# Supporting Information

## Double-Shell Microcapsules with Spatially Arranged Au Nanoparticles and Single Zn Atoms for Tandem Synthesis of Cyclic Carbonates

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## Section 1. Experimental section

**Chemicals:** Styrene (St), polyvinyl pyrrolidone (PVP), potassium persulfate (KPS), methanol (MeOH), 2-methylimidazole (2-MeIm), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), chloroauric acid hydrated ($HAuCl_4 \cdot 4H_2O$, 99%), sodium hydroxide (NaOH), tetrakis hydroxymethyl phosphonium chloride (THPC, 80% in water), ethanol (EtOH), aminopropyltriethoxysilane (APTES), cetyl trimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS, 99.5%), tetrabutylammonium bromide (TBAB), and tert-butyl hydroperoxide (TBHP, 70% in water) were purchased from Aladdin Industrial Corporation. St and TEOS monomers were purified by distillation under reduced pressure. All the other chemicals were used as received.

**Synthesis of polystyrene (PS) microspheres.** Monodispersed PS microspheres with ~ 380 nm diameter were prepared according to the reported work[1]. First, 125 mL ultrapure water and 0.15 g PVP were intensively mixed in a 250 mL round-bottomed flask. After adding 15 mL styrene monomers under constant stirring, the mixture was introduced with argon and fluxed at 75 °C for 30 min. Subsequently, 12.5 mL aqueous solution containing 0.05 g KPS as initiator was dropwise added into the solution. The polymerization lasted 24 h with continuous stirring (370 rpm) at an argon atmosphere. Finally, the monodispersed PS microspheres were collected by centrifugation from milk-liked product and dried at room temperature.

**Fabrication of PS@ZIF-8.** After mixing 0.06 g PS powder with 10 mL MeOH, the suspension was treated by ultrasound wave for 2 h, followed by the addition of 15 mL methanol solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 g) and 30 mL methanol solution of 2-MeIm (1.1 g) in turn under constant stirring. After stirring for 30 min, the obtained solution was allowed to stand and crystallize for 12 h at room temperature. The PS @ZIF-8 was collected by centrifugation, followed by washing with EtOH and drying at 60 °C.

**Preparation Au NPs.** Au NPs were synthesized according to the previous literature[2]. 54 mL ultrapure water was mixed with 20 mg NaOH and 1 mL aqueous solution containing 12 μL THPC. After vigorous stirring for 5 min, 2 mL aqueous solution of 20 mg $HAuCl_4 \cdot 4H_2O$

was added and continually stirred for another 30 min. Subsequently, the gold sol was stored at 4 °C for 24 h before use.

**Synthesis of PS@ZIF-8/Au.** 0.5 g PS@ZIF-8 and 0.05 g PVP were evenly dispersed in 25 mL MeOH via stirring and ultrasonic treatment. After stirring for 1 h, PS@ZIF-8/PVP was collected by centrifugation and washed with EtOH. Subsequently, the collection was redispersed in 50 mL MeOH, followed by the addition of 50 mL gold sol under constant stirring. After stirring for 1 h, the precipitated PS@ZIF-8/Au was washed with EtOH and dried at 60 °C.

**Fabrication of PS@ZIF-8/Au@SiO$_2$.** 0.2 g PS@ZIF-8/Au was redispersed in 40 mL mixed solvent of ethanol with ultrapure water (1/1 vol) containing 0.2 g CTAB and 0.16 g 2-MeIm. After stirring for 30 min, 0.4 mL TEOS was dropwise added into the mixture. After stirring for another 2 h, the product was collected by centrifugation and washed with EtOH. Finally, the PS@ZIF-8/Au@mSiO$_2$ was dried at 60 °C under a static vacuum.

**Preparation of Zn-N-C/Au@mSiO$_2$.** PS@ZIF-8/Au@SiO$_2$ was placed in a quartz boat and put into a tube furnace. The Zn-N-C/Au@mSiO$_2$ was obtained after calcination at 800 °C for 2 h under a nitrogen atmosphere with a flow rate of 60 mL min$^{-1}$.

**Synthesis of Zn-N-C/Au.** The as-synthesized PS@ZIF-8/Au without SiO$_2$ shell was calcined in the tube furnace at 800 °C for 2 h under nitrogen atmosphere to obtain Zn-N-C/Au (Scheme S1).

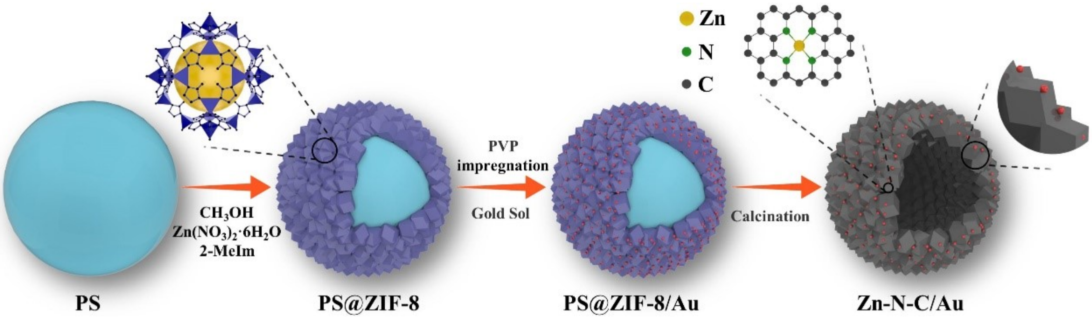
**Fabrication of Mixture of SiO$_2$-Au with Zn-N-C.** SiO$_2$ microspheres were synthesized according to well-known Stöber method. After that, 0.5 g SiO$_2$ microspheres were dispersed in 100 mL EtOH. Then 0.5 mL APTES was dropwise added and constantly stirred for 6 h at 70 °C. After washing with EtOH and drying at 50 °C, the SiO$_2$-NH$_2$ microspheres were obtained. Next, 0.2 g SiO$_2$-NH$_2$ powder was immersed in 20 mL methanol with ultrasonic treatment for 30 min. Then 20 mL gold sol was added under constant stirring. After stirring for 2 h, the SiO$_2$-Au was collected by centrifugation, washed with EtOH, and dried at 60 °C. ZIF-8 crystals were prepared by collecting precipitate of methanol mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 g) and 2-MeIm (1.1 g). Afterward, the ZIF-8 crystals were calcinated at 800 °C for 2 h under a nitrogen atmosphere with a flow rate of 60 mL $min^{-1}$ to obtain Zn-N-C. Then $SiO_2$-Au and Zn-N-C were ground in equal quality into powder together to get a mixture of $SiO_2$-Au with Zn-N-C (Scheme S2).

**Catalytic Test.** One-pot synthesis of styrene carbonate from styrene with $CO_2$ under normal pressure as a model tandem reaction was investigated. Typically, Zn-N-C/Au@m$SiO_2$ (25 mg), TBAB (25 mg), St (115 mg), and TBHP (430 mg) were added into the 20 mL glass bottle and a balloon filled with $CO_2$ was connected to the bottle. The bottle was purged with $CO_2$ to ensure a pure $CO_2$ atmosphere for the reaction. Subsequently, the reactor was maintained at the target temperature for 12 h. Finally, the Zn-N-C/Au@m$SiO_2$ and the liquid mixture were separated by centrifugation. The Zn-N-C/Au@m$SiO_2$ catalyst was reused in the cycle experiment and the liquid mixture was analyzed via $^1$H NMR. For the Zn-N-C/Au and mixture, the catalytic conditions were the same as above.

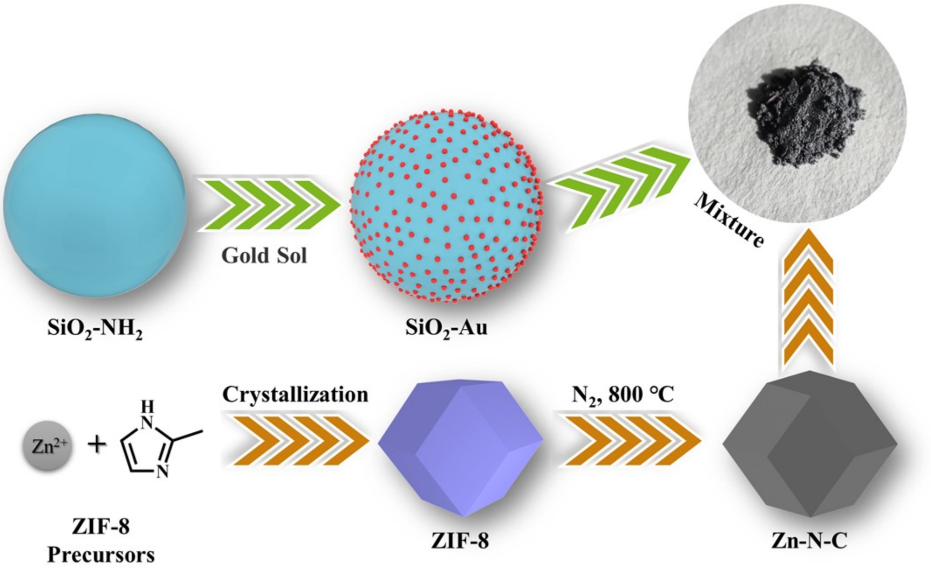
**Characterization.** Zeta potential was performed at a Malvern ZS90. Scanning electron microscopy (SEM) images were obtained on a FEI Nova Nano-SEM450 field-emission scanning electron microscope at different accelerating voltages. Transmission electron microscopy (TEM) images were taken on a JEM-2100F electron microscope. The content of Au and Zn in the nanoreactor was determined by inductively coupled plasma optical emission spectrometer (ICP-OES, PE Optima 8300). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken on a FEI-Titan Cubed Themis G2 300 electron microscope. X-ray diffraction (XRD) pattern was measured on an X-ray diffractometer (Bruker D8-Davinci). Nitrogen adsorption−desorption isotherms were performed at 77.3 K on a surface area and porosity analyzer (ASAP 2020 M + C). The pore volume and average pore size, and the specific surface area were respectively computed by using the Horvath−Kawazoe method and the Brunauer−Emmett−Teller (BET) method. Fourier transform infrared (FT-IR) spectroscopy was performed with a Bruker VECTOR-22 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Thermo Scientific

ESCALab250Xi spectrometer with monochromatic Al Kα radiation (1486.6 eV) and a spot size of 650 μm, and the binding energies were calibrated using the C 1s peak at 284.6 eV. Nuclear Magnetic Resonance (NMR) characterization was performed by Bruker AVANCE400.

## Section 2. Schemes



**Scheme S1.** Preparation process of single-shell microcapsules (Zn-N-C/Au).



**Scheme S2.** Preparation process of mixture of SiO$_2$-Au with Zn-N-C.

## Section 3. Figures

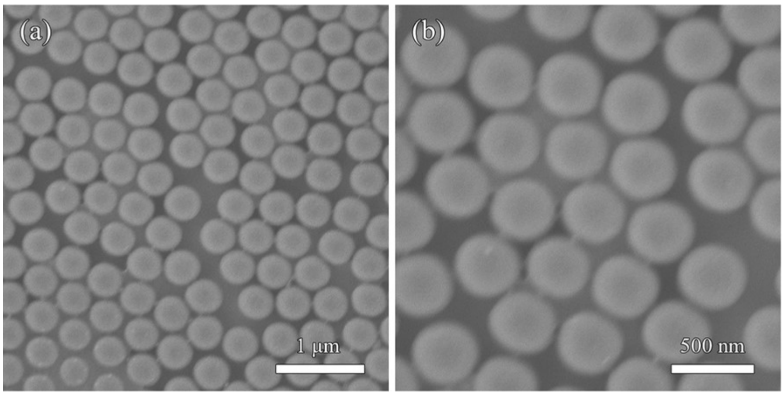


**Figure S1.** SEM images of PS microspheres.

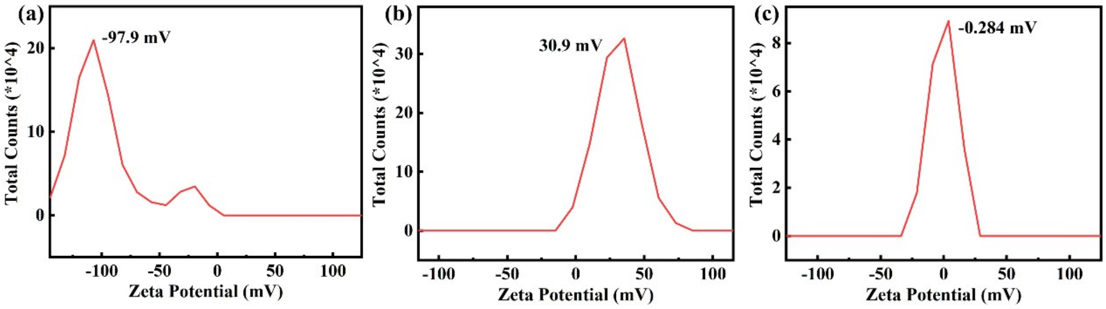


**Figure S2.** Zeta potential of (a) Au NPs, (b) PS@ZIF-8/PVP, and (c) PVP.

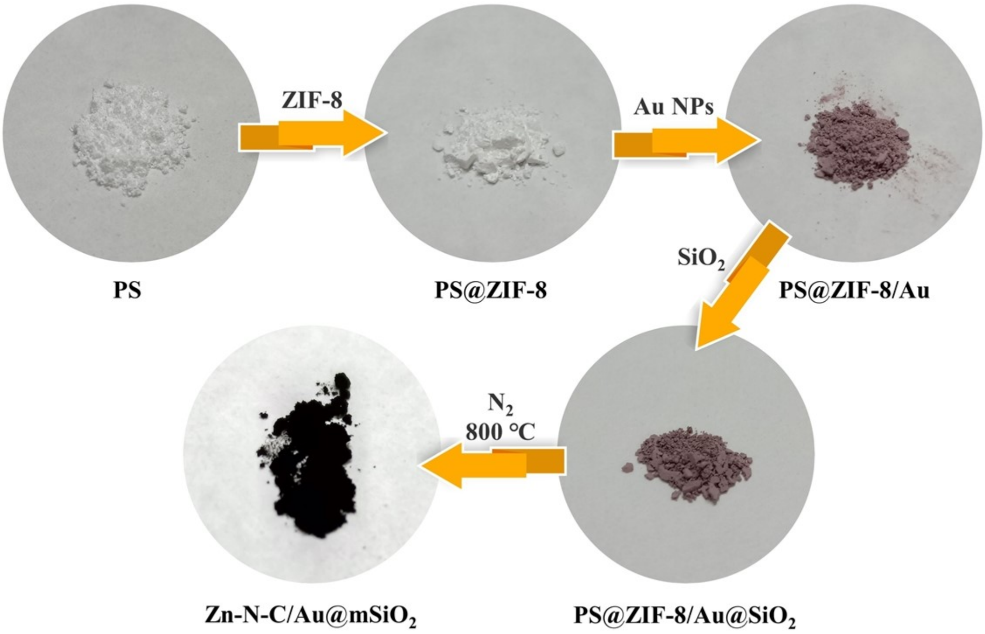


**Figure S3.** The color evolution during the preparation process of Zn-N-C/Au@mSiO$_2$.

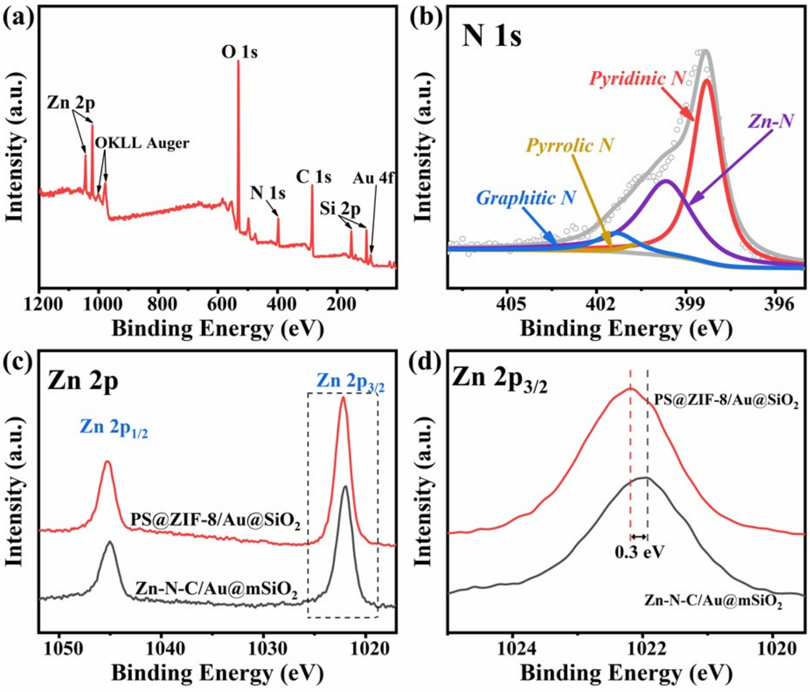


**Figure S4.** (a) XPS survey spectrum of Zn-N-C/Au@mSiO$_2$-2. (b) High-resolution XPS spectrum for N 1s of Zn-N-C/Au@mSiO$_2$-2, which was only coated with an incomplete SiO$_2$ shell. (c) High-resolution XPS spectrum of Zn from different sample. (d) Area magnified image of image c).

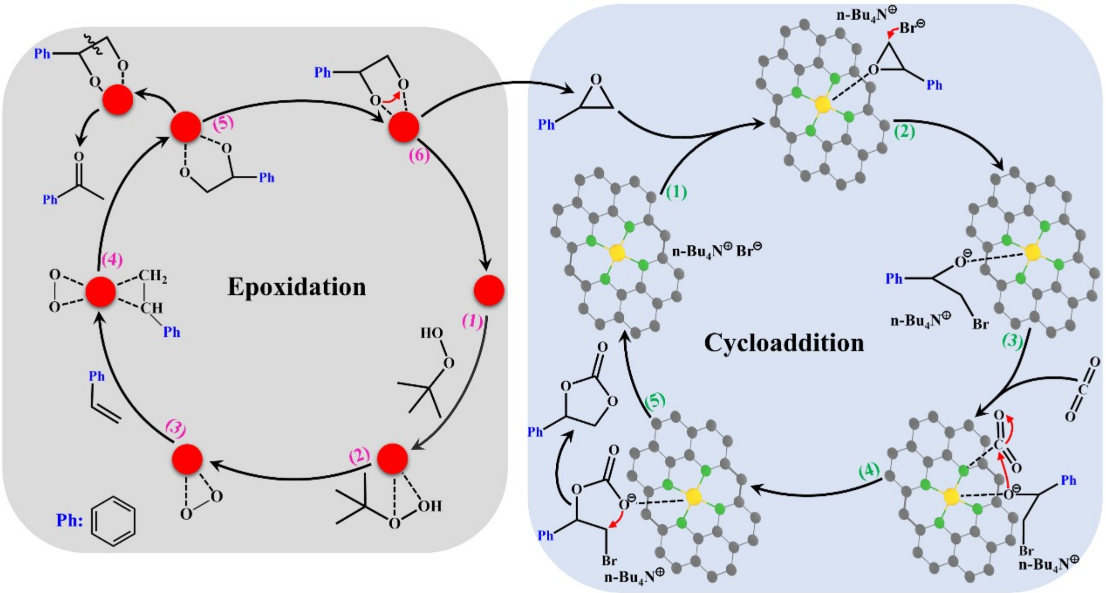


**Figure S5.** Proposed mechanism for tandem reaction from styrene to styrene carbonate catalyzed by Zn-N-C/Au@mSiO$_2$.

Firstly, the epoxide adsorbed and polarized by the Zn SAC, and CO$_2$ molecules were adsorbed and activated by the adjacent N atom. Then the nucleophilic bromide anion from the co-catalyst (TBAB) quickly attacks the less-hindered epoxide carbon to activate it for achieving ring-open step. Next, the C atom of the $CO_2$ activated by N atom is attacked by the ring-opened intermediate. Subsequently, $CO_2$ inserts into the ring-opened intermediate to obtain an acyclic ester. Finally, the intramolecular cyclization of the acyclic ester result in the formation of cyclic carbonate.

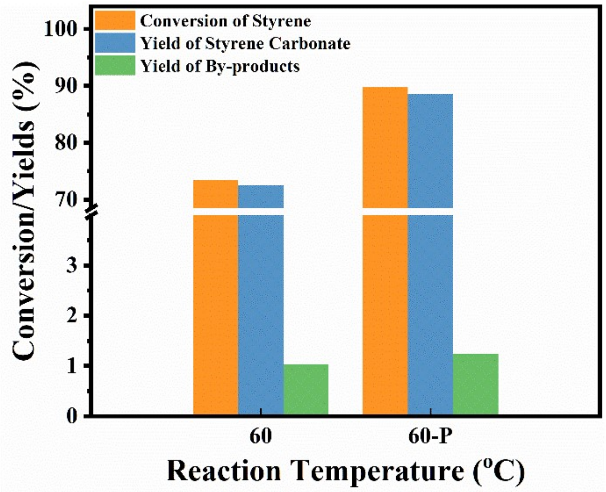


**Figure S6.** Conversion and yield versus reaction temperature curve for tandem trans-fromation of styrene into styrene carbonate catalyzed by Zn-N-C/Au@$mSiO_2$.

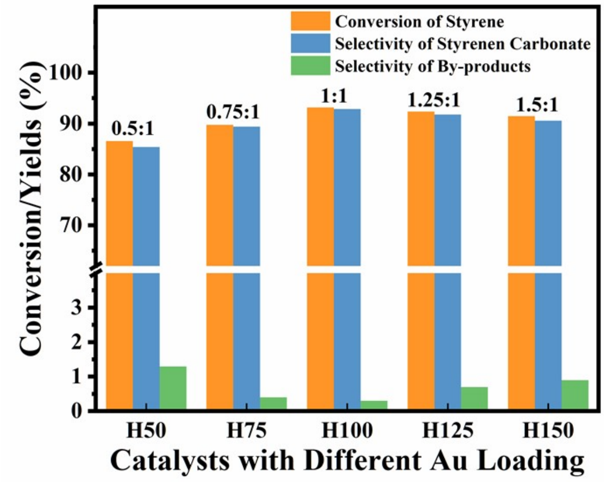


**Figure S7.** Conversion and yields versus different catalyst. We set H100 (10 mL Au Sol to 0.1 g PS@ZIF-8/PVP) as standard ratio (1:1). H50 to H150 represent the following ratios respectively: 0.5:1, 0.75:1, 1:1, 1.25:1, and 1.5:1.

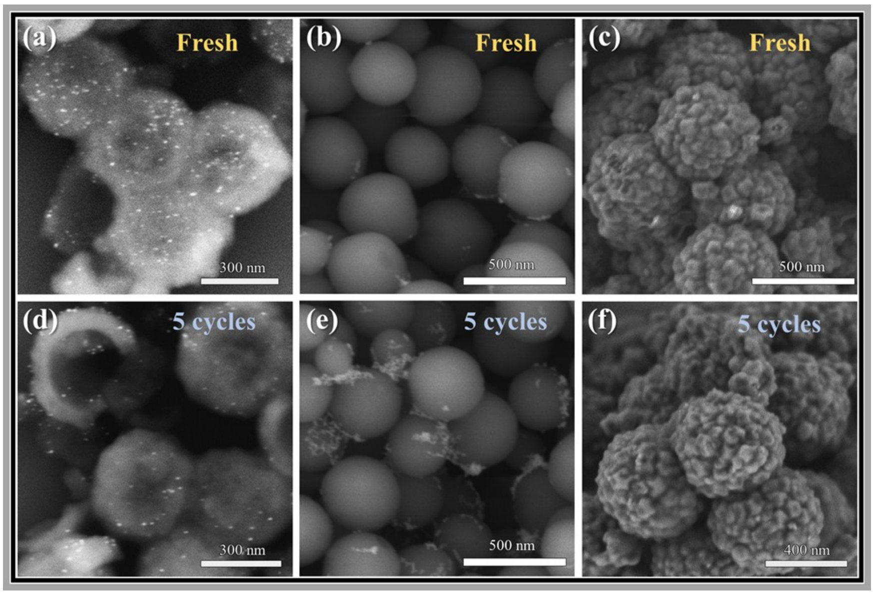


**Figure S8.** SEM images of (a,d) fresh and used (5 cycles) Zn-N-C/Au, (b,e) fresh and used (5 cycles) $SiO_2$-Au from mixture, and (c,f) fresh and used (5 cycles) Zn-N-C/Au@m$SiO_2$.

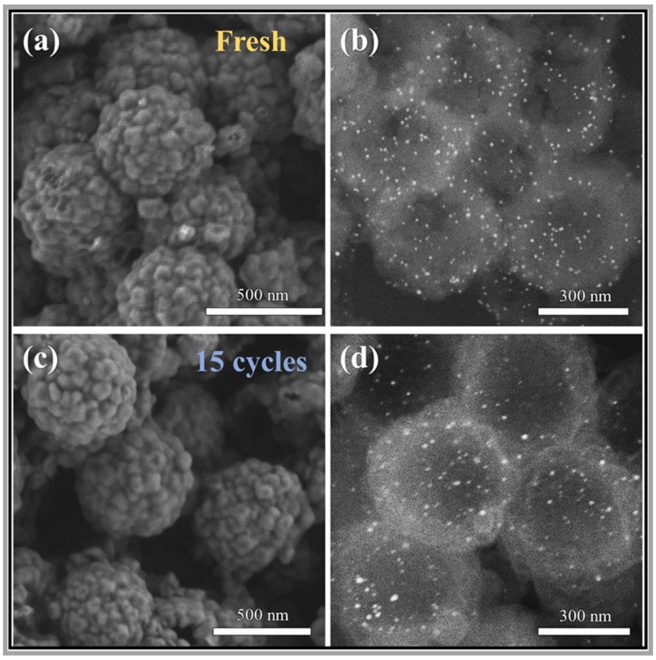


**Figure S9.** SEM images of (a,b) Fresh Zn-N-C/Au@m$SiO_2$, and (c,d) Zn-N-C/Au@m$SiO_2$ after 15 consecutive catalytic experiments at high voltage.

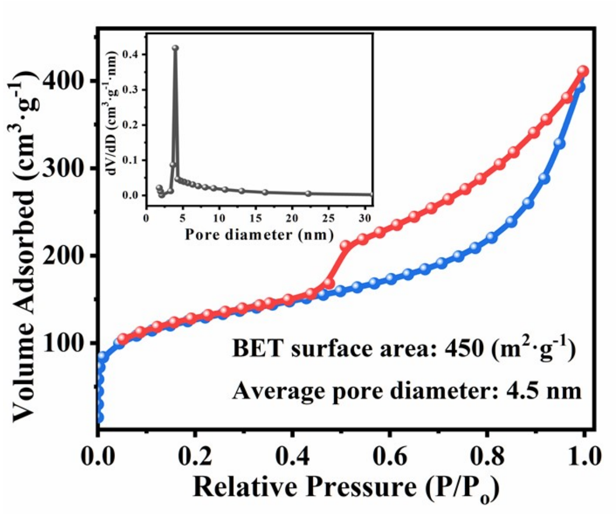


**Figure S10.** $N_2$ sorption-desorption isotherms and pore diameter distribution of Zn-N-C/Au@mSiO$_2$ after 15 consecutive catalyst experiments.

## Section 4. Tables

**Table S1**. Elemental content distribution detected by EDS.

| Element | Atomic Fraction (%) | Mass Fraction (%) |
|---|---|---|
| N | 7.49 | 6.06 |
| Zn | 2.74 | 10.34 |
| Au | 0.29 | 3.35 |
| Si | 12.45 | 20.22 |
| C | 48.60 | 33.74 |
| O | 28.43 | 26.29 |

**Table S2.** Comprison of Zn-N-C/Au@mSiO$_2$ against previous studies reported for the tandem synthsis of styrene carbonate from styrene.

| Catalyst | Co-catalyst, Solvent | Conditions | Conv. (%) | Yield (%) to carbonate | Recycles (Yield, %) | Ref. |
|---|---|---|---|---|---|---|
| **Zn-N-C/Au@mSiO$_2$** | **TBAB, No solvent** | **TBHP, 1 atm CO$_2$, 80 °C , 12 h** | **93.2** | **92.9** | **15 (92.9-89.2)** | **This work** |
| ImBr-MOF-545(Mn) | None | 5 bar O$_2$/IBA, 5 bar CO$_2$, 60 °C, 10 h | 99.2 | 94.8 | 5 (94.8-89.1) | 3 |
| Au@[IM$^+$]/[MIL-101-SO$_3^-$] | TBAB, DMF | 1 atm O$_2$, 10 atm CO$_2$, 80 °C , 12 h | 99.1 | 74.5 | 8 (74.5-61) | 4 |
| PN-CeO$_2$ | TBAB, No solvent | TBHP, 2 MPa CO$_2$, 80 °C, 18 h | 81.0 | 75.3 | 3 (75.3-75.2) | 5 |
| [C$_1$C$_4$Im][HCO$_3$] | None | TBHP, 2 MPa CO$_2$, 65 °C, 30 h | 91.4 | 75.4 | 5 (75.4-76.9) | 6 |

## Section 5. References

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