Supporting Information

Organic-Inorganic Bimetallic Hybrid Particles with Controllable Morphology for Catalytic Degradation of Organic Dyes

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1. Materials and treatment

The monomers, styrene (St, 98.0%, Tianjin Chemical Reagent Co., Ltd.) and glycidyl methacrylate (GMA, 99.5%, J&K Chemical Reagent Co., Ltd.) were distilled under reduced pressure at elevated temperatures to remove inhibitors. The purified St and GMA monomers were stored in a refrigerator prior to use. Acetoacetoxyethyl methacrylate (AAM, Beijing Baiyuan Chemical Co., Ltd., Beijing, China) monomer was used without further purification. Zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$, 99.0%), sodium hydroxide (NaOH, analytical grade), isopropanol (IPA, 99.7%), silver nitrate ($AgNO_3$, 99.8%), ethanol absolute (analytical grade) were all obtained from the Tianjin Chemical Reagent Co., Ltd. (Tianjin, China). Potassium persulfate (KPS, above 99.5%), sodium borohydride ($NaBH_4$, 98.0%) were achieved from China Medicine Group Chemical Reagent Co., Ltd. 2,2'-(ethylenedioxy)bis(ethylamine) (EDEA, 98.0%), Rhodamine B (97.0%), Rhodamine 6G (97.0%), methyl orange(analytical grade), cyclohexane (99.8%) were supplied by J&K Chemical Reagent Co., Ltd. The above chemical reagents were used as received. Distilled water was employed as the polymerization medium.

2. Synthesis of ZnO NPs

First, 0.0351gof $Zn(Ac)_2 \cdot 2H_2O$ salt was added into 20 mL of isopropanol in a three-necked round-bottom flask equipped with a condenser, a magnetic stirrer, and a thermometer. The mixture was stirred at 55 ^oC for 1.5 h to dissolve the salt absolutely.

Then,2 mL of NaOH aqueous solution(0.5 mM concentration) was added into the above mixture within 5 min.Afterward,the reaction solution was stirred at 55 ^{o}C for another 2 h. To remove the solvent and unreacted salt, the as-synthesized mixture was centrifuged at 10000 rpm for 10 min. The particles were re-dispersed into 10 mL of ethanol, and centrifuged to settle them again. Finally,the particles were used to make catalyst dispersion (1.0×10^{-5}mol/L).

3. Synthesis of Ag NPs

0.027g of $AgNO_3$ was put into 10 mLof ethanol with stirring at room temperature in the protection of N_2.After 15 min, 0.030g of $NaBH_4$ was added in the above mixture, thesolution color immediately changed from colorless to gray-black. The resultant particles were recovered by filtration and washed with ethanol. Finally, the obtained particles were dispersed in distilled water to make catalyst dispersion (1.0×10^{-5}mol/L).

4. Characterization

SEM-EDS analysis

For SEM observation, the dispersions of P(St-*co*-AAM), P(St-*co*-AAM)/PGMA, P(St-*co*-AAM)&ZnO/PGMA, P(St-*co*-AAM)/PGMA&Ag and P(St-*co*-AAM)&ZnO/ PGMA&Ag particles were diluted with distilled water, and ultra-sonicated for 40 min to achieve a translucent suspension. Then, they were aero-sprayed onto carbon-coated silicon wafers, and dried overnight under reduced pressure at room temperature prior to observation via scanning electron microscopy (FE-SEM, Nano 450, FEI, U.S.A., operated at 10 kV) coupled with an EDS.

Fourier transform infrared spectrum (FTIR)analysis

FTIR spectra of the samples were recorded in KBr disks using a Bruker Vector-22 FTIR spectrometer.

Particle size distribution measurement

Size distributions of the above particles in an aqueous dispersion were measured via Zeta-Sizer 90 type of dynamic light scattering particle size analyzer (DLS, Malvern, England) with 532 nm incident light. Before measurement, a drop of the synthesized latex was diluted with distilled water in a glass tube and ultra-sonicated for 0.5 h for DLS measurement, which was conducted at 25 ^{o}C with 90 ^{o} of scattering angle.

XPS measurement

The carbon, oxygen, zinc and silver element contents on the surface of the complex colloidal particles were determined by X-ray photoelectron spectroscopy (XPS, K-Aepna ThemoFisher, UK).

ICP detection

Inductively coupled plasma spectrometer (ICP, Optima 8300, USA) was used to detect load mass of Ag and Zn on the hybrid particle catalysts. The solid samples were calcined under 700 ^{o}Cin a muffle furnace for 4h, the residue was diluted with 10 mL of distilled water.The amounts of Ag and Zn contained in the samples were then determined using calibration curves and dilution factors.

5. Results and discussion

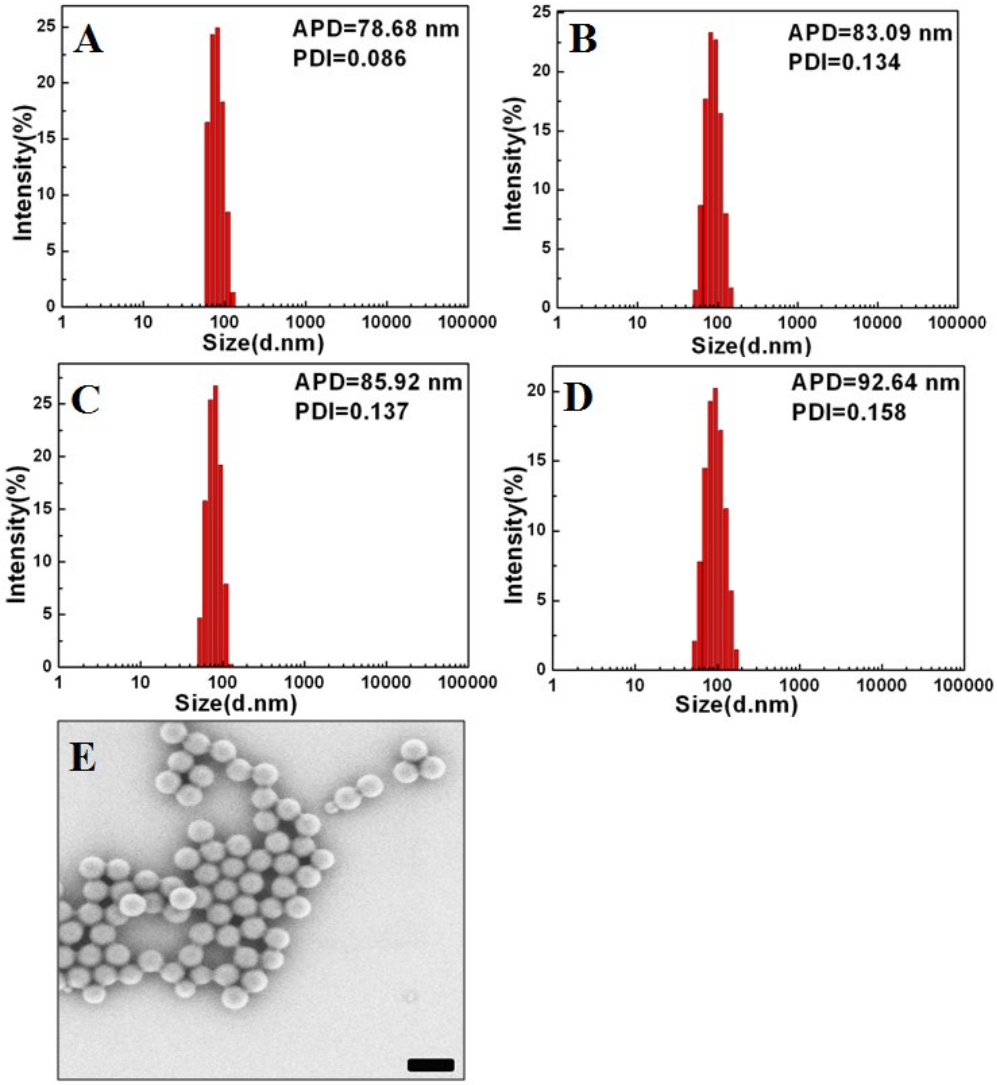


Fig. S1Average sizes and size distributions of P(St-*co*-AAM$_X$) particles tested by DLS where x =0 (A), 5 (B), 10 (C), 20wt% (D) based on St monomer, and SEM image of the P(St-*co*-AAM$_{20}$) particles (E). The

scale bar is 200 nm.

The minimum average size of synthesized particles, which came from the polymerization of pure styrene without AAM monomer, was 78.68 nm with PDI=0.086. With the increasing AAM monomers, the average sizes of obtained particles were slightly increasing, which might be attributed to the increase of hydrodynamic diameter of the particles caused by increasing hydrophilic AAM content. When the feed ratio of St/AAM was 3.0 g/0.6 g, the copolymer particles with maximum average size were achieved (APD=92.64 nm, PDI=0.158). Fig. S1-E shows the SEM image of P(St-*co*-AAM_{20}) particles, demonstrating that most of the particles are spherical.

For a better understanding of P(St-*co*-AAM) copolymer components, the reaction equation of synthesizing P(St-*co*-AAM) copolymer and FTIR spectra of synthesized several polymer particles are comparatively shown in Fig. S2.

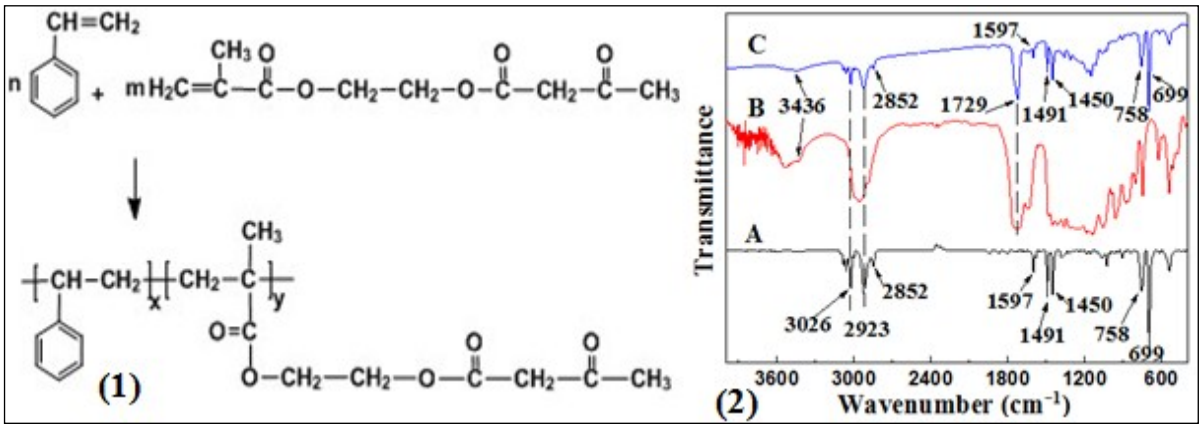


Fig. S2 Reaction equation of preparing P(St-*co*-AAM) (1) and FTIR spectra of several polymer particles synthesized for comparison(2): A, PS; B, PAAM; C, P(St-*co*-AAM).

As for the FTIR spectrum of pure PS displayed in Fig. S2(2)-A, the absorption bands at 758 and 699 cm^{-1} were attributed to =C–H folding vibration of single substituted benzene ring, and the peaks at 1450, 1491, and 1597 cm^{-1} were assigned to the C=C stretching vibration of benzene ring, while the bands at 2923 and 2852 cm^{-1} were due to the asymmetric/symmetric stretching vibrations of saturated C–H bond.[1] The band at 3026 cm^{-1} belonged to the stretching vibration of =C–H bond in benzene ring. All the above absorption peaks were from characteristic groups of PS. For the FTIR spectrum of PAAM (Fig. S2(2)-B),the typical absorption band displayed at 1729 cm^{-1} was assigned to the

stretching vibration of carbonyl groups (-C=O) in PAAM chain segments.[2] Besides, the absorption peak at around 3436 cm^{-1} could be ascribed to the -OH absorption of a little water in KBr. While for the P(St-*co*-AAM) particles, all the characteristic absorption peaks of PS and PAAM were reflected on the FTIR spectrum of P(St-*co*-AAM) (Fig. S2(2)-C). Thus, it can be concluded that the copolymerization of St and AAM was successfully conducted to make P(St-*co*-AAM) copolymer.

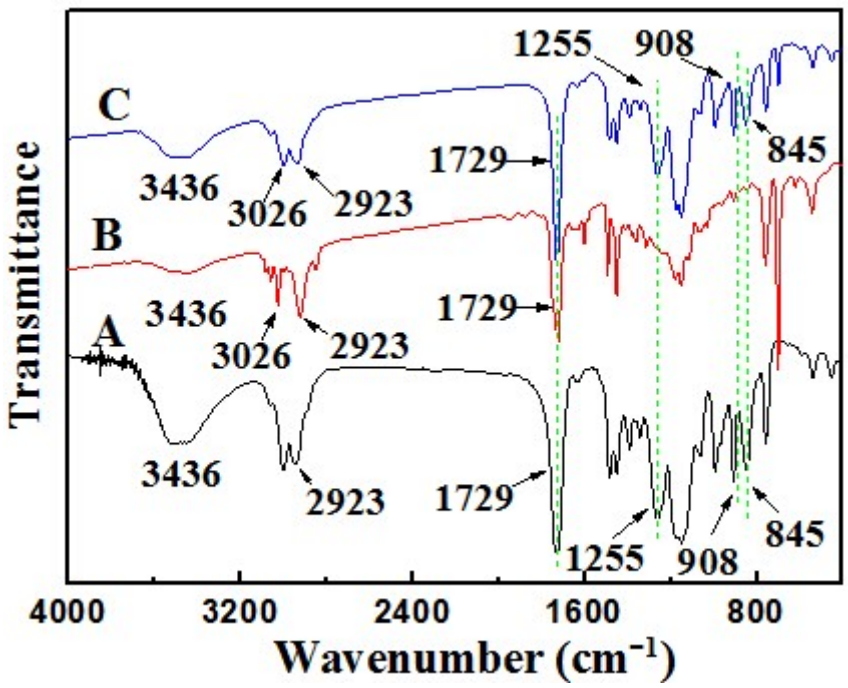
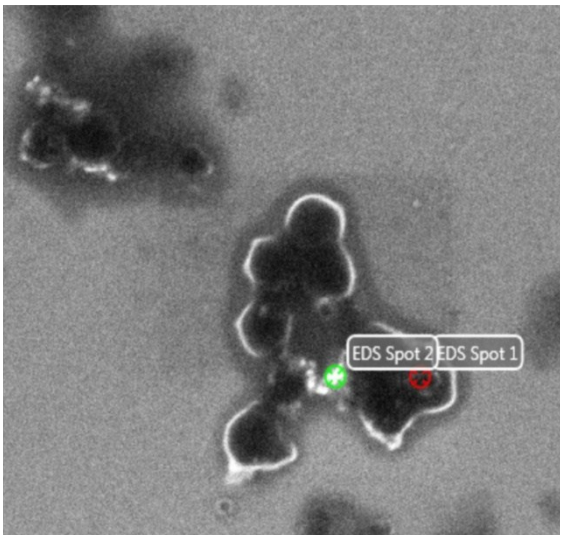
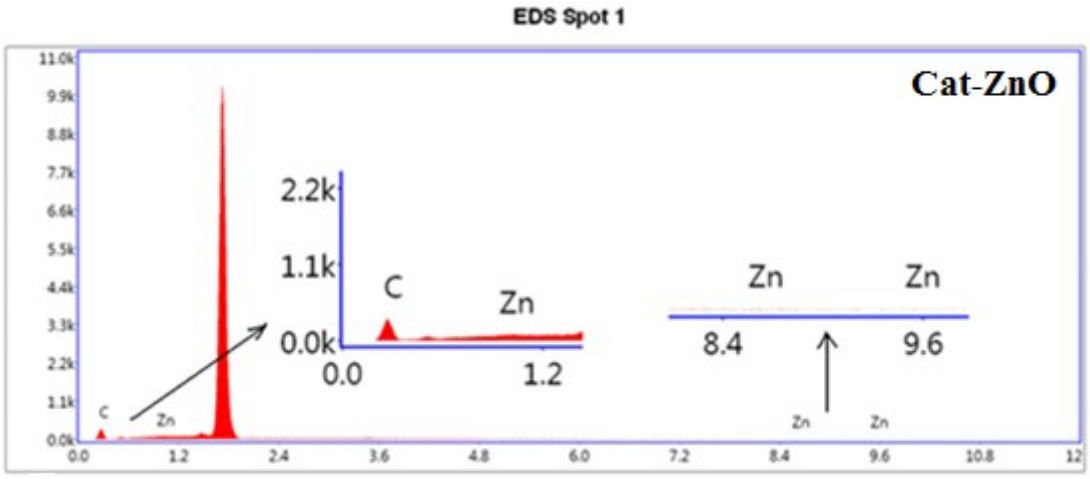


Fig. S3 FTIR spectra of PGMA (A), P(St-*co*-AAM) (B), and P(St-*co*-AAM)/PGMA (C).





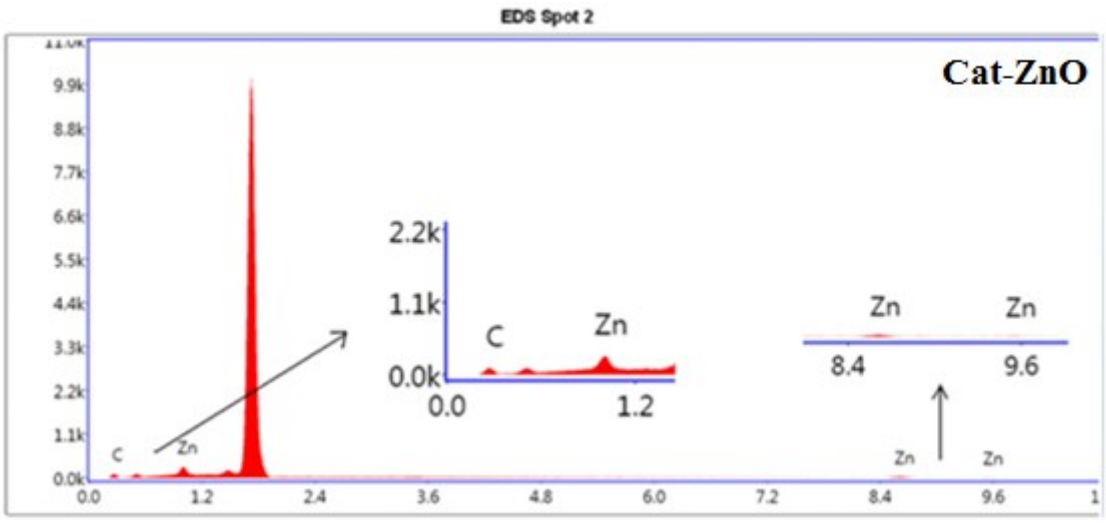


Fig. S4 EDS spectra of corresponding spot 1 and spot 2 of Cat-ZnO particles catalyst.

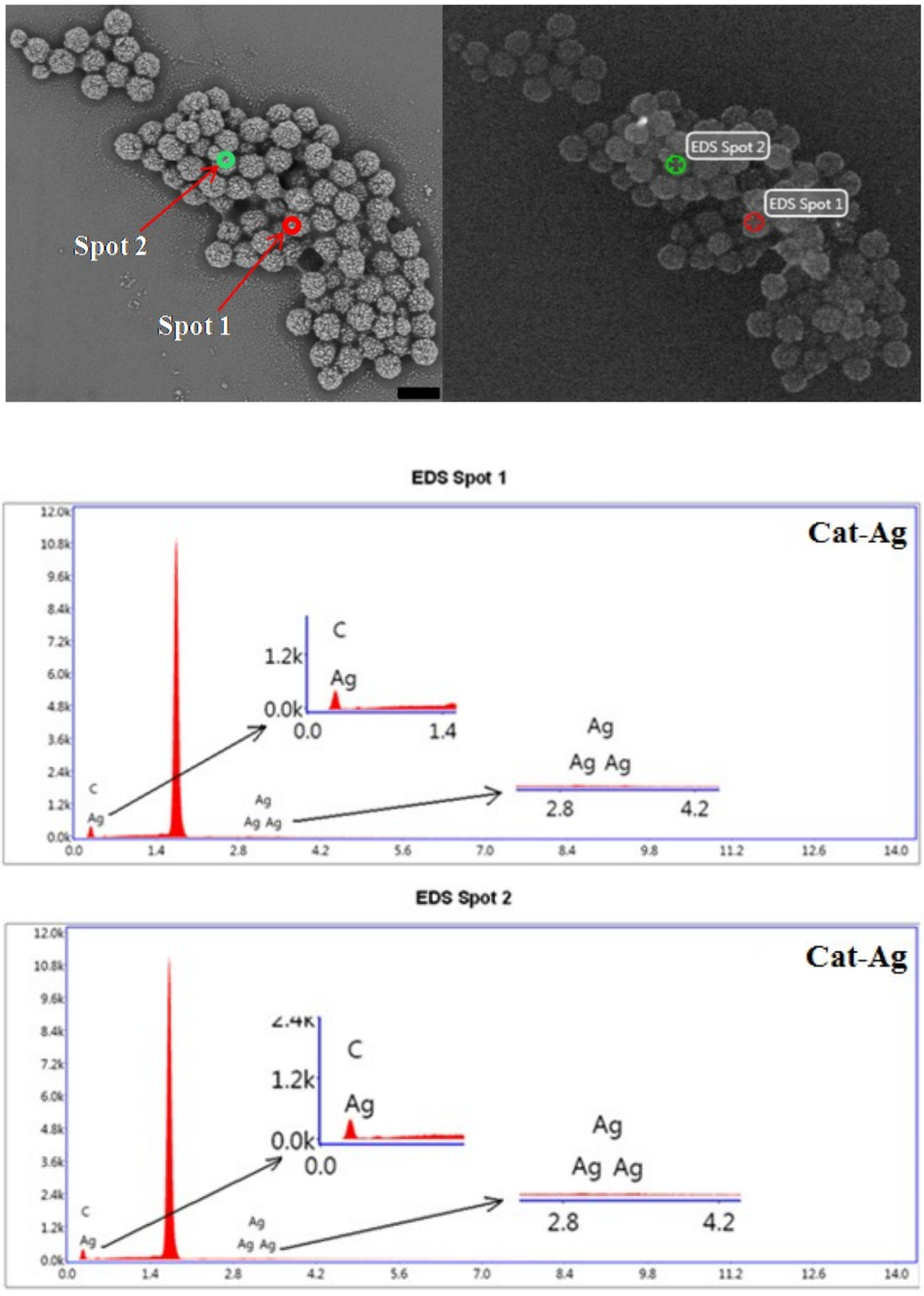


Fig. S5 SEM image and corresponding EDS spot scan characterization of Cat-Ag catalyst particles. The scale bar is 200 nm.

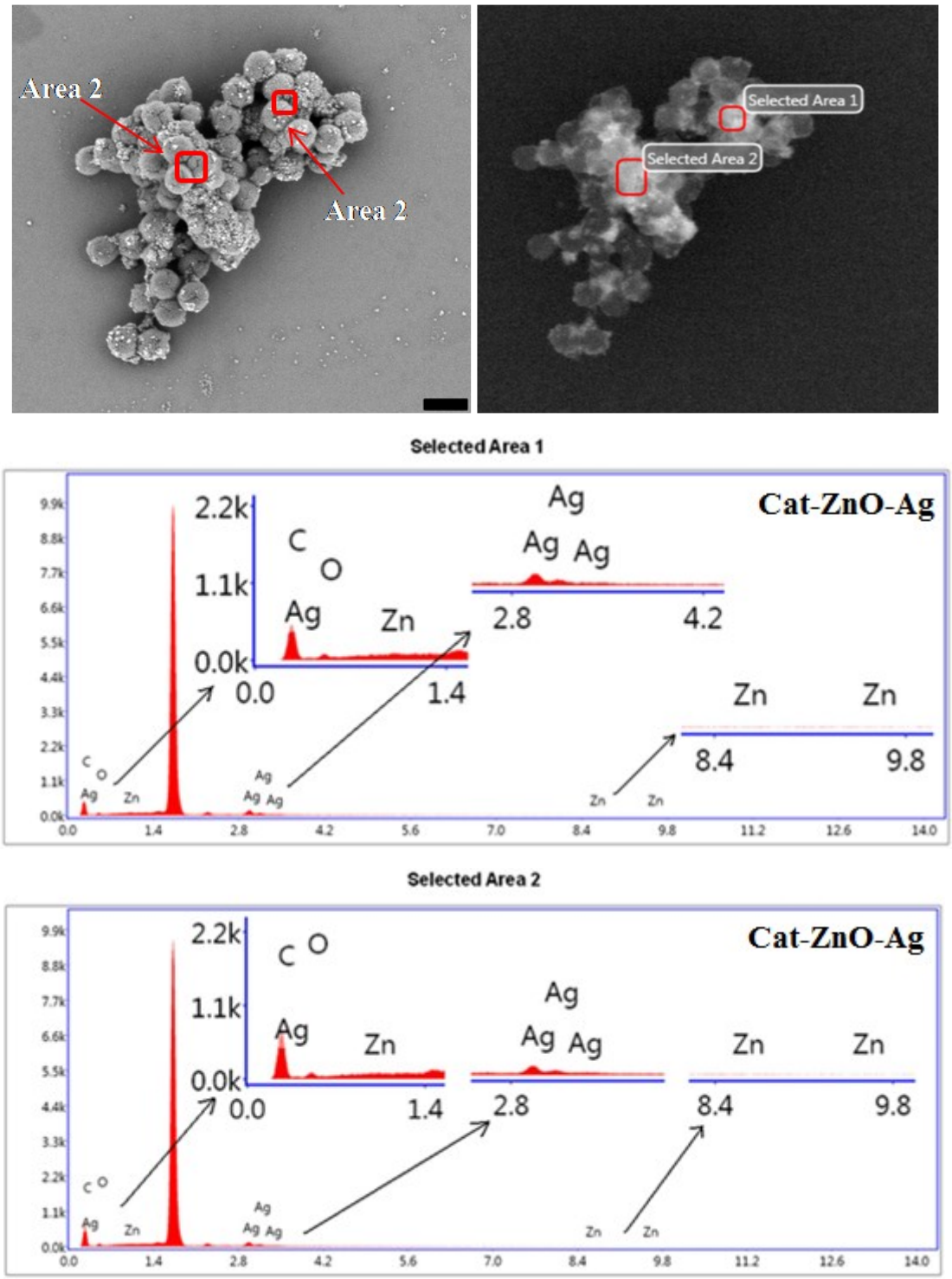


Fig. S6 SEM image and corresponding EDS spot scan characterization of Cat-ZnO-Ag catalyst particles.

The scale bar is 200nm.

Table S1 Apparent rate constants of the catalysts under different addition volumes of catalyst solutions in degradation of RhB

Catalyst type	Addition volume of catalyst solution (mL) **	K(min^{-1})
Cat-ZnO (Zn wt%=4.6%)	0.5	0.06
	1.0	0.08
	1.5	0.09
	2.0	0.10
	2.5	0.16
Cat-Ag (Ag wt%=1.3%)	0.5	0.18
	1.0	0.25
	1.5	0.30
	2.0	0.47
	2.5	0.63

**Reaction conditions: Using 10 mL of 2×10^{-5} mol/L RhB, 0.5 mLof 1.2mol/L $NaBH_4$ and keeping the same concentration of metal NPs through adding different volumes of water in the varying catalyst dispersions.

Table S2 Apparent rate constants of Cat-ZnO catalyst under different addition volumes of Cat-ZnO solution in degradation of Rh6G.

Catalyst type	Addition volume of catalyst solution (mL) **	K(min^{-1})
Cat-ZnO (Zn wt%=4.6%)	0.5	0.14
	1.0	0.15
	1.5	0.16
	2.0	0.17
	2.5	0.22

**Reaction conditions: Using 10 mL of 2×10^{-5} mol/L Rh6G, 0.5 mLof 1.2mol/L $NaBH_4$ and keeping the same concentration of metal NPs through adding different volumes of water in the varying catalyst dispersions.

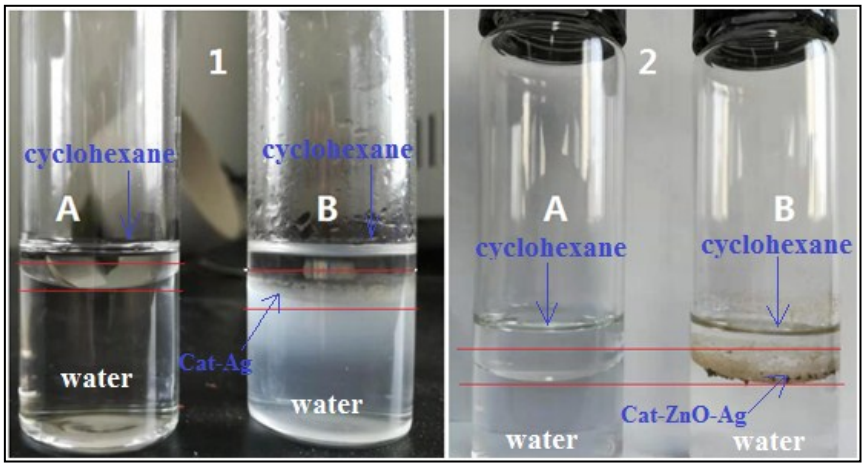


Fig. S7 Distribution states of Cat-Ag (1-B) and Cat-ZnO-Ag (2-B) particles in oil-water mixture of cyclohexane and water. 1-A/2-A: oil-water mixture with no catalyst.

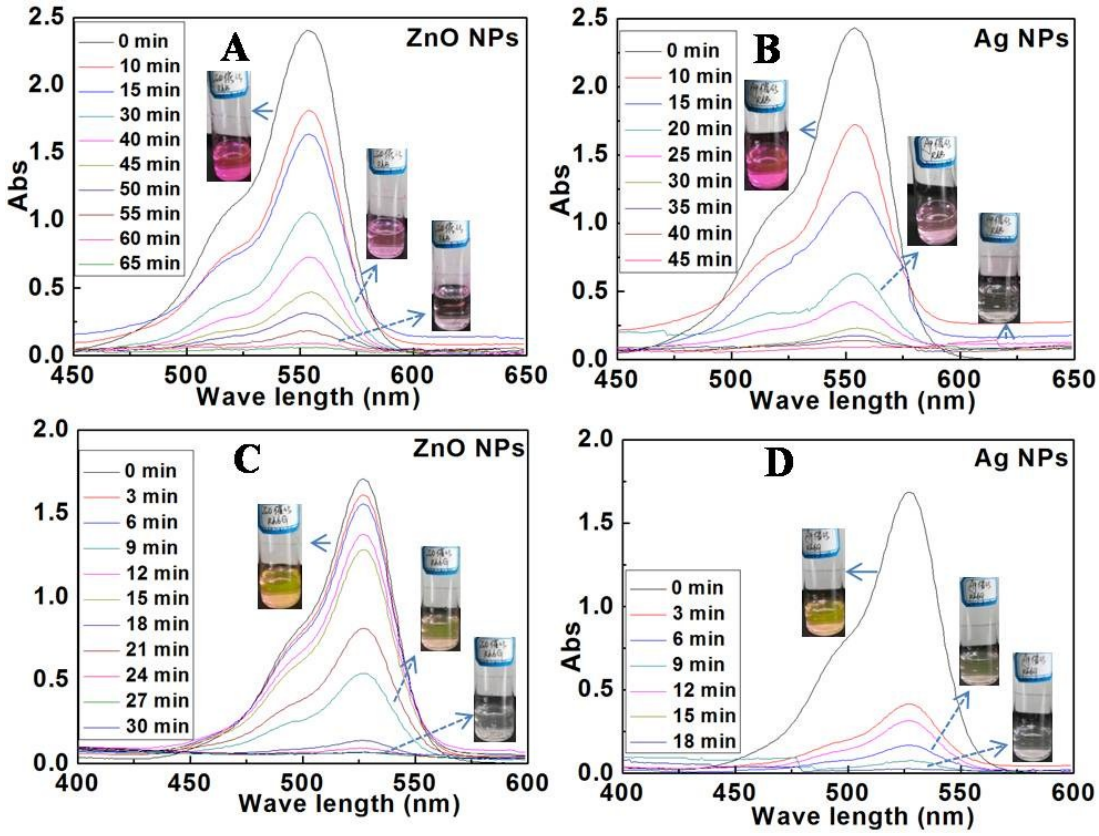


Fig. S8 UV-visible spectra of RhB (A/ B) or Rh6G (C/ D) solution reduced by $NaBH_4$ and the catalyst as function of reaction time with 10 mL of RhB or Rh6G solution (2×10^{-5} mol/L) and 0.5 mL of $NaBH_4$ solution (1.2 mol/L): 0.5 mL of ZnO NPs dispersion (A/ C), 0.5 mL of Ag NPs dispersion (B/ D). The concentrations of metal NPs were all the same in the solutions of catalysts.

From Fig. S8, when taking pure ZnO particles as catalyst to degrade RhB, it would take about 65 min to achieve above 99% degradation efficiency (Fig. S8-A), which took more time than that of Cat-ZnO (50 min, Fig. 6-B). For pure Ag particles, when putting 0.5 mL of the catalyst dispersion into RhB solution, only 45 min was needed to get the same degradation efficiency (Fig. S8-B), but the cost time was still greater than that of Cat-Ag (25 min, Fig. 6-C). Besides, the color of both RhB solutions gradually became lighter and lighter.

When the dispersions of two kinds of metal particles were added into Rh6G solution, respectively, and other conditions were kept same as those of degradation of RhB, it took about 30 min for the ZnO particles catalyst to get above 99% degradation efficiency of Rh6G (Fig. S8-C), which was about 15 min greater than that of Cat-ZnO catalyst (Fig. 8-B). For Ag particles, it only needed 18 min to acquire the same effect (Fig. S8-D), but the activity of Ag particles was still inferior to that of Cat-Ag, in which the time to gain 99% degradation efficiency was about 5 min (Fig. 8-C). Similarly, the color of both Rh6G solutions changed from the orange yellow to colorless.

6. References

[1] C.Y. Loo, P.M. Young, W.H. Lee, R. Cavaliere, C.B. Whitchurch, R. Rohanizadeh, *Acta Biomater*., 2012, 8, 1881-1890.

[2] V. Boyko, A. Pich, Y. Lu, S. Richter, K.F. Arndt, H.J.P. Adler, *Polymer*, 2003, 44, 7821-7827.