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Electronic Supplementary Information

A general route to coat poly(cyclotriphosphazene-co-4,4’-sulfonyldiphenol) on various substrates and derived N, P, S-doped hollow carbon shell for catalysis

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Experimental Section

Materials: Hexachlorocyclophosphazene (98%) and 4,4'-sulfonyldiphenol (99%), Ethylbenzene (99%), anisole (99%), 4-ethylanisole (98+%), cumene (99%), diphenylmethane (99+%), fluorene (98+%), tert-butyl hydroperoxide (70% aqueous solution), Sodium acetate trihydrate (99+%) and sodium fluoride (99+%) were provided by Acros. 2-Ethylnaphthalene (99%) was provided by TCI. 1-Ethyl-4-nitrobenzene (98%+) was produced by Adamas. L-ascorbic acid (99+%) and zinc nitrate hexahydrate (98%) were provided by Alfa-Aesar. Graphene oxide (GO) was a product of Tianjin Plannano Technology Co., LTD. MWCNT (d = 60~100 nm, L = 5~15 um) was purchased from Shenzhen Nanotech Port Co. Ltd (NTP), China. Potassium palladium (II) chloride (K_2PdCl_4) and ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$) were provided by Aladdin. Triethylamine (99%), 2-methylimidazole (99%) and *N*,*N*-dimethylformamide (SuperDry, 99.8%) were produced by J&K scientific Co., Ltd. Anatase TiO_2 and rutile TiO_2 were purchased from Beijing Dk Nano technology Co., LTD. ZrO_2 nanopowder (<100 nm particle size (TEM)), tin nanopowder (<150 nm particle size (SEM), ≥99% trace metals basis), oleylamine (technical grade, 70%), poly(vinyl pyrrolidone) (PVP, average Mw~55,000), F-127 and palladium(II) acetate (reagent grade, 98%) were provided by Sigma-Aldrich. Sodium carbonate (A.R.), glucose (A.R.), ethylenediamine (anhydrous), potassium bromide (A.R.) and $FeCl_3\ 6H_2O$ were provided by Sinopharm Chemical Reagent Beijing Co. Ltd.

Synthesis of Fe_3O_4 colloidal nanocrystal clusters: The Fe_3O_4 colloidal nanocrystal clusters (CNC) were prepared according to a previous report with minor modification.[1, 2] In a typical experiment, $FeCl_3\ 6H_2O$ (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL) to obtain a clear brown solution. Then CH_3COONa (3.6 g) and anhydrous ethylenediamine (10mL) were added. The resulting reaction mixture was stirred for 30 min and then sealed in a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 ℃ for 8 h. After cooling to room temperature, the black products were collected by magnet, and washed with ethanol three times. The obtained samples were further dried under vacuum at room temperature for 6 h.

Synthesis of α-Fe_2O_3 nanospindles: The α-Fe_2O_3 nanospindles were prepared according to a previous report.[3, 4] In a typical experiment, $FeCl_3\ 6H_2O$ (0.405 g, 1.5 mmol) was dissolved in 75 mL 0.45 mmol/L NaH_2PO_4 solution, then the obtained orange solution was transferred to a 100 mL teflon autoclave, and heated at 105 ℃ in an electric oven for 48 h.

Synthesis of X-shaped α-FeOOH: The X-shaped α-FeOOH nanocrystals were obtained through a simple hydrothermal process.[5] Typically, 53 mg of sodium fluoride and 20 mg of sodium carbonate were added in an 80 mL aqueous solution of iron chloride hexahydrate (0.12 mM) under stirring for 15 min to form transparent solution. Then the mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed, and kept at 150 ℃ for 12 h. The yellow products were collected by centrifugation at 5000 r/min and rinsed several times with deionized water before drying at 80 ℃ overnight.

Synthesis of carbon nanospheres: The carbon nanospheres were prepared according to a previous report.[6, 7] Glucose (4.5 g) was dissolved in 30 mL water to form a clear solution and then transferred into a 40mL Teflon-sealed autoclave. The autoclave was maintained at 190 ℃ for 4h. The products were separated by centrifugation, followed by washing three times using water and ethanol and finally oven-dried at 80 ℃ for further use.

Synthesis of Pd nanostructures: The Pd nanostructures were prepared according to a previous report with modification.[8] In a typical experiment, 210 mg poly(vinyl pyrrolidone) (PVP, M.W.=55,000), 120 mg L-ascorbic acid and 600 mg KBr were dissolved into 16 mL water at 80 ^{o}C oil bath. After stirring for 30 min, 3.0 mL potassium palladium (II) chloride aqueous solution was added with a pipette, followed by the injection of 1.0 mL ruthenium chloride hydrate aqueous solution. The reaction was allowed to continue at 80 ℃ for 30 min. The product was collected by centrifugation and washed three times with deionized water. The potassium palladium (II) chloride aqueous solution was prepared through dissolving 189 mg potassium palladium(II) chloride into 9 mL water. The ruthenium chloride hydrate aqueous solution was prepared through dissolving 40 mg ruthenium chloride hydrate into 8 mL water.

Synthesis of Pt nanoframes: The Pt nanoframes were prepared according to a previous report with modification.[9] In a typical experiment, 6.0 mg of $H_2PtCl_6 \cdot 6H_2O$ and 2 mL of oleylamine were added into 8 mL of N, N-Dimethylmethanamide. After stirring for 1 h, the resultant homogeneous and transparent solution (10 mL) was transferred into a 50 mL Teflon-lined autoclave. The autoclave was maintained at 160 ℃ for 12 h, and then cooled down to room temperature. The black products were collected by centrifugation and washed with ethanol and acetone several times.

Synthesis of ZIF-8 polyhedrons: The ZIF-8 polyhedrons ($Zn(MeIM)_2$, MeIM = 2-methylimidazole) were prepared according to a previous report with minor modification.[10] In a typical experiment, 1.758 g of zinc nitrate hexahydrate was dissolved into 30 mL of methanol to obtain a clear solution. Then 3.888 g of 2-methylimidazole was dissolved in 30 mL of methanol. Then the 2-methylimidazole solution was poured into the zincous solution under magnetic stirring. After stirring for 1.5 h, the resulting white precipitates were centrifuged and washed thoroughly with methanol three times and dried under vacuum at room temperature for 12 h.

Preparation of ZIF-8@PZS: 1.758 g of zinc nitrate hexahydrate was dissolved into 30 mL of methanol to obtain a clear solution. Then 3.888 g of 2-methylimidazole was dissolved in 30 mL of methanol. Then the 2-methylimidazole solution was poured into the zincous solution under magnetic stirring. After stirring for 1.5 h, the resulting white precipitates were centrifuged and washed thoroughly with methanol three times. The above synthesized ZIF-8 polyhedrons were dispersed into 80 mL methanol under ultrasound for 5 minutes. Then another solution was prepared by dissolving 200 mg of hexachlorocyclophosphazene and 450 mg of 4, 4'-sulfonyldiphenol into 10 mL of methanol to obtain a clear solution. Next, the clear solution was added into the above-mentioned ZIF-8 suspensions drop by drop. After stirring for 5 minutes, 550 μL of triethylamine was added dropwise and the solution was continued to stir for 8 h. When the reaction time was reached, the white precipitates were collected and washed with methanol for three times and dried under vacuum at room temperature for 12 h. The obtained product was denoted as ZIF-8@PZS.

Preparation of GO@PZS: Typically, 20 mg of graphene oxide (GO) was dispersed in 50 mL methanol under ultrasound for 25 minutes. Then another solution containing 70 mg of hexachlorocyclophosphazene and 158 mg of 4, 4'-sulfonyldiphenol in 10 mL of methanol was added drop by drop. After stirring for 5 minutes, 185 μL of triethylamine was added dropwise and the solution was continued to stir for 6 h. When reaction time was reached, the products were collected and washed with methanol for three times and dried under vacuum at room temperature for 12 h. The obtained product was denoted as GO@PZS.

Preparation of C Sphere@PZS: Typically, 100 mg of carbon sphere was dispersed in 40 mL methanol under ultrasound for 15 minutes. Then another solution containing 70 mg of hexachlorocyclophosphazene and 158 mg of 4, 4'-sulfonyldiphenol in 10 mL of methanol was added drop by drop. After stirring for 5 minutes, 185 μL of triethylamine was added dropwise and the solution was continued to stir for 6 h. When reaction time was reached, the products were collected and washed with methanol for three times and dried under vacuum at room temperature for 12 h. The obtained product was denoted as C Sphere@PZS.

Preparation of MWCNT@PZS: Typically, 100 mg of multi-walled carbon nanotube (MWCNT) was dispersed in 40 mL methanol under ultrasound for 15 minutes. Then another solution containing 270 mg of hexachlorocyclophosphazene and 608 mg of 4, 4'-sulfonyldiphenol in 20 mL of methanol was added drop by drop. After stirring for 5 minutes, 715 μL of triethylamine was added dropwise and the solution was continued to stir for 6 h. When reaction time was reached, the products were collected and washed with methanol for three times and dried under vacuum at room temperature for 12 h. The obtained product was denoted as MWCNTs@PZS.

Preparation of Pd@PZS: Typically, 9 mL Pd dispersion was collected by centrifugation and washed three times with deionized water. The obtained black solid was dispersed in 20 mL acetonitrile under ultrasound for 7 minutes. Then another solution was prepared by dissolving 5 mg of hexachlorocyclophosphazene and 11 mg of 4, 4'-sulfonyldiphenol into 5 mL of acetonitrile to obtain a clear solution. The clear solution was added into the above-mentioned suspensions drop by drop. After stirring for 2 minutes, 111 μL of triethylamine was added dropwise and the solution was continued to stir for 8 h. When reaction time was reached, the products were collected and washed with acetonitrile for three times and dried under vacuum at room temperature for 12 h.

Preparation of Pt@PZS: Typically, the above prepared Pt nanoframes were dispersed into 20 mL acetonitrile under ultrasound for 7 minutes. Then another solution was prepared by dissolving 3 mg of hexachlorocyclophosphazene and 7 mg of 4, 4'-sulfonyldiphenol into 4 mL of methanol to obtain a clear solution. Next, the clear solution was added into the above-mentioned suspensions drop by drop. After stirring for 2 minutes, 70 μL of triethylamine was added dropwise and the solution was continued to stir for 6 h. When reaction time was reached, the products were collected and washed with acetonitrile for three times and dried under vacuum at room temperature for 12 h.

Preparation of MWCNT-Fe_3O_4@PZS: In a typical procedure, 300 mg Fe(acac)$_3$ and 80 mg MWCNTs were added to 48 mL triethylene glycol (TREG) which was loaded in a 100 mL flask and then the mixture was ultrasonicated for 10 min. The resulting composites were rapidly heated to 190 ^{o}C, maintained there for 30 min under argon protection, then rapidly heated to 278 ^{o}C, and held there for an additional 30 min. After cooling to room temperature, the obtained mixture was centrifugated and washed with ethyl acetate for 5 times and dried in vacuum at room temperature for 3 h. The above prepared MWCNT-Fe_3O_4 composites were dispersed into 80 mL methanol under ultrasound for 3 minutes. Then another solution was prepared by dissolving 500 mg of hexachlorocyclophosphazene and 1125 mg of 4, 4'-sulfonyldiphenol into 20 mL of methanol to obtain a clear solution. Next, the clear solution was added into the above-mentioned suspensions drop by drop. After stirring for 5 minutes, 1300 μL of triethylamine was added dropwise and the solution was continued to stir for 9 h. When reaction time was reached, the precipitates were collected and washed with methanol for three times and dried under vacuum at room temperature for 12 h. The obtained product was denoted as MWCNT-Fe_3O_4@PZS.

Exploration of the solvent effect: Typically, 100 mg ZrO_2 was dispersed in 50 mL solvent (solvents including methanol, ethanol, acetone, acetonitrile, water, hexane, DMF and DMSO) under ultrasound for 15 minutes. Then another mixture containing 70 mg of hexachlorocyclophosphazene (0.2 mmol) and 158 mg of 4, 4'-sulfonyldiphenol (0.63 mmol) in 10 mL of solvent was added drop by drop. After stirring for 5 minutes, 185 μL of triethylamine was added dropwise and the solution was continued to stir for 6 h. When reaction time was reached, the products were collected and washed with solvent for three times. The coating results were ascertained by transmission electron microscope (TEM).

Preparation of PZS-900-2 h: 300 mg of hexachlorocyclophosphazene and 675 mg of 4, 4'-sulfonyldiphenol were dissolved into 20 mL of methanol to obtain a clear solution. Next, 1 mL of triethylamine was added dropwise and the solution was continued to stir for 18 h. When the reaction time was reached, the white precipitates were collected and washed with methanol for three times and dried under vacuum at room temperature for 12 h. The white product was calcined at 900 ℃ with heating rate of 2 ℃/min for 2 h in a tubular furnace under argon atmosphere. The obtained sample was denoted as PZS-900.

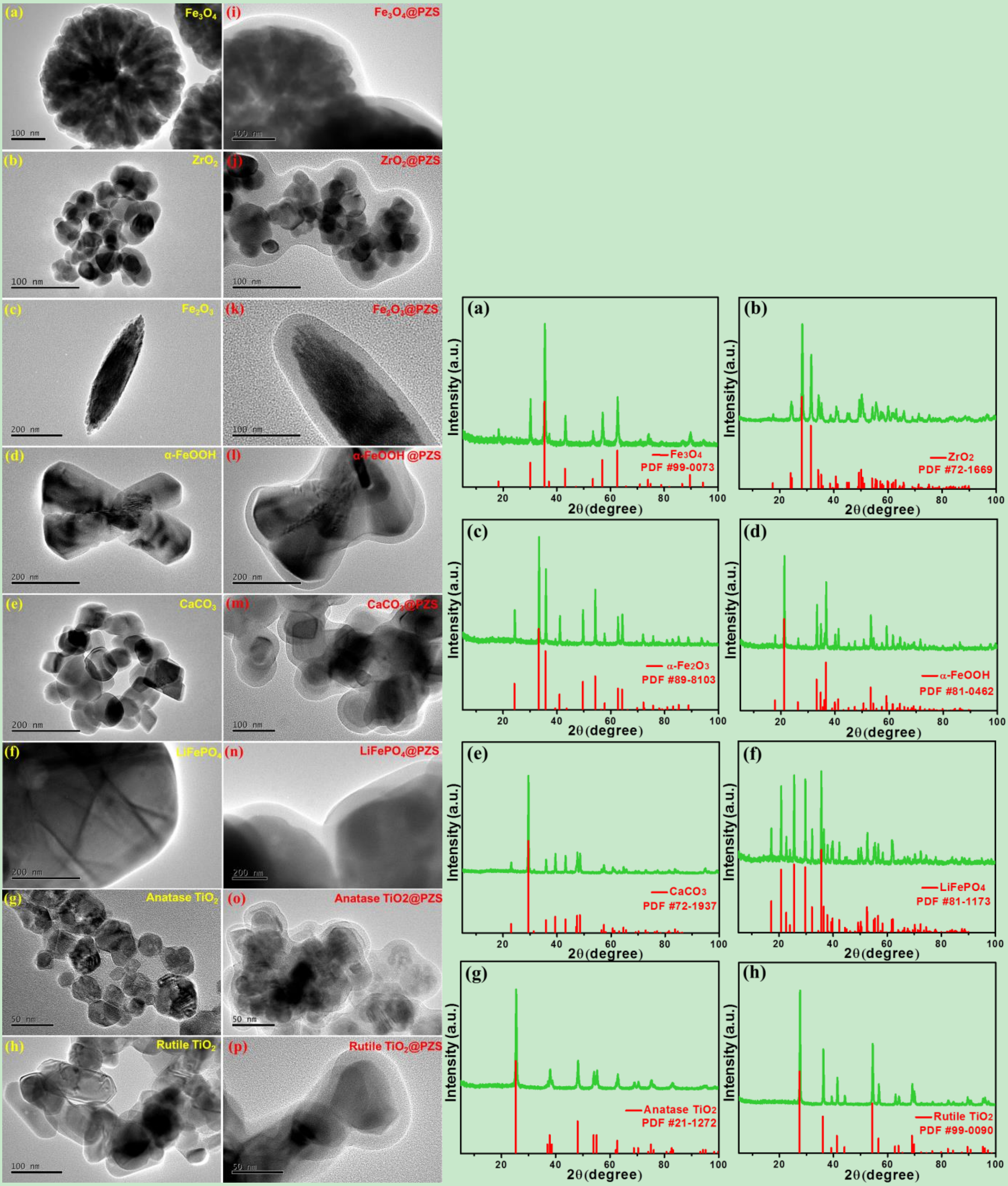


Fig. S1 Left: TEM images of the Fe_3O_4 (a), ZrO_2 (b), α-Fe_2O_3 (c), α-FeOOH (d), $CaCO_3$ (e), $LiFePO_4$ (f), anatase TiO_2 (g), rutile TiO_2 (h) and the corresponding Fe_3O_4@PZS (i), ZrO_2@PZS (j), α-Fe_2O_3@PZS (k), α-FeOOH@PZS (l), $CaCO_3$@PZS (m), $LiFePO_4$@PZS (n), anatase TiO_2@PZS (o), rutile TiO_2@PZS (p) core-shell nanostructures. **Right:** XRD patterns of the Fe_3O_4@PZS (a), ZrO_2@PZS (b), α-Fe_2O_3@PZS (c), α-FeOOH@PZS (d), $CaCO_3$@PZS (e), $LiFePO_4$@PZS (f), anatase TiO_2@PZS (g) and rutile TiO_2@PZS (h) core-shell nanostructures.

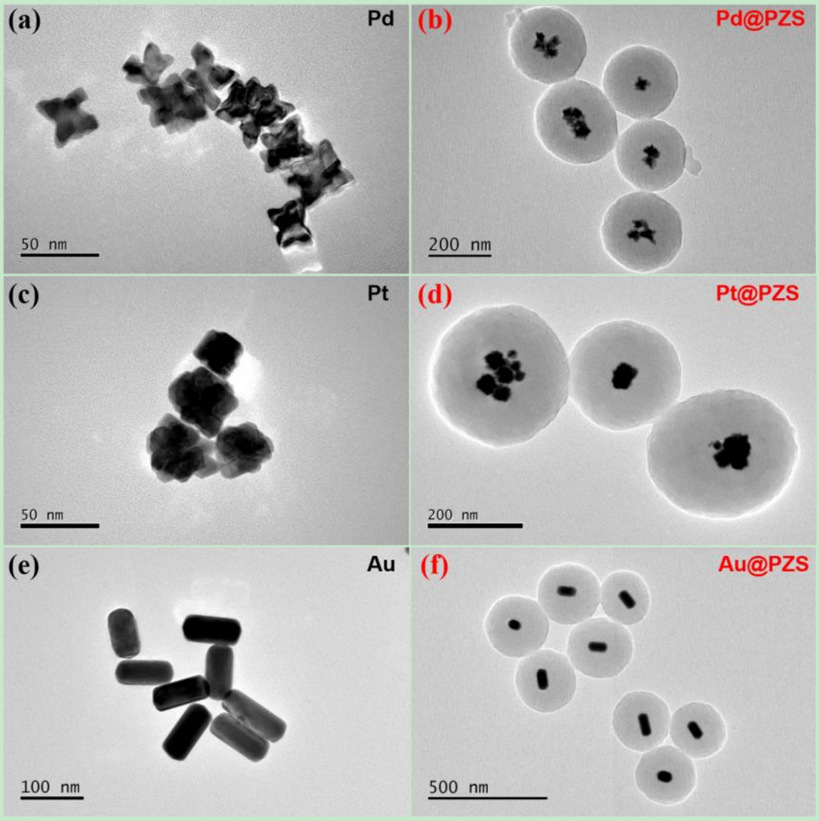


Fig. S2 TEM images of the Pd (a), Pt (c), Au (e) and the corresponding Pd@PZS (b), Pt@PZS (d), Au@PZS (f) core-shell nanostructures.

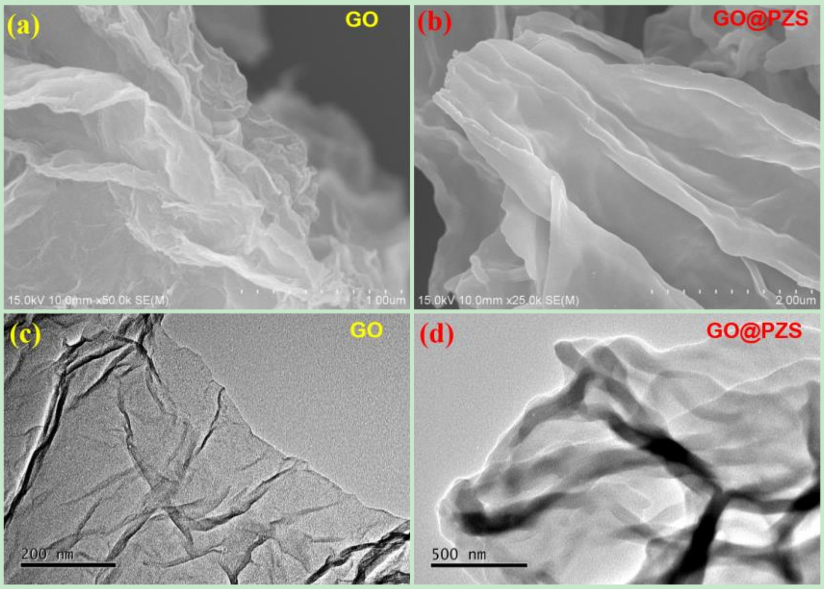


Fig. S3 SEM and TEM images of the GO (a, c) and the corresponding coated GO@PZS (b, d).

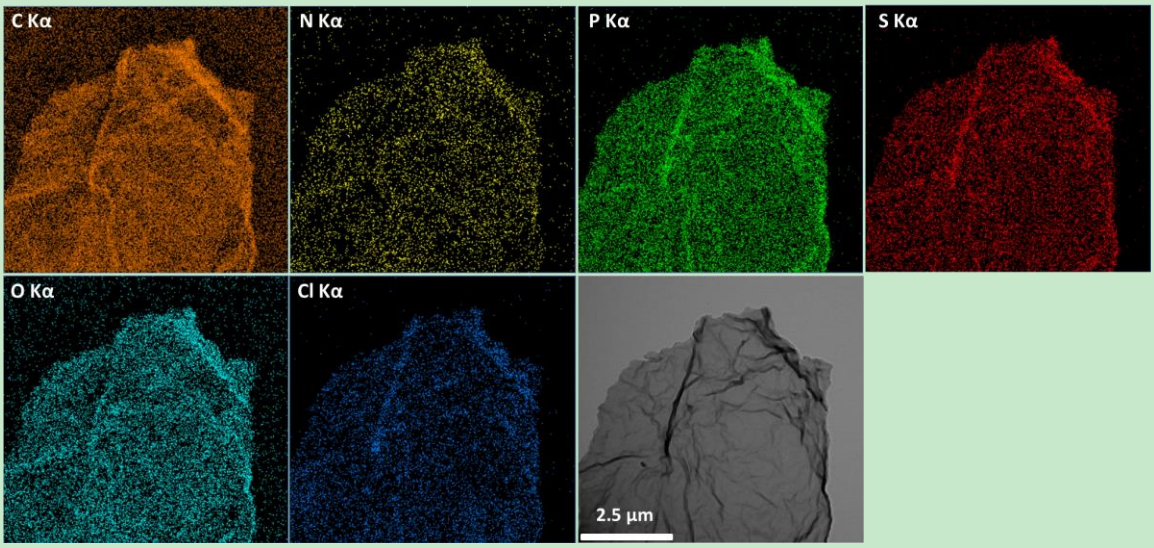


Fig. S4 EDS mapping of the GO@PZS structure.

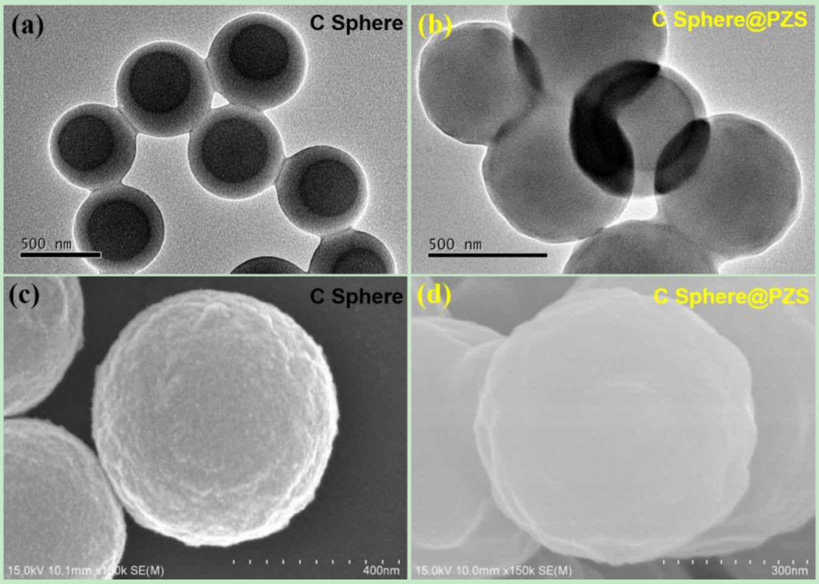


Fig. S5 SEM and TEM images of the C sphere (a, c) and the corresponding coated C sphere@PZS (b,d).

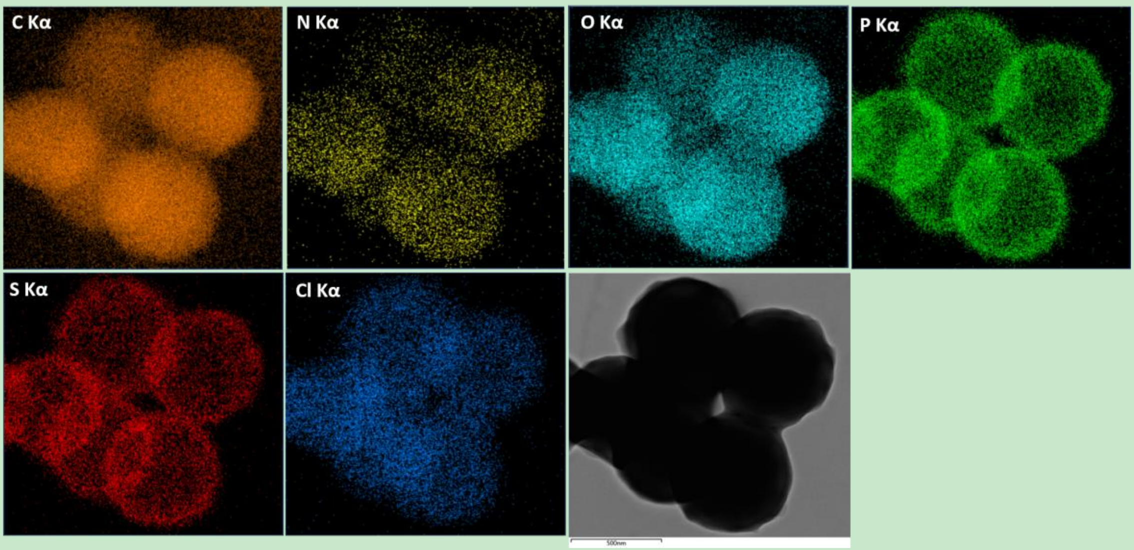


Fig. S6 EDS mapping of the C sphere@PZS core-shell structure.

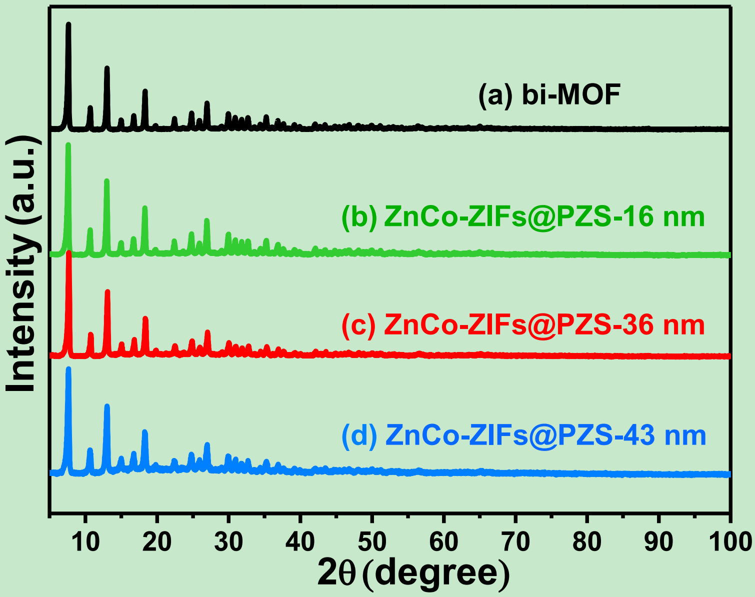


Fig. S7 XRD patterns of the ZnCo-ZIFs (a), ZnCo-ZIFs@PZS-16 nm (b), ZnCo-ZIFs@PZS-36 nm (c), ZnCo-ZIFs@PZS-43 nm (d).

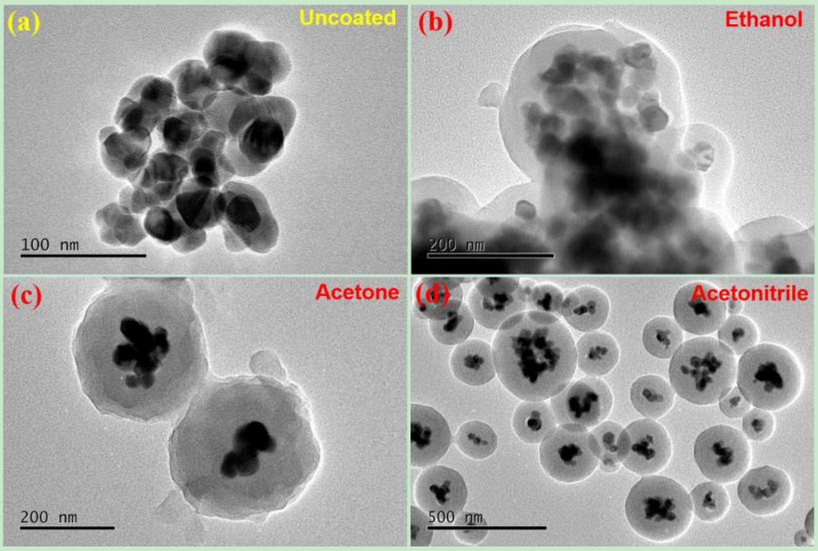


Fig. S8 TEM images of the ZrO_2 (a) and ZrO_2@PZS using ethanol (b), acetone (c) and acetonitrile (d) as solvent, respectively.

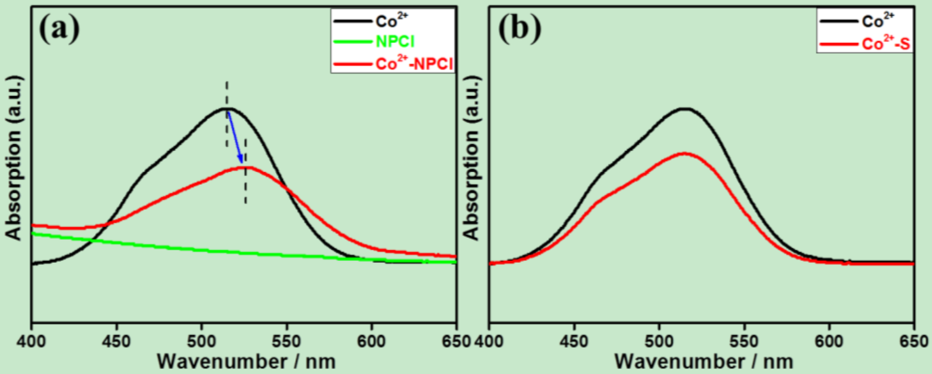


Fig. S9 UV-Vis spectra of $Co(NO_3)_2$•$6H_2O$ methanol solution (denoted as Co^{2+}), phosphonitrilic chloride trimer methanol solution (denoted as NPCl), $Co(NO_3)_2$•$6H_2O$-4,4'-sulfonyldiphenol methanol solution (denoted as Co^{2+}-S), and $Co(NO_3)_2$•$6H_2O$-phosphonitrilic chloride trimer methanol solution (denoted as Co^{2+}-NPCl).

As for the mechanism of monomers being adsorbed onto the ZIF-67surface, when phosphonitrilic chloride trimer was mixed with Co^{2+} solution in methanol, red shift of absorption peak was found (please see the image a), while this phenomenon was not observed in 4,4'-sulfonyldiphenol (image b). The red shift should ascribe to coordination between Co^{2+} and phosphonitrilic chloride trimer. In addition, 4,4'-sulfonyldiphenol could form hydrogen bond with N-containing surface (*Langmuir*, **2014**, *30*, 13861-13868). Thus, we think these two kinds of interactions enable the adsorption of phosphonitrilic chloride trimer on the surface of ZIF-67, and then polycondensation with 4,4'-sulfonyldiphenol to form PZS layer.

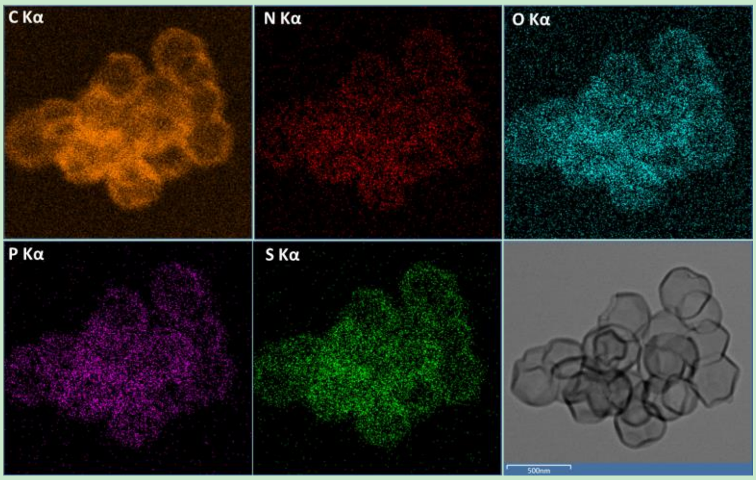


Fig. S10 Compositional EDS mapping of the ZnCo-ZIFs@PZS-36 nm-900-6 h hollow structures using STEM.

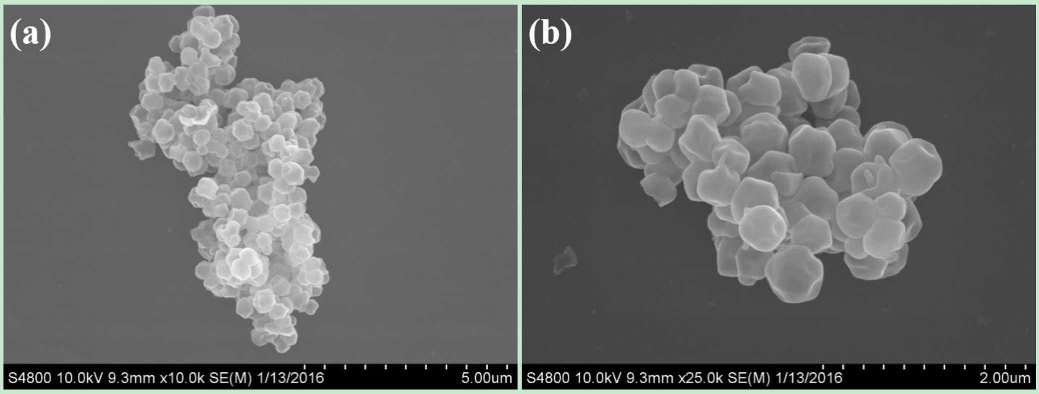


Fig. S11 SEM images of the ZnCo-ZIFs@PZS-36 nm-900-6 h after 5 runs for selective oxidation of ethylbenzene.

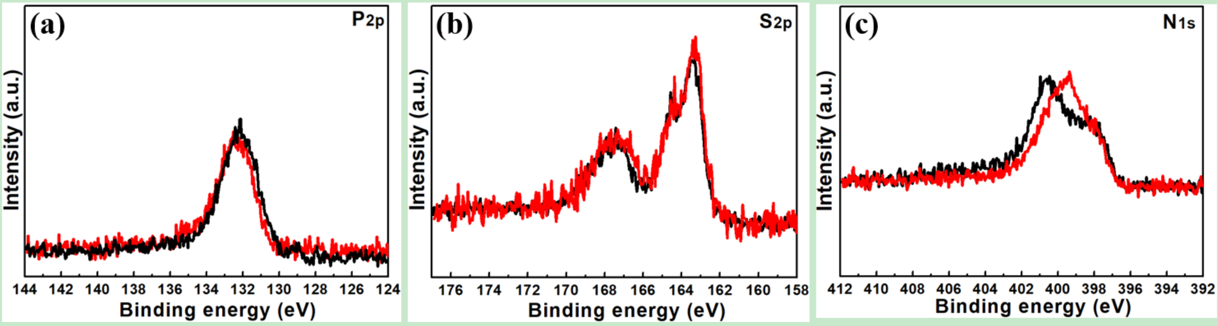
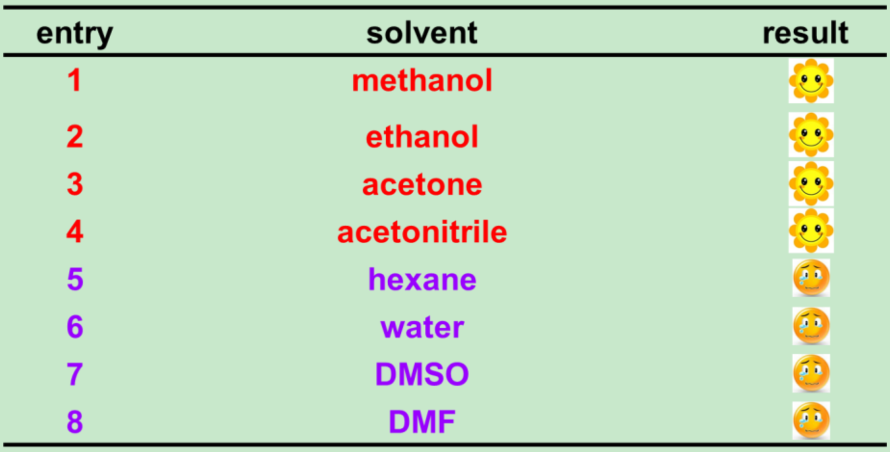


Fig. S12 High-resolution XPS spectra of (a) P_{2p}, (b) S_{2p} and (c) N_{1s} of fresh ZnCo-ZIFs@PZS-36 nm-900-6 h catalyst (black lines) and after 5 runs (red lines).

Table S1 Solvent effects on the coating results^a



entry	solvent	result
1	methanol	☺
2	ethanol	☺
3	acetone	☺
4	acetonitrile	☺
5	hexane	☹
6	water	☹
7	DMSO	☹
8	DMF	☹

^{a} Coating conditions: ZrO_2 (100 mg), hexachlorocyclophosphazene (70 mg), 4, 4'-sulfonyldiphenol (158), triethylamine (185 µL), solvent (60 mL), 25 °C, 6 h. Happy faces and sad faces mean forming PZS layer successfully and unsuccessfully, respectively.

Table S2 The atomic ratio (calculation from XPS analysis) of the fresh ZnCo-ZIFs@PZS-36 nm-900-6 h catalyst and after 5 runs.

Sample	C	O	N	P	S
Fresh ZnCo-ZIFs@PZS-36 nm-900-6 h catalyst	87.00	7.69	3.26	0.93	1.12
Used ZnCo-ZIFs@PZS-36 nm-900-6 h catalyst	80.82	15.26	2.95	0.51	0.46

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