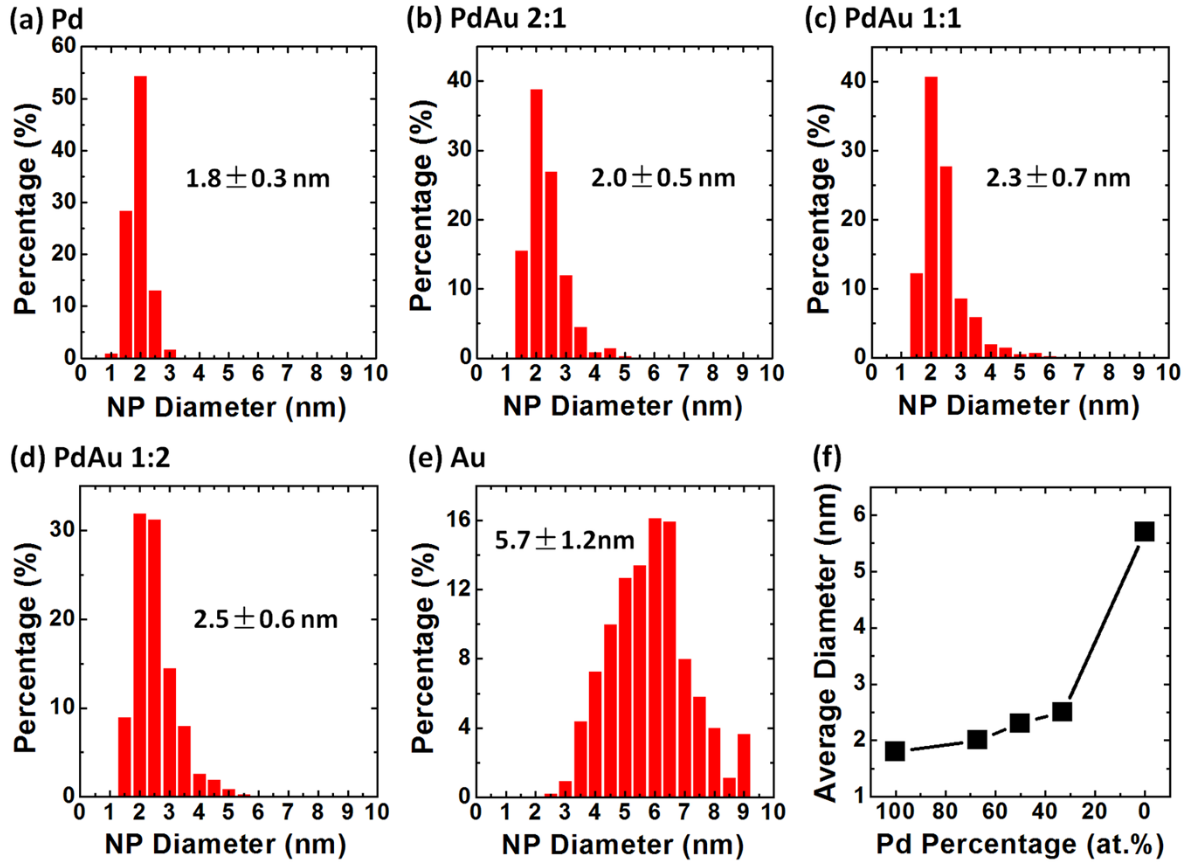


Fig. S2 Size distribution of graphene-supported PdAu NPs with different Pd-to-Au ratio: (a) Pd only, (b) Pd:Au = 2:1, (c) Pd:Au = 1:1, (d) Pd:Au = 1:2 and (e) Au only. (f) Average NP diameter vs Pd percentage based on the data in (a)–(e). Upon the addition of Pd to Au, the bimetallic NP size is greatly decreased compared with the monometallic Au NPs.

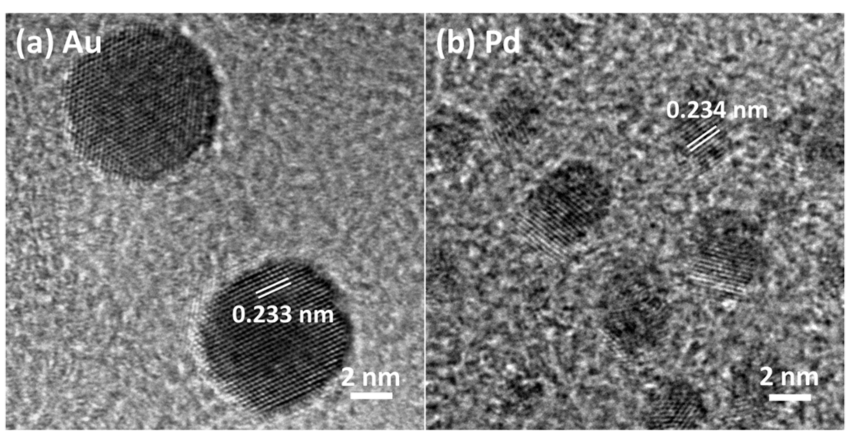


Fig. S3 HRTEM images of graphene-supported monometallic (a) Au NPs and (b) Pd NPs.

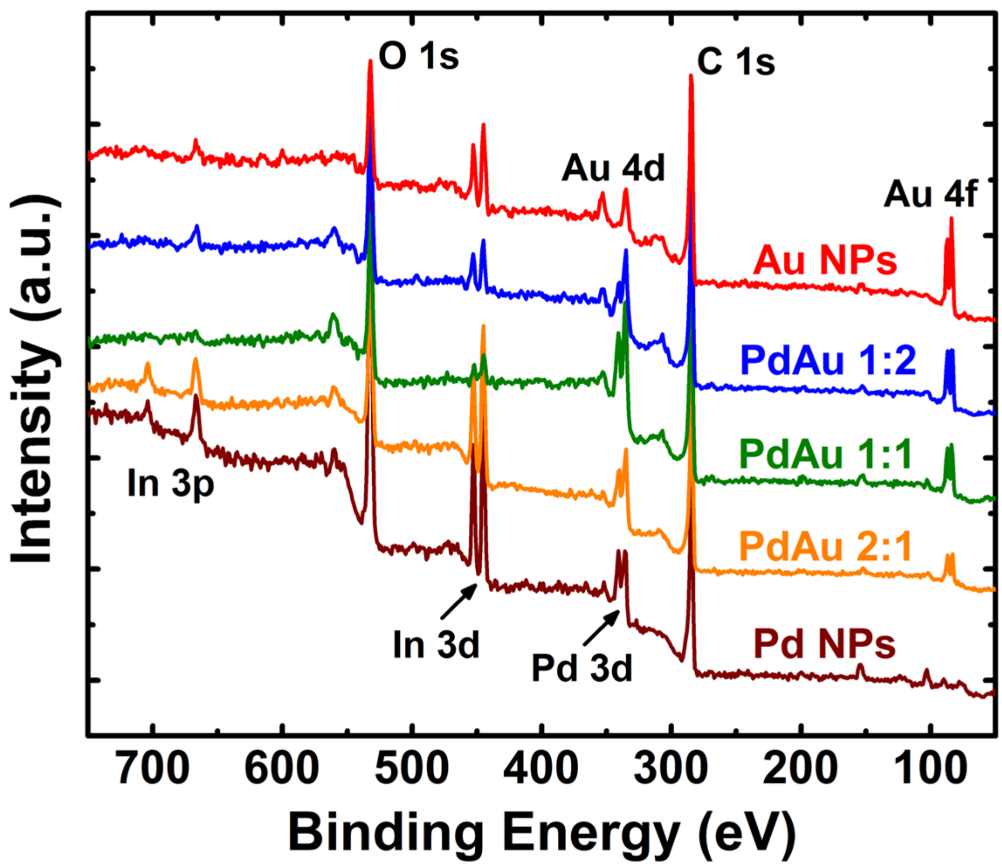
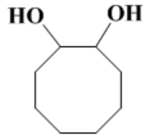
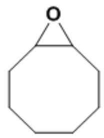
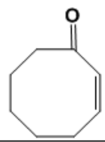
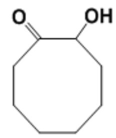


Fig. S4 XPS survey spectra of graphene-supported PdAu NPs with different Pd-to-Au ratio, where In signal is from In flake as the powder sample substrate.

Table S1 Oxidation of *cis*-cyclooctene with O_2 in absence of a solvent.

Catalysts	Conv. (%)	Selectivity (%)					
						Σ_{sel}C8☆	Σ_{yield}C8★
Pd*	6.5	35.5	10.4	8.7	35.4	90	5.8
Pd/Au=4:1*	8.8	36.3	12.1	8.8	34.5	91.7	8.1
Pd/Au=2:1*	9.5	37.4	11.7	9.2	33.8	92.1	8.8
Pd/Au=4:3*	10.7	37.8	11.3	9.8	32.5	91.4	9.8
Pd/Au=3:4*	14.6	38.0	10.5	10.4	32.0	90.9	13.3
Pd/Au=1:2*	18.5	39.2	9.1	11.4	29.3	89	16.5
Pd/Au=1:4*	16.3	38.6	9.8	10.9	30.9	90.2	14.7
Au*	8.6	40.1	8.6	12.8	28.4	89.9	7.7

☆ Total selectivity to C8 partial oxidation products

★ Total yield of C8 partial oxidation products

✳ Reaction conditions: Catalyst (20 mg), *cis*-cyclooctene (10 mL, 0.066 mol), TBHP (0.12 g), atmosphere pressure, 80 °C, 24 h.

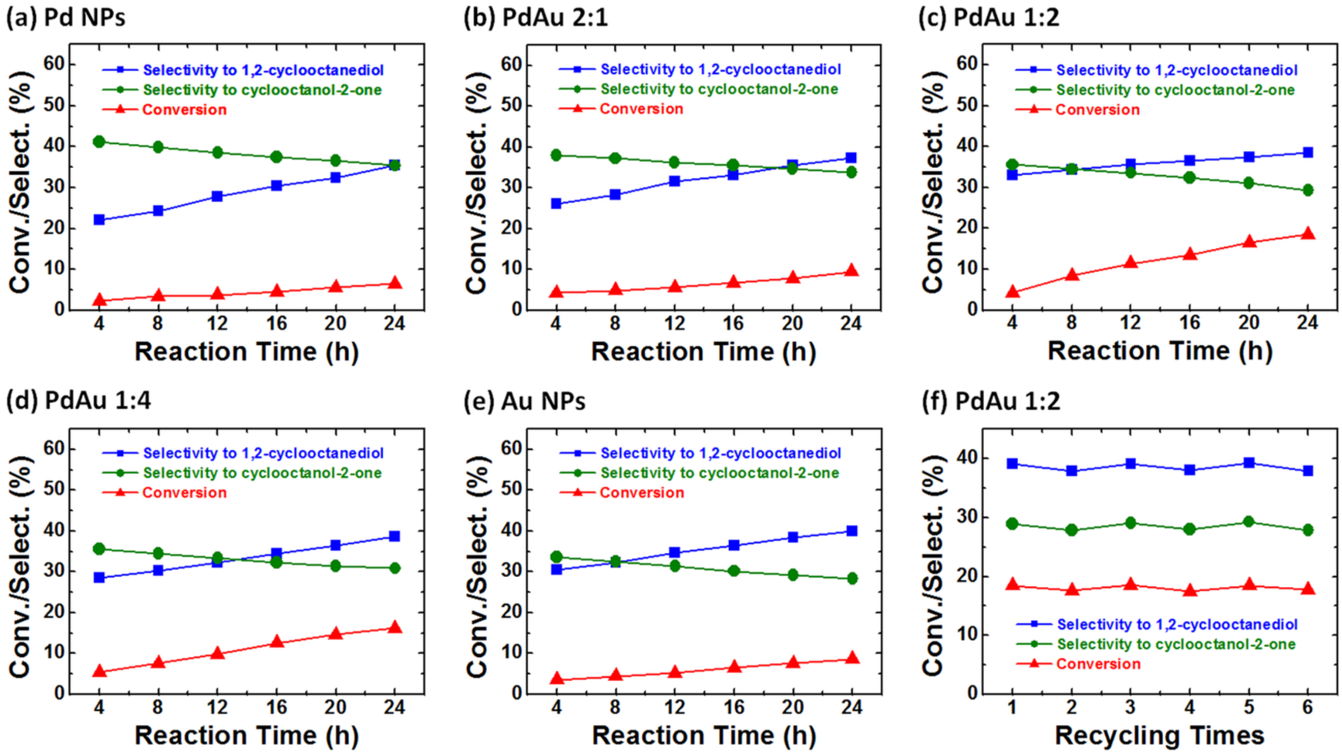


Fig. S5 Catalytic performance for oxidation of *cis*-cyclooctene using graphene-supported PdAu NPs with different Pd-to-Au ratio: (a) Pd only, (b) Pd:Au = 2:1, (c) Pd:Au = 1:2, (d) Pd:Au = 1:4 and (e) Au only. (f) Catalytic stability of graphene-supported PdAu NPs at Pd-to-Au ratio of 1:2.

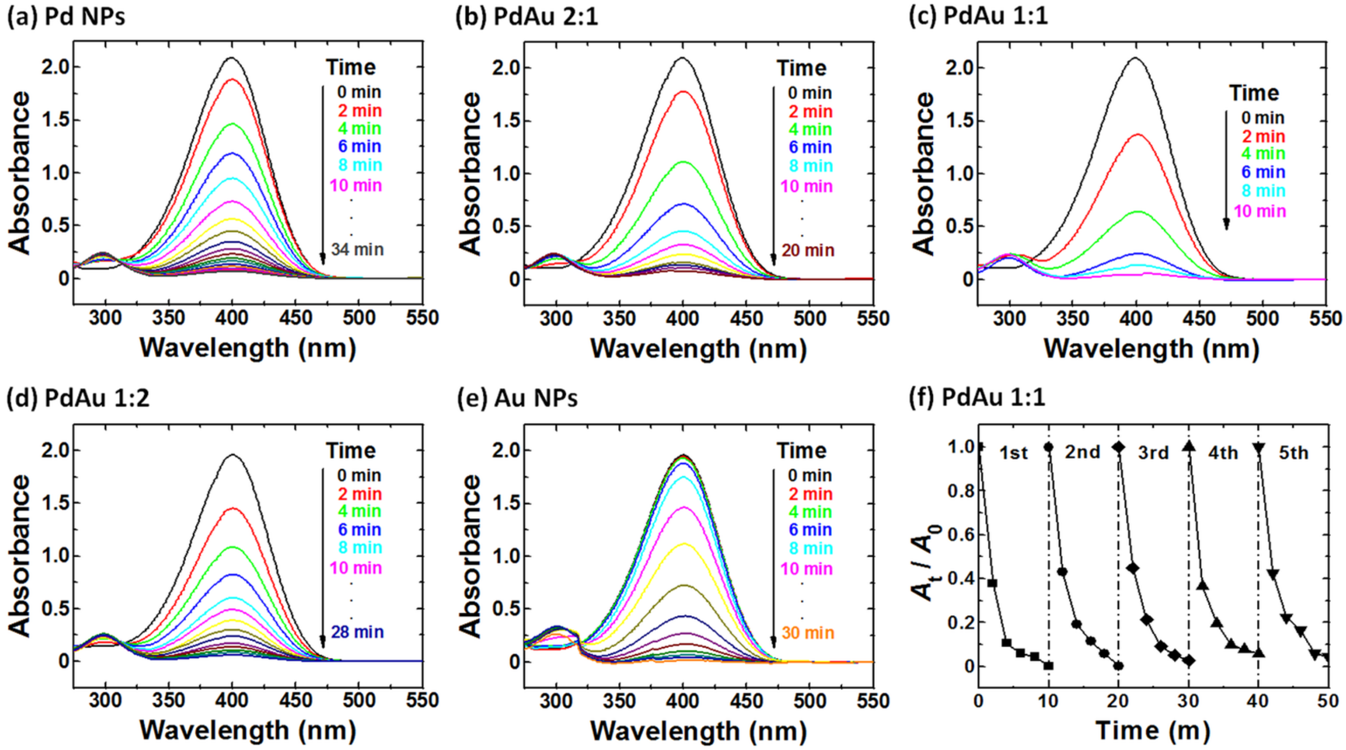


Fig. S6 Time-dependent UV-vis absorption spectra for reduction of 4-nitrophenol using graphene-supported PdAu NPs with different Pd-to-Au ratio: (a) Pd only, (b) Pd:Au = 2:1, (c) Pd:Au = 1:1, (d) Pd:Au = 1:2 and (e) Au only. (f) Catalytic stability of graphene-support PdAu NPs at Pd-to-Au ratio of 1:1.

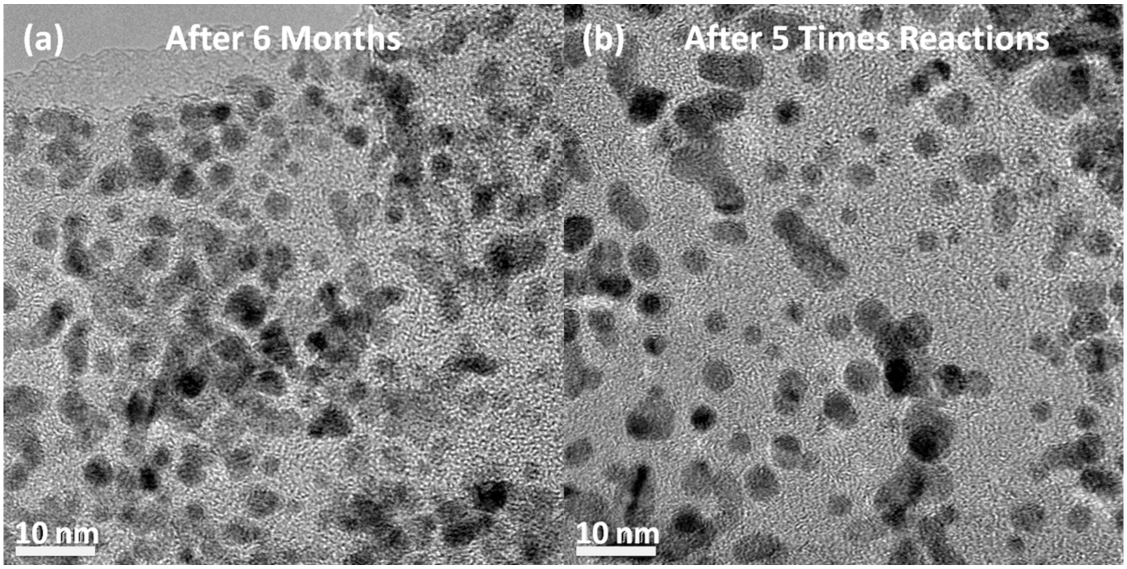


Fig. S7 TEM images of PdAu-NP-graphene hybrid (Pd-to-Au ratio of 1:1) measured (a) after storage in dry air for 6 months and (b) after 5 times catalytic reduction reactions.

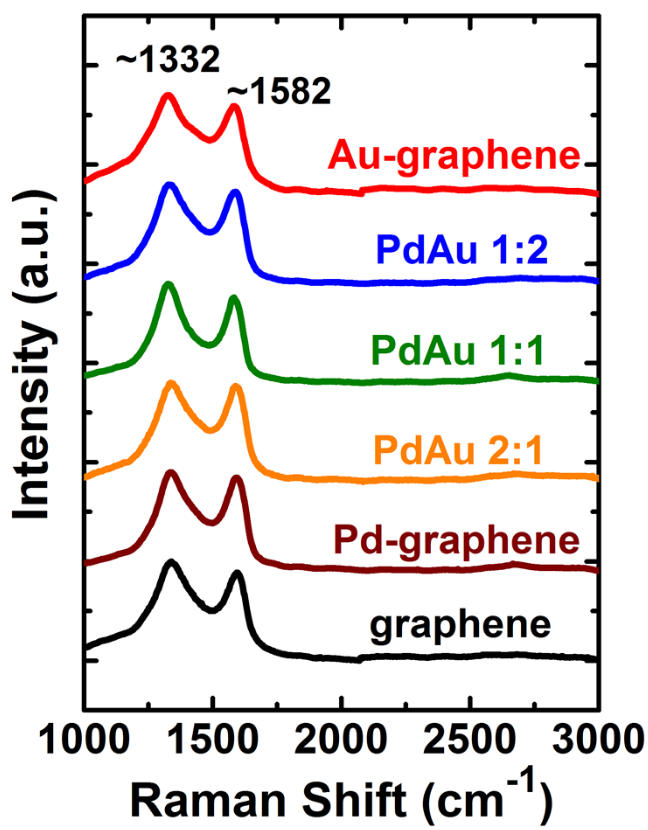


Fig. S8 Raman spectra of pristine graphene and metal-NP-graphene hybrids studied in the present case.