Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Synergistically Enhanced Photocatalysis from Plasmonics and Co-catalyst in Au@ZnO-Pd Ternary Core-Shell Nanostructures

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SUPPORTING METHODS

Preparation of the Au Nanospheres. Au nanospheres (NSs) were synthesized by a seed-mediated growth method reported previously. In a typically procedure, 0.25 mL of $HAuCl_4$ aqueous solution (0.01 M) was added to 9.75 mL of CTAB aqueous solution (0.1 M), then quickly injection of 0.60 mL of freshly-prepared, ice-cold $NaBH_4$ aqueous solution (0.01 M) under vigorous stirring. The mixed resultant aqueous solution was kept at room temperature for 3 h under mild stirring to the formation of the seed 1. After the gradual addition of 9.75 mL of CTAB aqueous solution, 4 mL of $HAuCl_4$ aqueous solution (0.01 M), and 15 mL ascorbic acid (0.1 M) to 190 mL of water, 0.12 mL of seed 1 was put into the growth mixed aqueous solution. The mixed aqueous solution was gently shaken and then kept at room temperature for overnight to form the seed 2. In addition, the seed 2 was obtained by four times into water by centrifugation and then re-dispersion with water for further use. The seed 2 was first added into a growth aqueous solution, which is made up of 30 mL of CTAC aqueous solution (0.025 M), 0.75 mL of ascorbic acid (0.1M), and 1.5 mL of $HAuCl_4$ aqueous solution (0.01 M). Followed by the mixed aqueous solution was placed in an air-bath shaker at 45 °C for 3 h, then was centrifuged and re-dispersed in 30 mL of CTAB aqueous solution (0.02 M). Finally, 1.5 mL of $HAuCl_4$ aqueous solution (0.01 M) was added into the CTAB aqueous solution and then was placed in an air-bath shaker at 45 °C for 2 h to produce Au NSs. The synthesized Au NSs were centrifuged and re-dispersed in water before further use.

SUPPORTING FIGURES

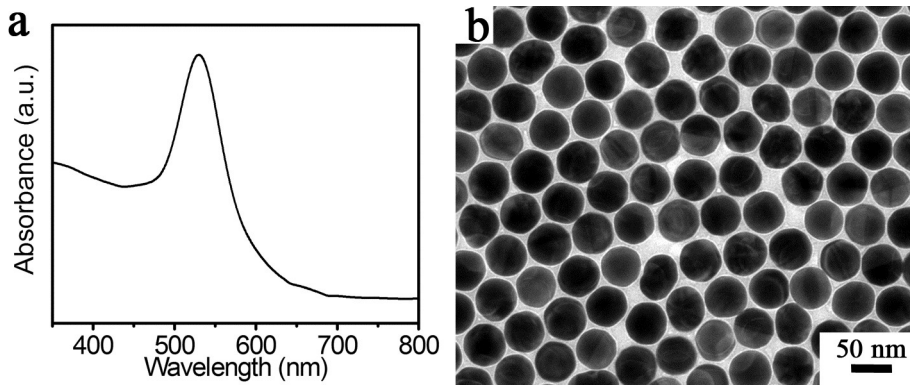

Fig. S1. (a) Extinction spectrum and (b) TEM image of the Au nanospheres used for preparing Au@ZnO core-shell nanostructures.

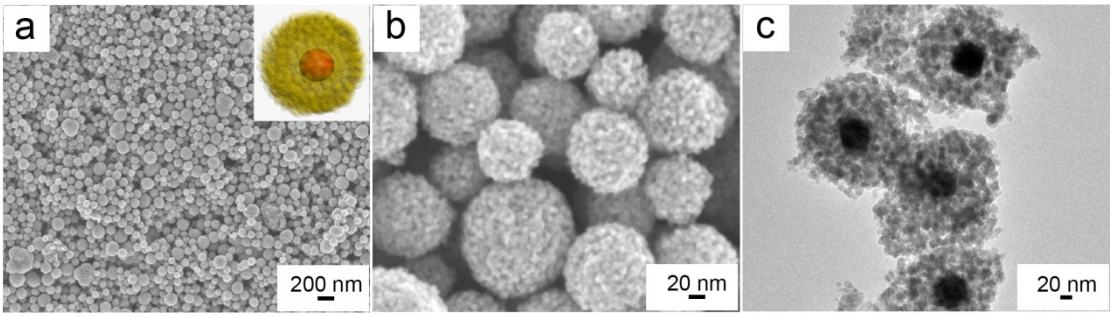

Fig. S2. (a-b) SEM and (c) TEM images of Au@ZnO core-shell nanostructures for preparing Au@ZnO-Pd ternary hybrid photocatalyst. Inset in (a) is the structural illustration of an Au@ZnO core-shell nanostructure.

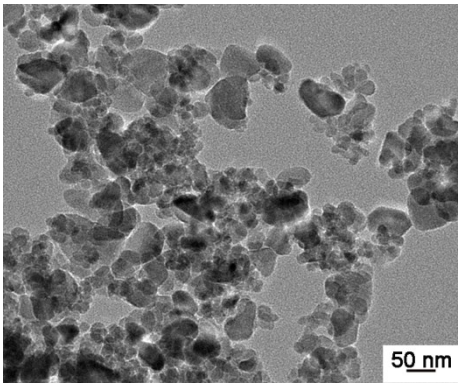

Fig. S3. TEM image of the pure ZnO sample prepared by the same method for Au@ZnO sample, without adding Au nanospheres.

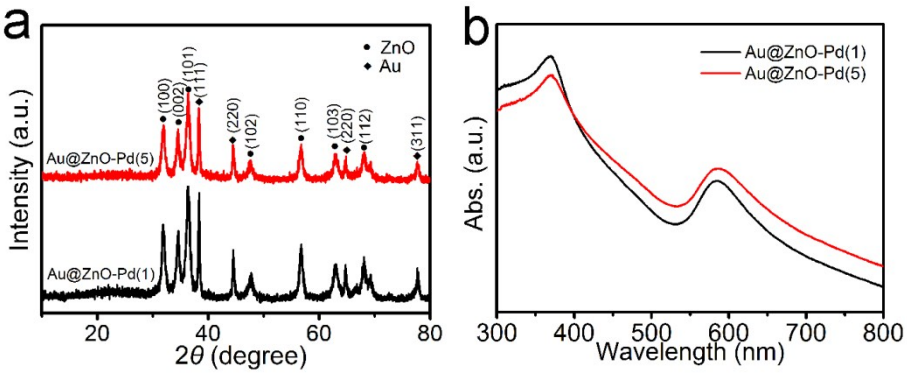

Fig. S4. (a) XRD patterns and (b) UV-vis absorption spectra of the Au@ZnO-Pd(*1*) and Au@ZnO-Pd(5) photocatalysts, respectively.

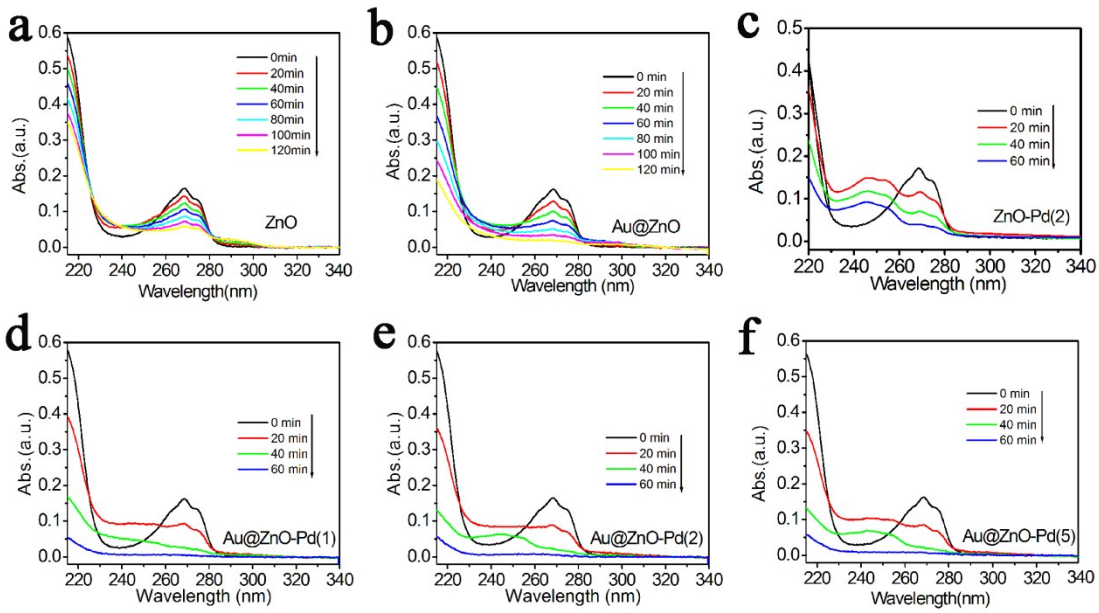

Fig. S5. The time-dependent absorption spectra of phenol solution in the presence of (a) pure ZnO nanoparticles, (b) Au@ZnO core-shell nanostructures, (c) ZnO-Pd(*2*), (d) Au@ZnO-Pd(*1*), (e) Au@ZnO-Pd(*2*), and (f) Au@ZnO-Pd(*5*), respectively, under the UV-visible light irradiation.

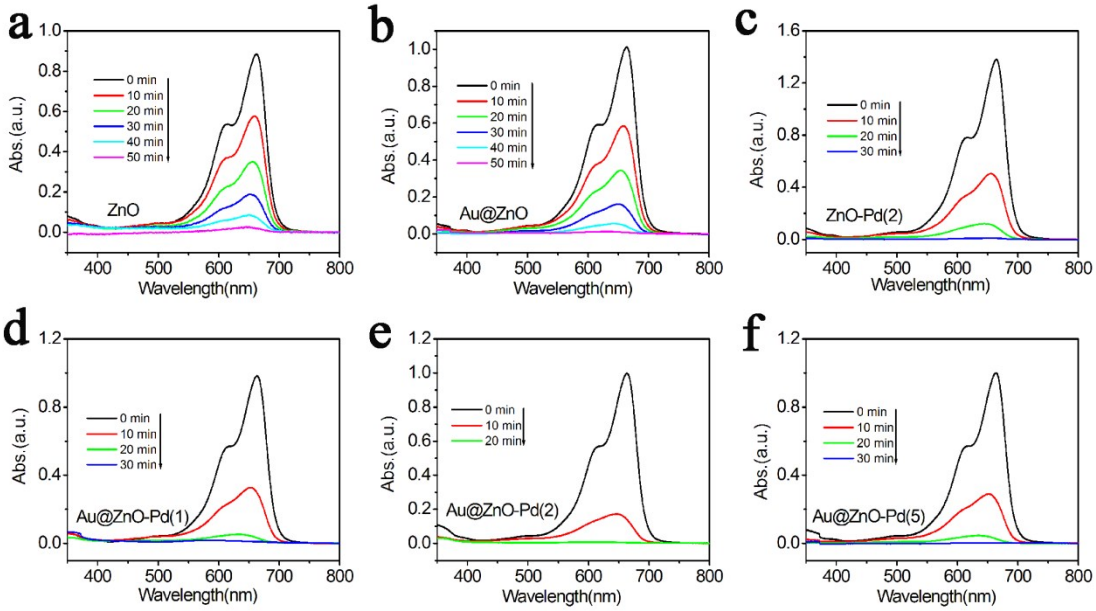

Fig. S6. The time-dependent absorption spectra of MB solution in the presence of (a) pure ZnO nanoparticles, (b) Au@ZnO core-shell nanostructures, (c) Pd-modified ZnO nanoparticles (ZnO-Pd(*2*)), (d) Au@ZnO-Pd(*1*), (e) Au@ZnO-Pd(*2*), and (f) Au@ZnO-Pd(*5*), respectively, under the UV-visible light irradiation.

Table S1 Theoretical and ICP-OES measured Pd loading amounts of Au@ZnO-Pd(*x*) samples.

Sample	Theoretical Pd loading (wt.%)[a]	Measured Pd loading (wt.%)[b]
Au@ZnO-Pd(*1*)	1.0	0.8
Au@ZnO-Pd(*2*)	2.0	1.8
Au@ZnO-Pd(*5*)	5.0	4.5

[a] The theoretical Pd loading mass percent calculated from the experimental dosage of $(NH_4)_2PdCl_4$ for each sample.

[b] The actual mass percent of Pd in each sample from the ICP-OES measured results.

Table S2. Lifetimes (τ_1, τ_2 and τ_m) and relative intensities (A_i) obtained by fitting the time-resolved PL decay spectra (Fig. 6b) of ZnO, Au@ZnO and Au@ZnO-Pd(*2*) to a biexponential decay function.

Sample	τ_1/ns (A_1)	τ_2/ns (A_2)	τ_m/ns
ZnO	0.162 (0.835)	1.34 (0.165)	0.356
Au@ZnO	0.139 (0.716)	1.149 (0.284)	0.426
Au@ZnO-Pd(*2*)	0.165 (0.705)	1.137 (0.295)	0.452

Table S3. The results of photocatalytic phenol degradation in the presence of Au@ZnO-Pd(*2*) photocatalyst with adding different scavengers.

No.	Scavenger	Scavenged radicals	Degradation rate (%)
1	No	No	100
2	IPA	•OH	51.2
3	EDTA-2Na	h^+	28.0
4	BQ	$•O_2^-$	62.2