Supporting Information

Synergistic Effect of Bimetallic PdAu Nanocrystals on Oxidative Alkyne Homocoupling

Experimental Details

Preparation for PdAu nanocrystals:

In a typical preparation of PdAu(1:1) nanocrystals, 0.1 g L^{-1} aqueous $HAuCl_4$ (270 ml) and $Pd(acac)_2$ (10 mg) were dissolved in OAm(10 mL) at 60 ^oC under vigorous stirring for 10 min. Then, a solution of borane-tert-butylamine (100 mg, 1.15 mmol) in OAm (1 mL) was added quickly into the previous solution, and the reaction mixture immediately turned black. After 1 min, the flask was heated to 80 ^oC for a further 1 h. After cooling to room temperature, the solution was washed with ethanol (40 mL×3) and then dispersed in cyclohexane for future use.
The PdAu nanocrystals with other metal ratios were synthesized in the similar way but use related stoichiometric precursors. The pure Pd and Au nanocrystals were synthesized by using single precursor source.

Preparation for mpg-C_3N_4:

5 g of cyanamide and 12.5 g of Ludox-HSO_4 silica dispersion are mixed together until complete dissolution of cyanamide. The mixture is heated in an oil bath at 100 ^oC upon stirring for ca .3h until removal of water and formation of a white solid. The powder is then grounded in a mortar, transferred into a crucible and heated under air at 2.3 $^oC\ min^{-1}$ (4h) up to 550 ^oC and then treated at 550 ^oC for 4h. The as-obtained yellow powder is grounded in a mortar and then treated under stirring during 2 days in a NH_4HF_2 4 mol L^{-1} solution. The dispersion is then filtered; the precipitate is washed with distilled water and ethanol. After filtering, the yellow compound is dried under vacuum at 100 ^oC overnight.

Preparation for NCs/mpg-C_3N_4:

For the preparation of Pd/mpg-C_3N_4, PdAu/mpg-C_3N_4, and Au/mpg-C_3N_4 catalysts, mpg-C_3N_4 is added into the dispersions of Pd, PdAu, and Au at a loading of 2 wt. % (based on Pd and Au), and the mixtures are stirred overnight. The catalysts are obtained through centrifugation and drying under vacuum.

Typical procedure for catalyzing oxidative homocoupling of phenylacetylene:

1mmol phenylacetylene is dissolved in 5ml DMF in air condition, 50 mg NPs/ mpg-C_3N_4 catalyst (2 mmol% based on total metal) is mixed with the reactant, then the solution is stirred at 80 ^oC (or 100 ^oC) for 12 hours, the conversion and selectivity are determined by GC using biphenyl as internal

Materials Characterization:

The Powder XRD patterns is recorded by a Bruker D8 ADVANCE X-ray powder diffractometer with CuKa radiation (l=1.5406 Å). The sample compositions are determined by EDX, and the particle size and dispersion are investigated with a Hitachi H-800 transmission electron microscope (TEM).
X-ray photoelectron spectroscopy (XPS) is conducted with a Thermo Fisher ESCALAB 250Xi spectrometer equipped with a monochromatic Al X-ray source.

Supplementary Figures:

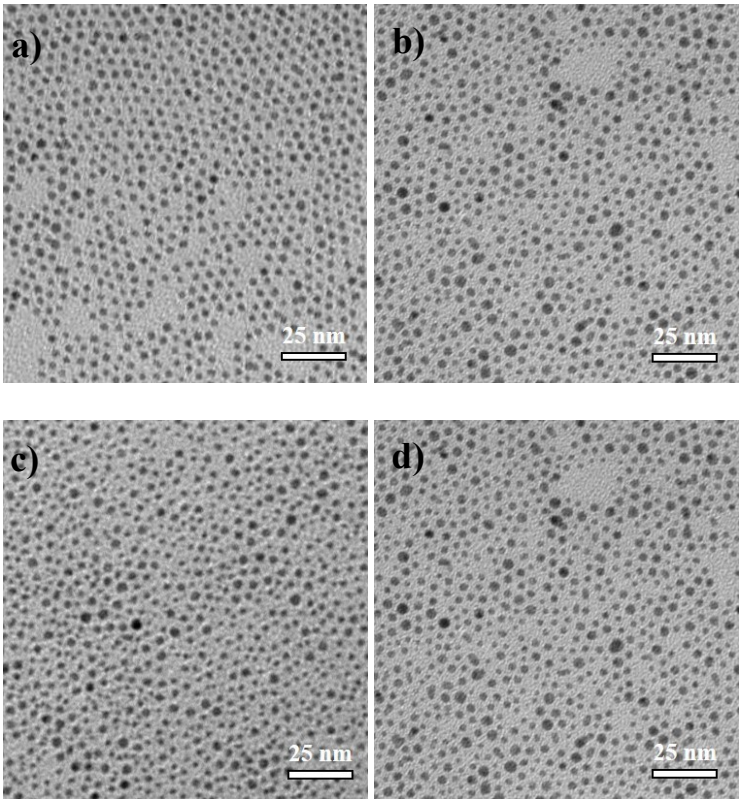


Fig. S1 TEM images of Pd_3Au (**a**), Pd_2Au (**b**), $PdAu_2$ (**c**), $PdAu_3$ (**d**).

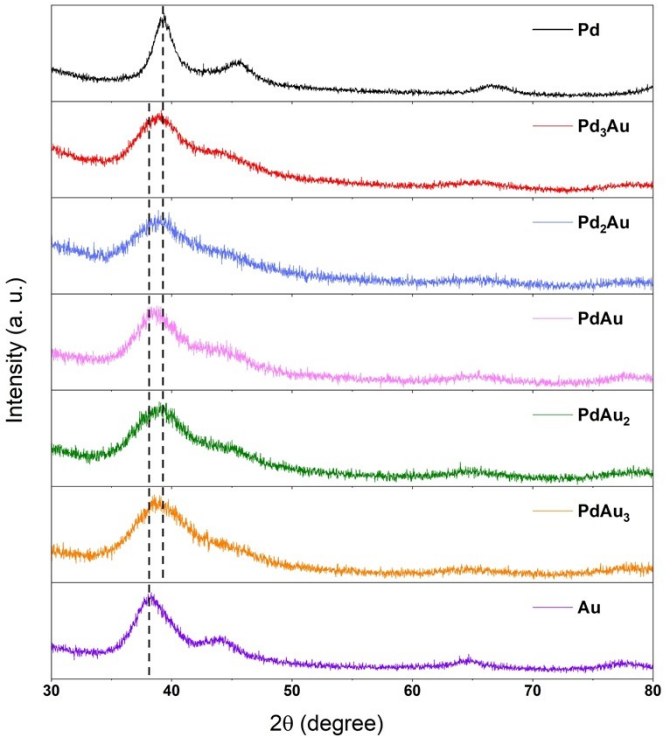


Fig. S2 The XRD patterns of all metallic NPs, the dash lines indicate the (111) peak positions of Pd and Au

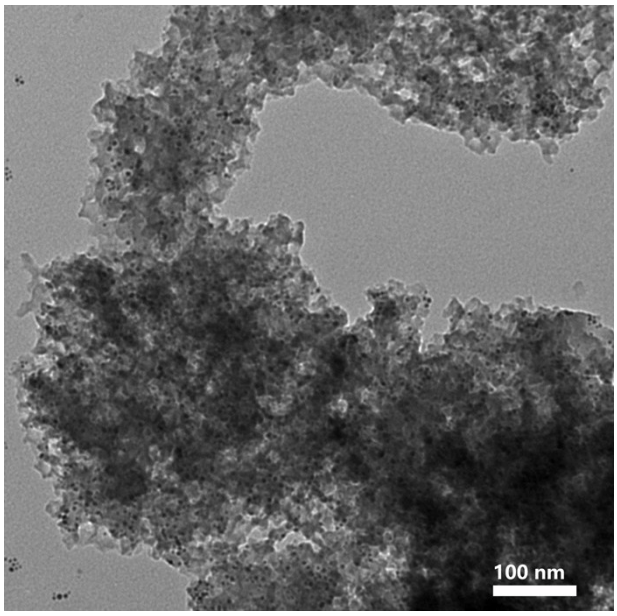


Fig. S3 TEM image of PdAu/mpg-C_3N_4

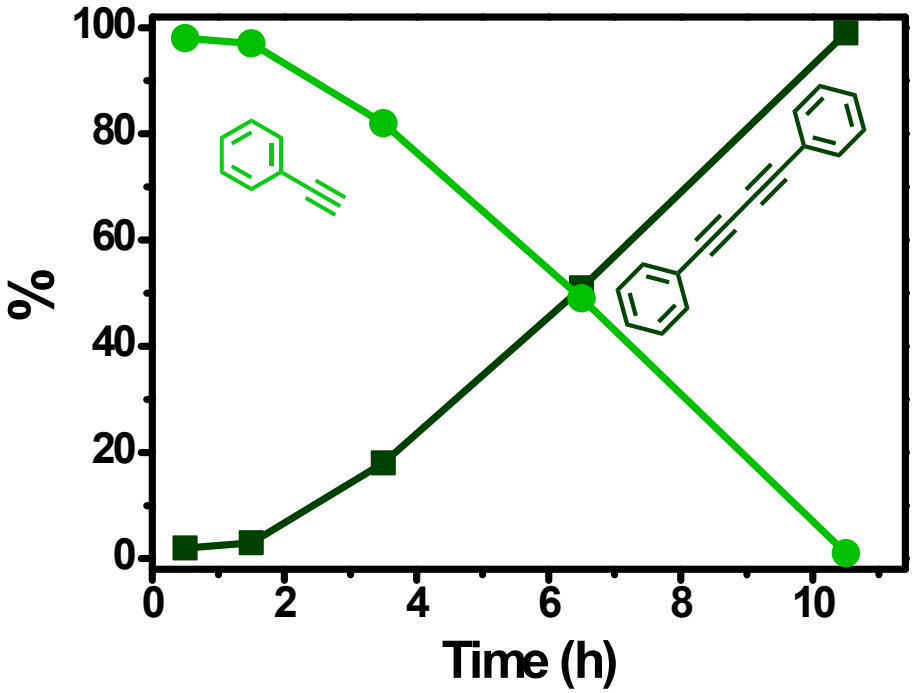


Fig. S4 The ratios of substrate and product versus reaction time.

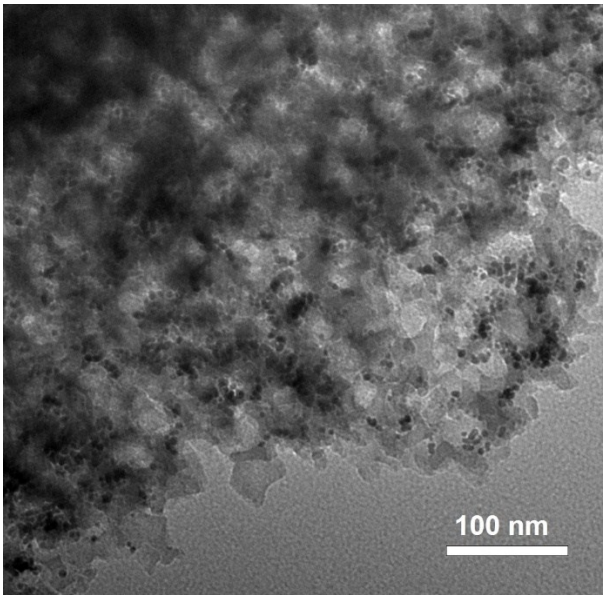


Fig. S5 TEM image of PdAu/mpg-C_3N_4 after five cycles.

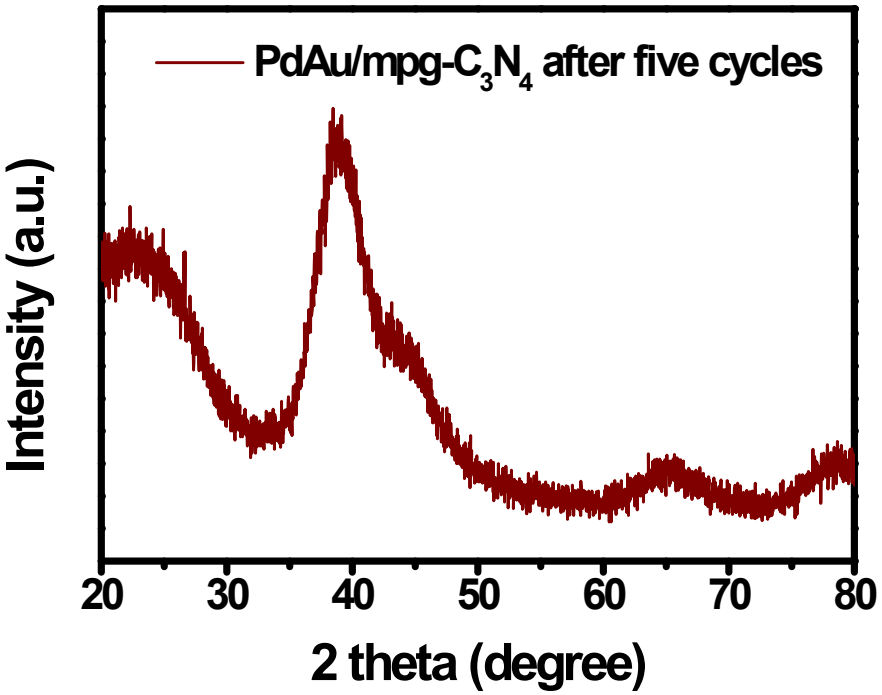


Fig. S6 XRD pattern of PdAu/mpg-C_3N_4 after five cycles.

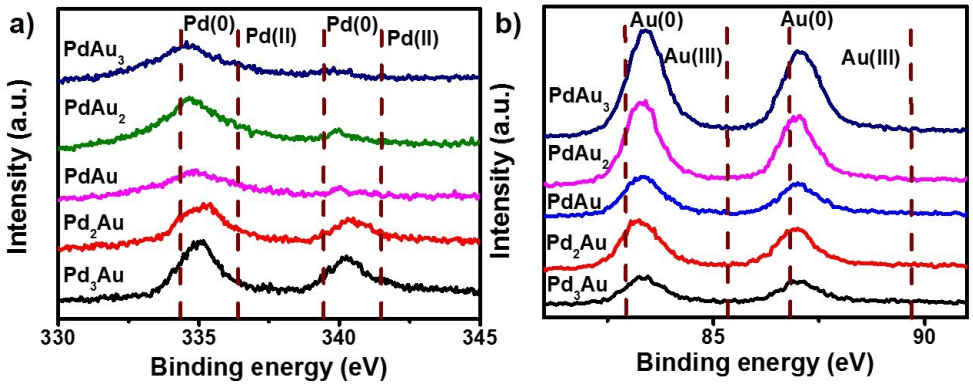
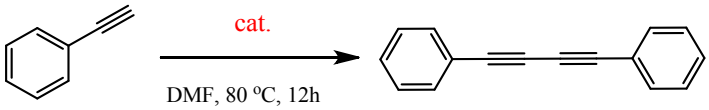


Fig. S7 XPS characterization of PdAu/mpg-C_3N_4 with different metal ratios about Pd 3d and Au 4f spectra.

Supplementary Tables:

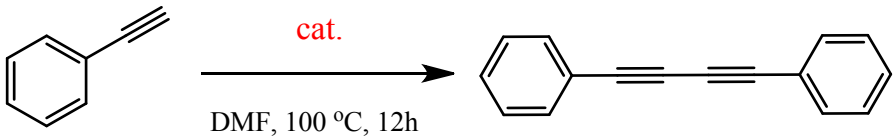
Table S1 Oxidative homocoupling of phenylacetylene over various heterogeneous catalysts.



Entry [a)]	Catalysts[b)]	Yields (%) [c)]	Selectivity (%) [d)]
1	Pd	2.2	>99
2	Au	-	-
3	Pd + Au	6.3	>99
4	Pd_3Au	61	79
5	Pd_2Au	78.9	>99
6	PdAu	41	>99
7	$PdAu_2$	11	>99
8	$PdAu_3$	-	-
9	Mpg-C_3N_4	-	-

a) phenylacetylene: 1mmol, DMF: 5ml, air, catalyst: 50mg with 12h; b) catalyst: 2% mmol based on metal (Pd and Au); c) determined by GC using biphenyl as internal; d) other products: benzaldehyde/acetophenone.

Table S2 Oxidative homocoupling of phenylacetylene over Pd_2Au loaded on different supports



Entry [a)]	Support [b)]	Yields (%) [c)]	Selectivity (%) [d)]
1	C_3N_4	100	>99
2	TiO_2	42.9	>99
3	ZnO	31.7	>99
4	SiO2	83.1	>99
5	C	91.2	>99
6	Fe_3O_4	58.9	>99
7	CeO_2	31.5	76.1

a) phenylacetylene: 1mmol, DMF: 5ml, air, catalyst: 50mg with 12h; b) different catalyst: 2% mmol based on metal (Pd and Au); c) determined by GC using biphenyl as internal; d) other products: benzaldehyde/acetophenone.

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