Supporting Information

Reduced graphene oxide nanosheets decorated with Au-Pd bimetallic alloy nanoparticles towards efficient photocatalytic degradation of phenolic compounds in water

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Experimental

Materials:

Platinum (II) chloride (98%, Alfa Aesar, Great Britain), zinc chloride (99%, Merck, India), sodium carbonate anhydrous (SRL Chemicals, India) and sodium hydroxide (Qualigens, India), titanium (IV) oxide (anatase nanopowder, <25 nm particle size, 99.7%, Sigma Aldrich, Germany)

Synthesis of Pt/rGO

For typical synthesis of Pt/rGO nanocomposite, $PtCl_2$ (0.0638 g) was dissolved in 10 mL of ethanol solution. To the above solution 10 mL GO solution (10 mg/L) was added and stirred for 20 min. The entire reaction mixture was stirred for 8 h under a hydrogen atmosphere. The resulting composite material was filtered and repeatedly washed with water followed by ethanol and dried in an air oven at 65 ºC to obtain solid black Pt/rGO nanocomposite.

Characterization of Pt/rGO

The XRD spectra of Pt/rGO is shown in Fig. S8. The distinct diffraction peaks at 2θ value of 40.1, 46.4, 67.6, 81.4 and 86.0 are assigned to (111), (200), (220), (311) and (222) crystallographic planes of *fcc* Pt nanoparticles respectively with *d*-spacing values 2.24, 1.95, 1.38, 1.18 and 1.12 Å. The broad diffraction peak at 2θ ~ 24.2 is due to the presence of rGO nanosheets in Pt/rGO nanocomposite.

The morphology, size and the crystalline nature of the Pt/rGO nanocomposites is studied from TEM and HRTEM images. Fig. S9(a) shows that spherical Pt nanoparticles are well distributed on the rGO nanosheets with an average size distribution of 3.16 nm (Fig. S9(c)). The HRTEM image reflects the crystalline nature of Pt/rGO nanocomposite. Clear lattice fringes with an interplanar spacing of 0.23 nm corresponding to (111) plane of *fcc* Pt is displayed in Fig. S9(b) thus confirming formation of Pt nanoparticles on rGO sheets.

Synthesis of ZnO nanoparticles

For synthesis of ZnO without support, $ZnCl_2$ (0.05 g) was dissolved in 50 mL H_2O solution. To the above solution, Na_2CO_3 (1 M) was added until a white precipitate was obtained. The entire reaction mixture was stirred for 1 h at room temperature. The white precipitate was

continuously washed with deionized water and ethanol to remove any impurities present and dried in an air oven at 110 ºC for 4-5 h to obtain ZnO nanoparticles.

Characterization of ZnO nanoparticles

The XRD profile (Fig. S10) of ZnO nanoparticles without support displays nine major diffraction peaks that can be indexed to (100), (002), (101), (102), (110), (103), (112), (004) and (202) planes appearing at 2θ value of 31.8, 34.4, 36.3, 47.5, 56.5, 62.9, 67.9, 72.4 and 77.2, respectively. The crystalline nature of the ZnO nanoparticles was also reflected from the XRD patterns.

The information regarding morphology, size and crystallinity of the ZnO nanoparticles was further obtained from TEM and HRTEM images. The TEM images (Fig. S11(a)) represent the formation of spherical ZnO nanoparticles with an average size distribution of 6.9 nm as shown in Fig. S11(c). The HRTEM image of a single ZnO nanoparticle is depicted in Fig. S11(b) which shows clear lattice fringe with an interplanar spacing of 0.28 nm corresponding to (100) plane of ZnO nanoparticle. The HRTEM image also clearly reflects the crystalline nature of ZnO nanoparticle.

Synthesis of ZnO/rGO nanocomposite

In a typical preparation procedure, 0.05 g $ZnCl_2$ was added to 15 mL of GO suspension (10 mg/L) in water. The pH of the reaction mixture was adjusted at pH 9 using an alkaline NaOH solution (1 M) until a brownish-black suspension is obtained. The entire reaction mixture was stirred for 20 min and then transferred into a Teflon lined autoclave and subjected to hydrothermal treatment for 8 h at 120 ºC. The product obtained was filtered and washed repeatedly with deionized water and ethanol and dried in an air oven at 65 ºC to obtain ZnO/rGO nanocomposite.

Characterization of ZnO/rGO nanocomposite

The XRD profile (Fig. S12) of ZnO/rGO nanocomposites displays eleven major diffraction peaks. These diffractions can be indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes appearing at 2θ value of 31.7, 34.4, 36.2, 47.5, 56.5, 62.7, 66.3, 67.8, 69.0, 72.4 and 76.8, respectively. Moreover, another peak at 2θ ~ 24.2 suggest successful conversion of GO to rGO during nanoparticle formation. The crystalline nature of the ZnO nanoparticles was also reflected from the XRD patterns.

The TEM and HRTEM images provide information on the size, morphology and crystallinity of ZnO/rGO nanocomposites. The TEM images clearly depict the formation of ZnO nanoparticles on rGO sheets (Fig. S13(a)). The size distribution curve (Fig. S13(c)) shows the formation of ZnO nanoparticles with an average size of 13.28 nm. The HRTEM images also clearly reflects the crystal lattice of (100) plane of ZnO with an interplaner spacing of 0.28 nm (Fig. S13(b)).

Results

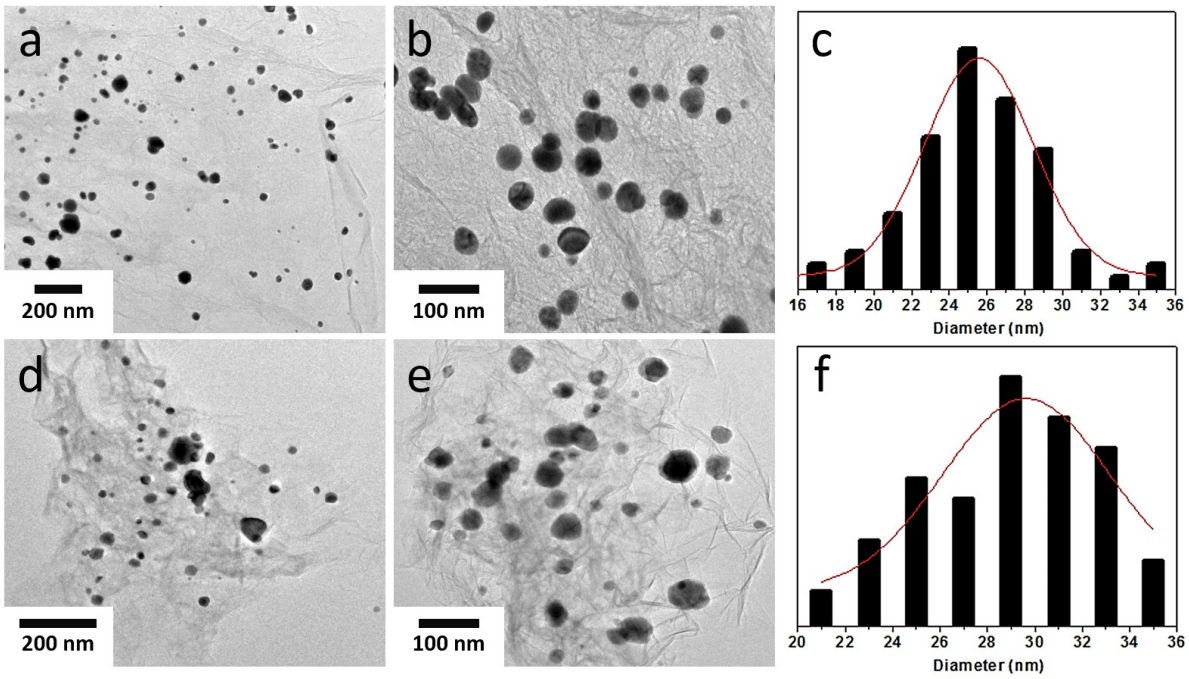

Fig. S1. (a,b) TEM images of Au/rGO nanocomposite (c) Size distribution of Au/rGO (d,e) TEM images of Pd/rGO nanocomposite (f) Size distribution of Pd/rGO

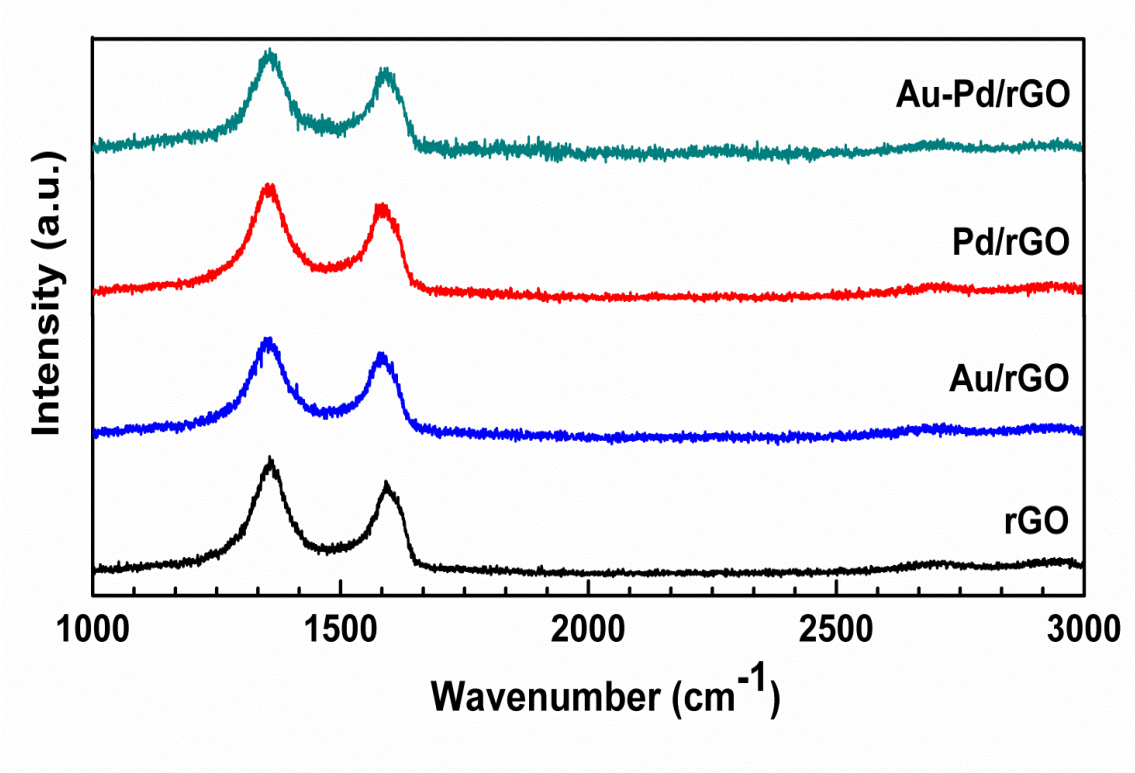

Fig. S2. Raman spectra of rGO, Au/rGO, Pd/rGO and Au-Pd/rGO

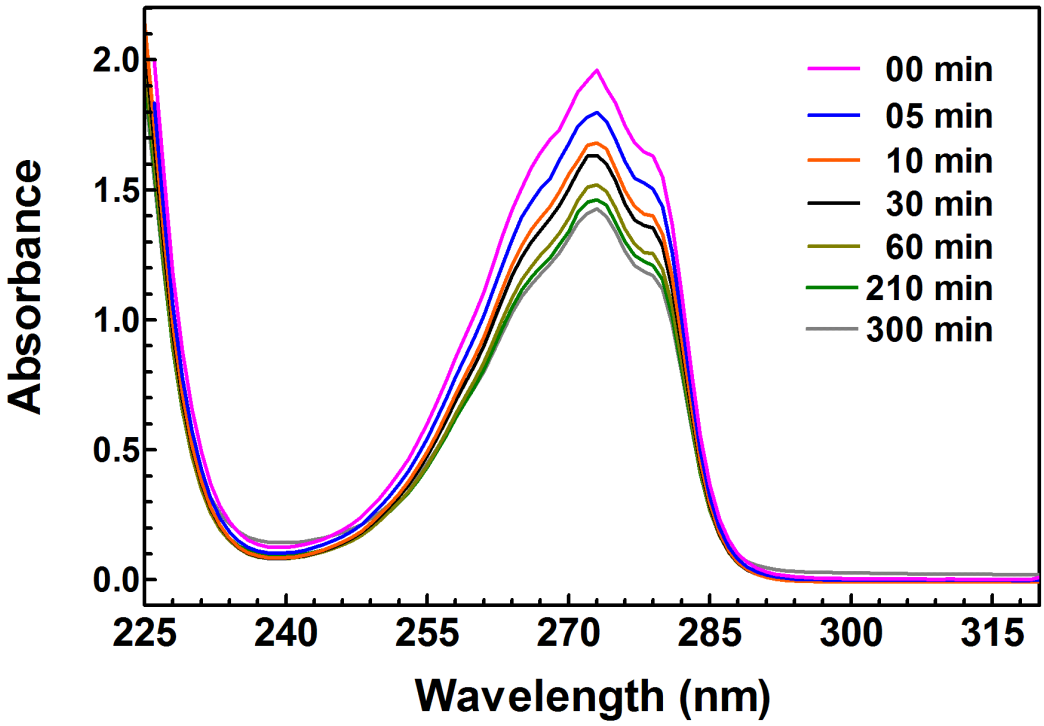

Fig. S3 UV-visible absorbance spectra of phenol in absence of Au-Pd/rGO nanocomposites

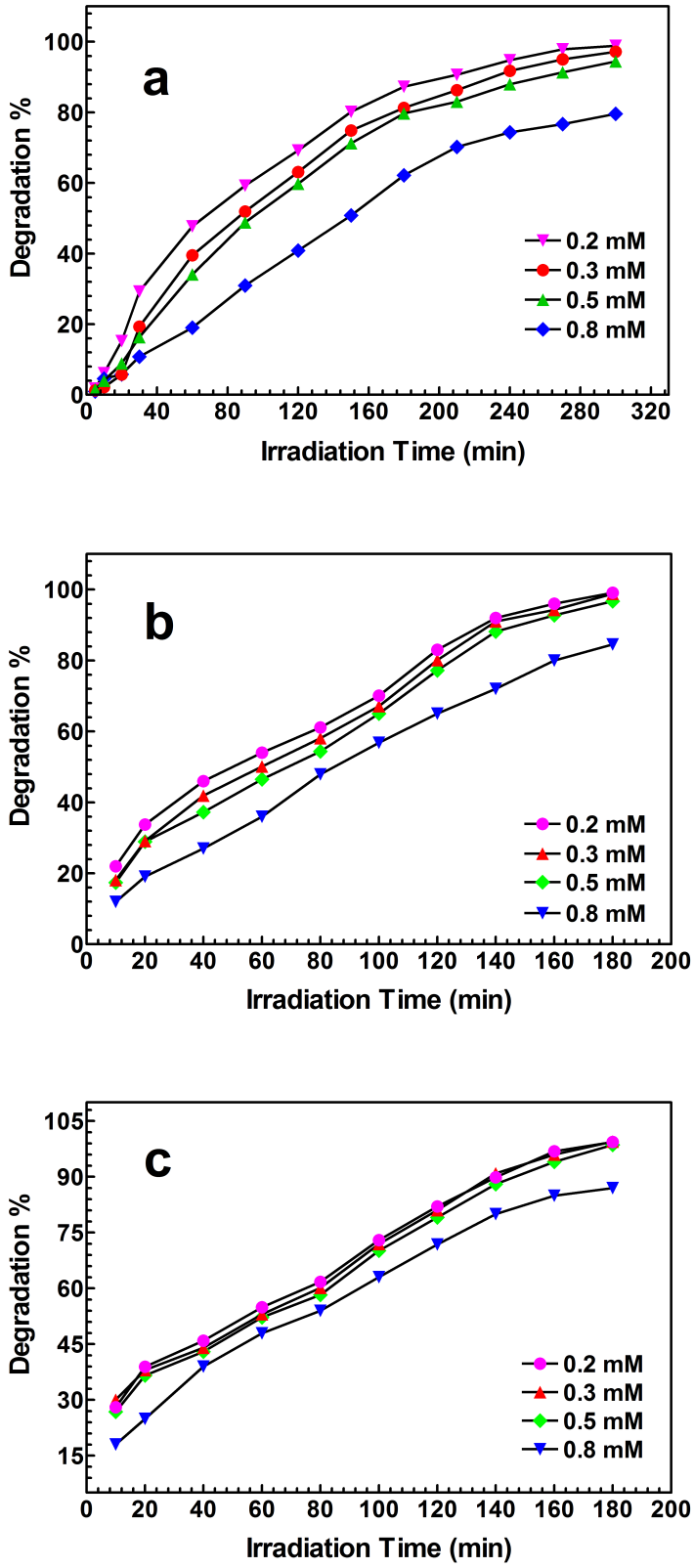

Fig. S4 Photodegradation of (a) phenol, (b) 2-CP and (c) 2-NP at different substrate concentrations using Au-Pd/rGO nanocomposites (0.5g L^{-1} and pH 7)

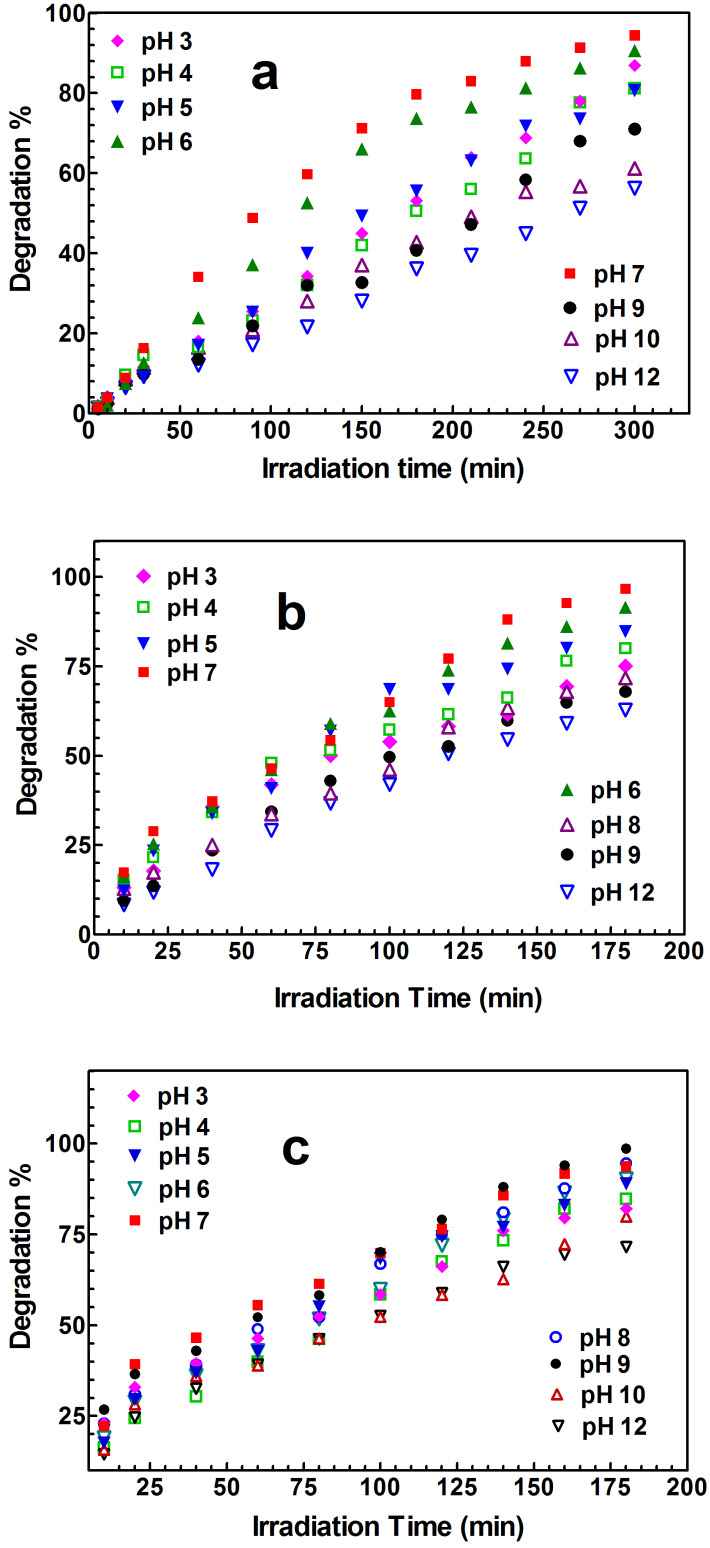

Fig. S5 Effect of varying pH (a) phenol (b) 2-CP (c) 2-NP at 0.5 mM concentration of phenolic substrates and 0.5 gL^{-1} of catalyst loading

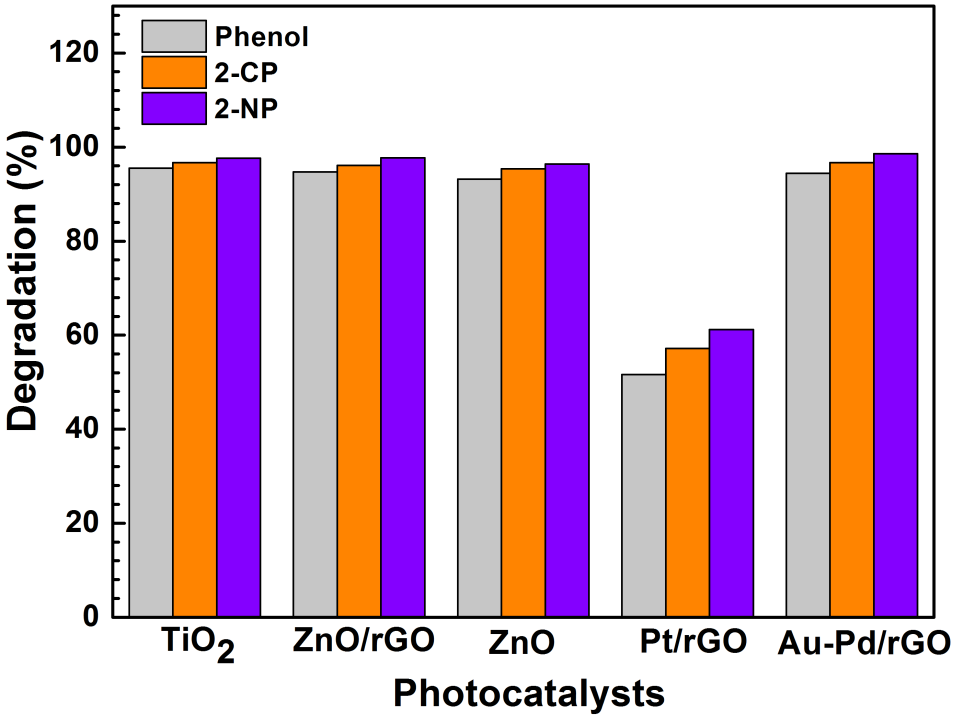

Fig. S6 Comparison of degradation efficiency for different semiconductor and non-semiconductor photocatalyst towards phenol, 2-CP and 2-NP

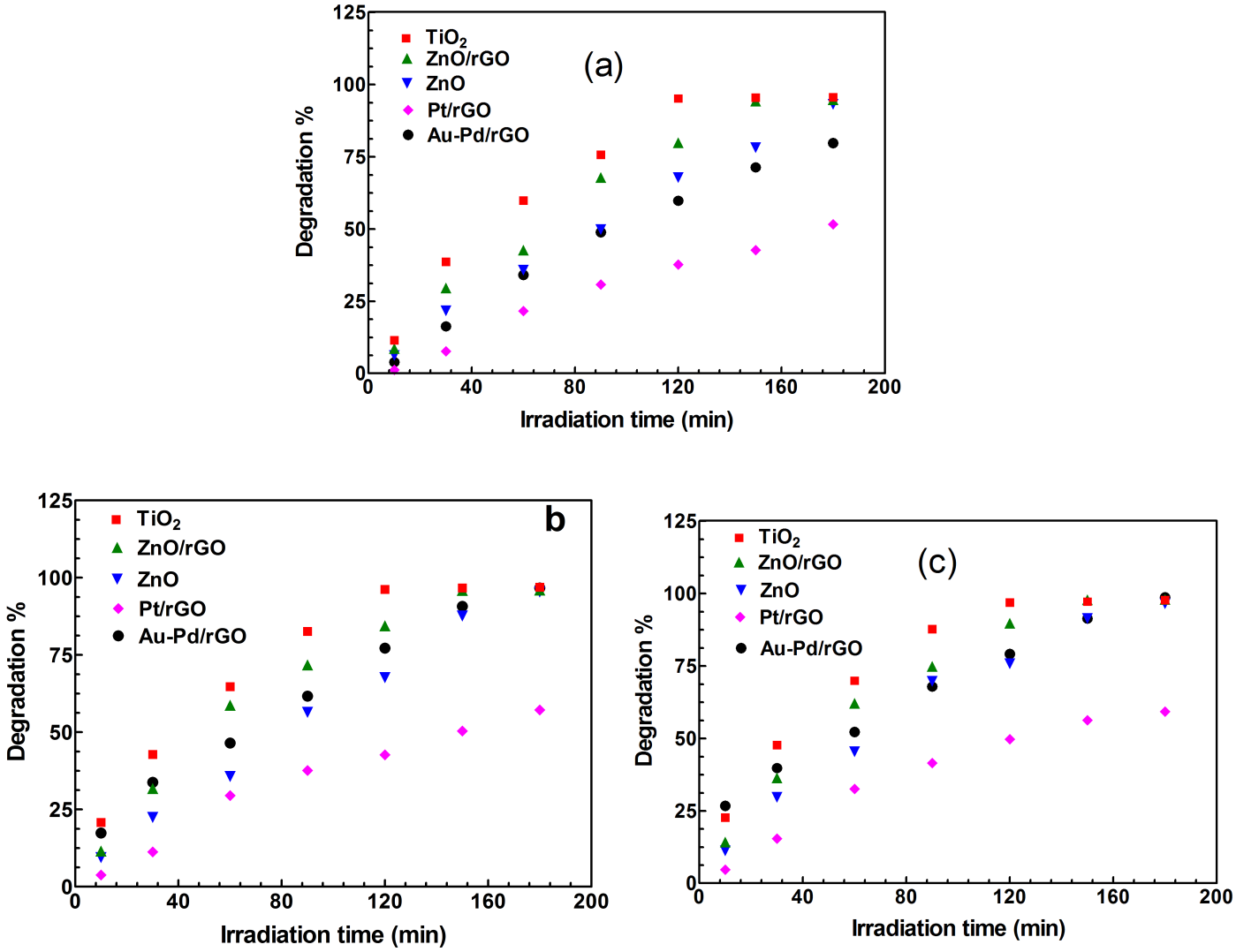

Fig. S7 Degradation efficiency of semiconductor and non-semiconductor photocatalyst towards degradation of (a) phenol (b) 2-CP and (c) 2-NP

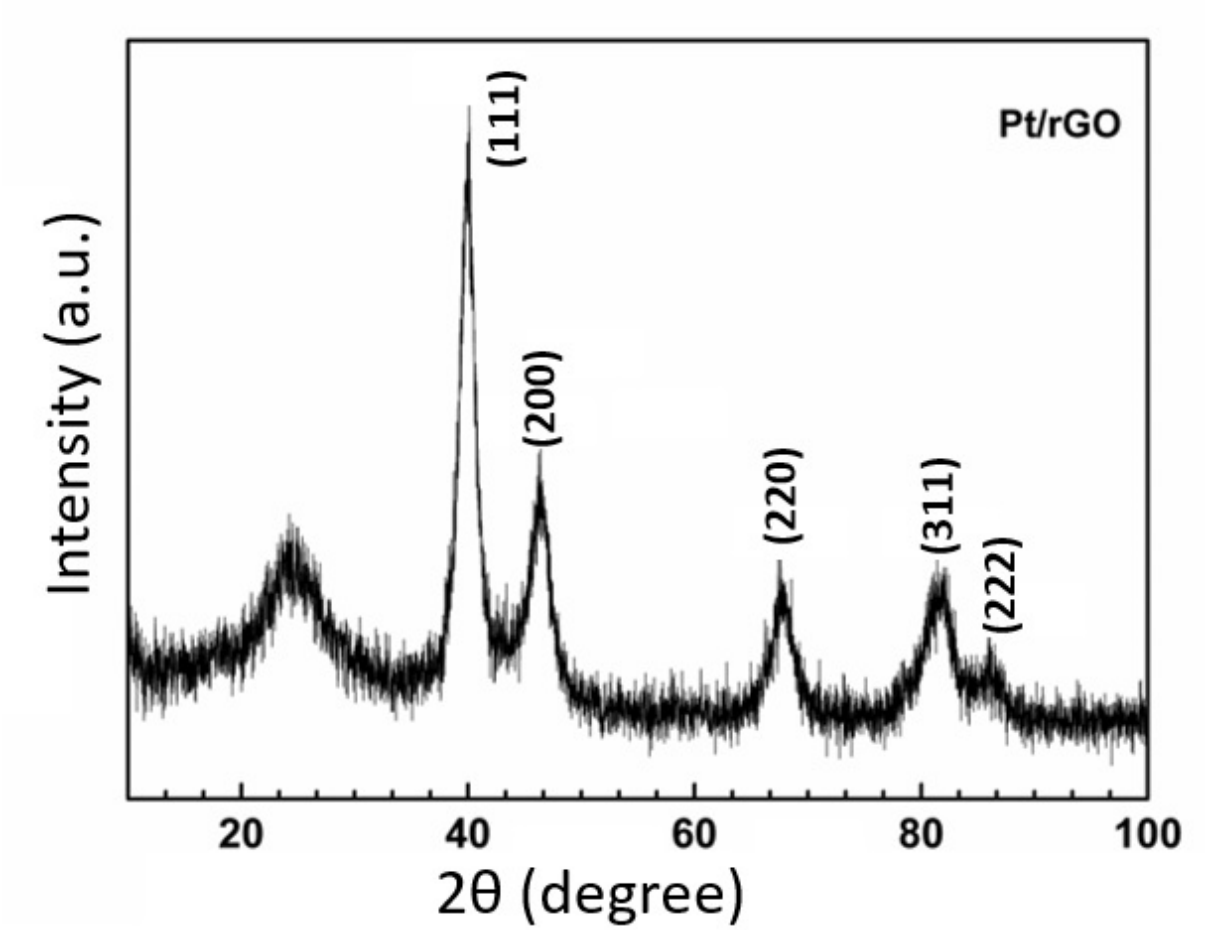

Fig. S8 XRD pattern of Pt/rGO nanocomposite

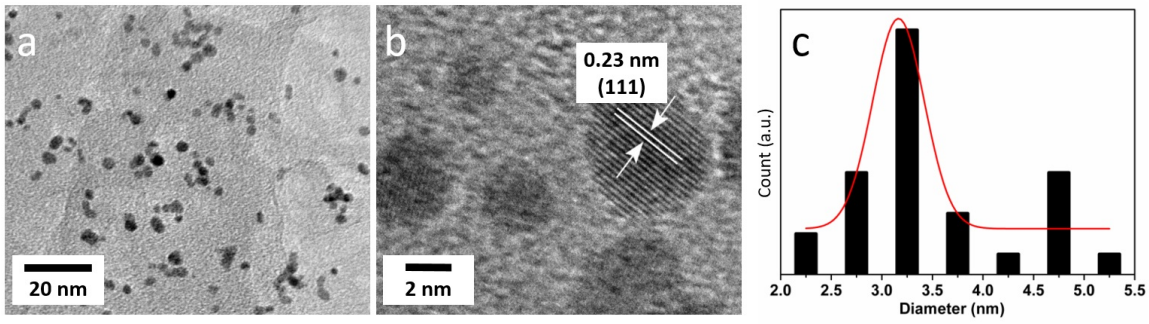

Fig. S9 TEM and HRTEM images of Pt/rGO (a,b); Size distribution curve of Pt/rGO (c)

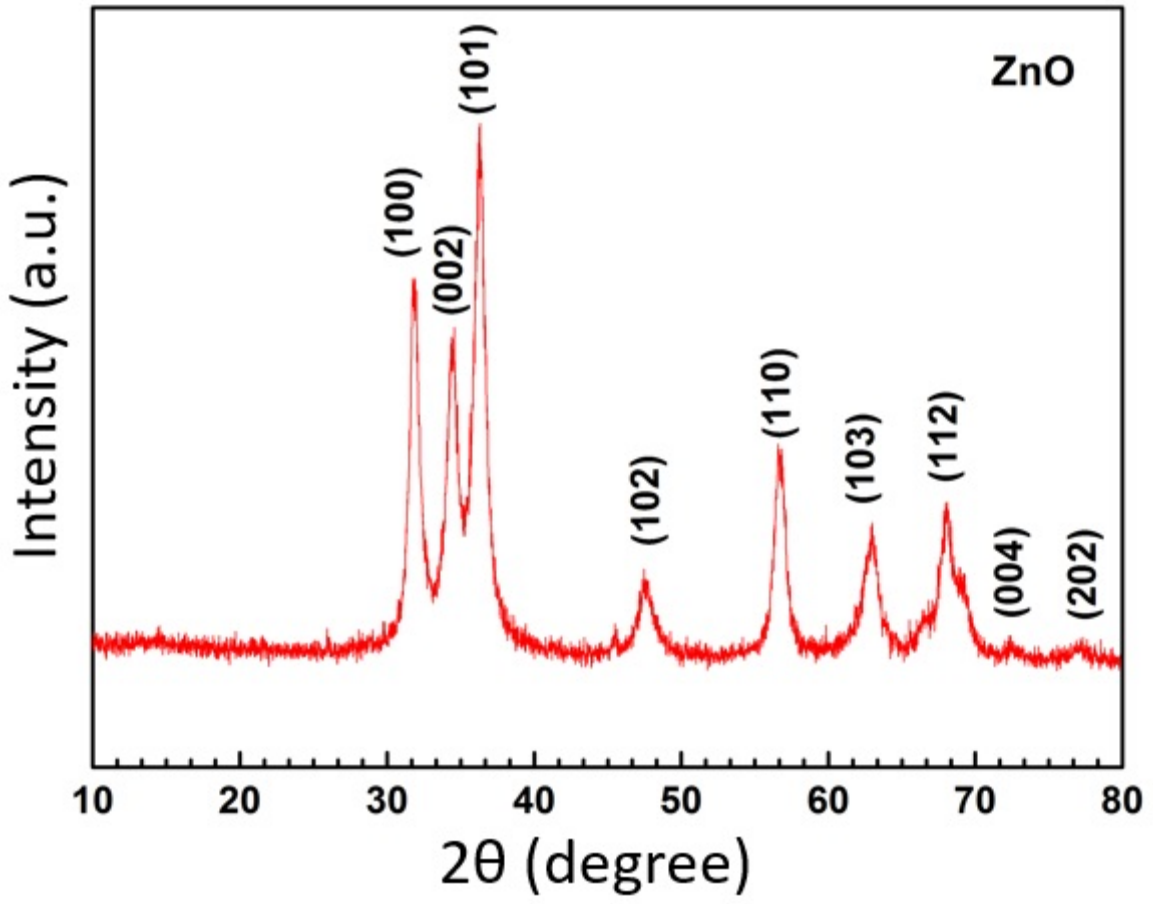

Fig. S10 XRD pattern of ZnO nanoparticles

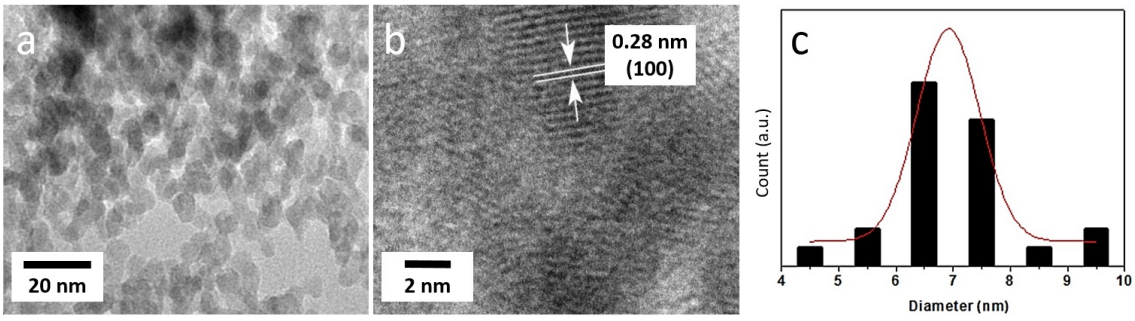

Fig. S11 TEM and HRTEM images of ZnO nanoparticles (a,b); Size distribution curve of ZnO nanoparticles (c)

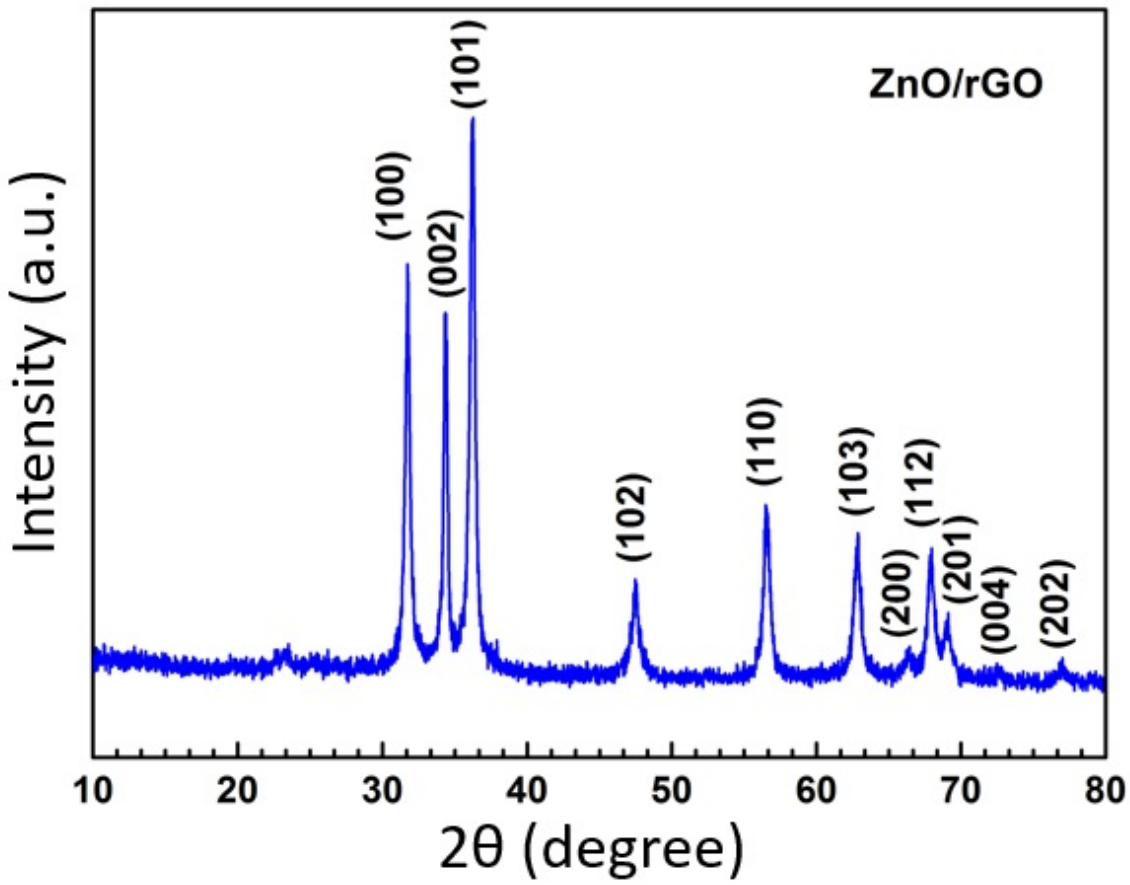

Fig. S12 XRD pattern of ZnO/rGO nanocomposites

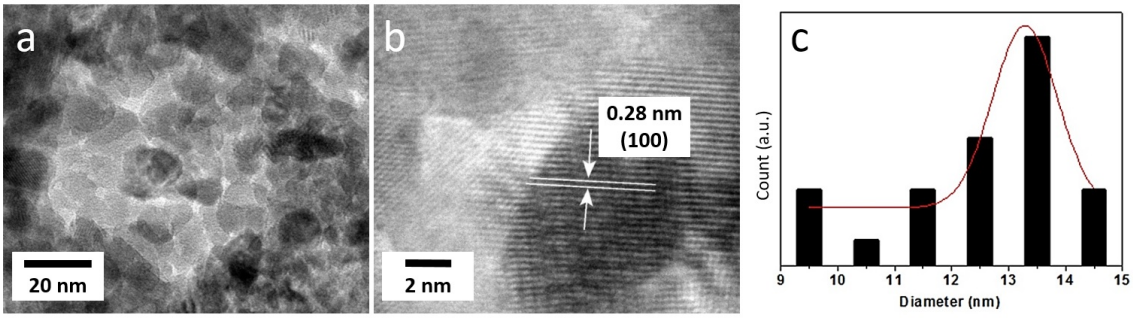

Fig. S13 TEM and HRTEM images of ZnO/rGO nanocomposites (a,b); Size distribution curve of ZnO/rGO nanocomposites (c).

Table S1: Parameters of pseudo first order kinetics model for the degradation of Phenol, 2-CP and 2-NP under sunlight irradiation

Substrate	pH	K (min^{-1})	Degradation (%)	R^2
Phenol	3	0.0061	86.91	0.9568
	4	0.0045	81.17	0.9758
	5	0.0054	80.66	0.9851
	6	0.0096	90.61	0.9939
	7	0.0078	94.43	0.9904
	9	0.0034	71.00	0.9775
	10	0.0031	61.22	0.9926
	12	0.0027	56.23	0.9842
2-CP	3	0.0077	75.16	0.9818
	4	0.0093	80.01	0.9883
	5	0.0104	84.84	0.9839
	6	0.0119	91.49	0.9931
	7	0.0172	96.69	0.9882
	8	0.0070	71.78	0.9757
	9	0.0063	67.92	0.9966
	12	0.0054	62.72	0.9968
2-NP	3	0.0095	82.09	0.9888
	4	0.0104	84.71	0.9710
	5	0.0111	88.99	0.9874
	6	0.0118	90.23	0.9624
	7	0.0137	93.71	0.9957
	9	0.0117	94.57	0.9772
	10	0.0181	98.59	0.9924
	12	0.0069	71.43	0.9941

Table S2: Comparative degradation efficiency of semiconductor and non-semiconductor photocatalyst towards degradation of phenol, 2-CP and 2-NP

Photocatalysts	Light Source	Irradiation Time (min)	Degradation efficiency (%)		
			Phenol	2-CP	2-NP
TiO_2	Sunlight	120	95.1	96.2	96.8
ZnO/rGO	Sunlight	150	94.2	95.9	97.8
ZnO	Sunlight	180	93.2	95.4	96.4
Pt/rGO	Sunlight	180	51.6	57.2	59.2
Au-Pd/rGO	Sunlight	300	94.4	96.7	98.5