

Supplementary information for
**Entrapment of a chiral cobalt complex within silver:
a novel heterogeneous catalyst for asymmetric
carboxylation of benzyl bromides with CO₂**

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1. Materials and Instruments

All reagents were used as received.

Asymmetric carboxylation was performed using a direct current-regulated power supply (HY3002D, HYelec®, China).

The product yield, the ee value and chiral cobalt complex amount in filtrate were determined by a high performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) equipped with a UV (RS Variable Wavelength) detector and a chiralcel OD-H column [DAICEL Chiral technologies (China) CO., LTD.].

Microstructure and EDX mapping of [Co]@Ag were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK).

X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu K α radiation ($k=1.5406 \text{ \AA}$).

N₂ adsorption was carried out at 77 K on a BELSORP-MAX instrument after

outgassing the samples for 10 h under vacuum at 573 K.

Infrared spectra were achieved by a Fourier transform infrared spectrometer (FT-IR, NEXUS 670, Nicolet).

The amounts of Ag and Co in the [Co]@Ag composite were determined quantitatively by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a USA Thermo IRIS Intrepid II XSP ICP spectrometer.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin–Elmer PHI 5000C ESCA system.

2. General methods

Synthesis of [Co]@Ag and pure Ag: $\text{Co}^{\text{II}}\text{-(R, R)}$ (salen) (23.4 mg, 0.072 mmol) was dissolved in 100 mL distilled water and then 1.70 g (0.01 mol) of AgNO_3 (the molar ratio [Co]: Ag is 1:139) was added under stirring. After 5 min of stirring, zinc powder was added and the combined slurry was stirred at room temperature for 5 hours. Silver is formed while entrapping the chiral cobalt complex. Precipitation of [Co]@Ag begins immediately. The precipitate was filtered, washed with 10 mL water 5 times, and dried over night at 40 °C under vacuum. Fine and dark powder was achieved after filtration and drying (Fig. S2). S-[Co]@Ag was prepared the same method except for the utilization of $\text{Co}^{\text{II}}\text{-(S, S)}$ (salen) as dopant. Pure Ag nanoparticles (Fig. S3) were prepared in the same way except for the absence of chiral cobalt complex in reducing solution. Coarse and shine powder was obtained.

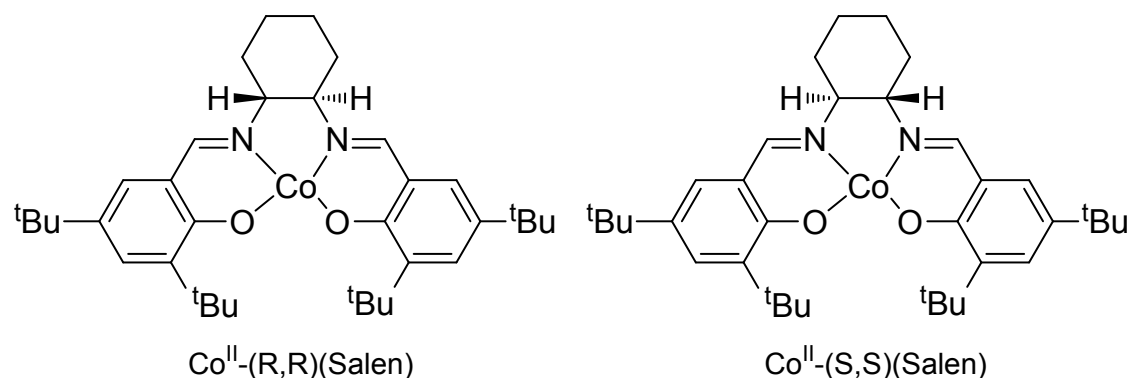


Fig. S1 Structures of chiral cobalt complex.

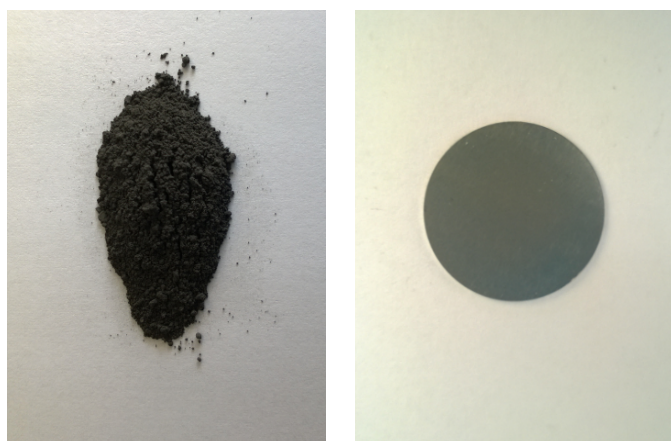


Fig. S2 [Co]@Ag before (left) and after (right) press.

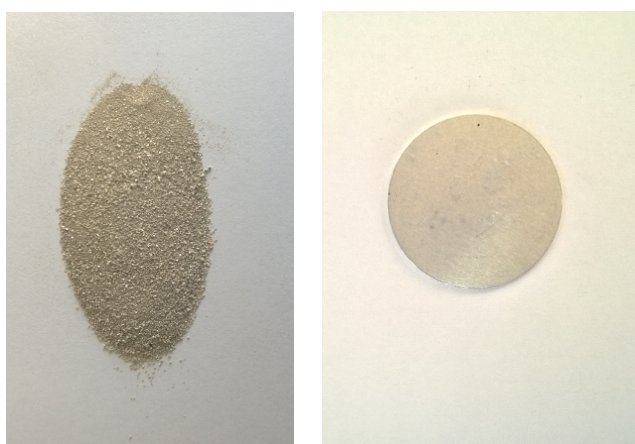


Fig. S3 Pure Ag NPs before (left) and after (right) press.

Asymmetric carboxylation procedure: Powder of [Co]@Ag was pressed into coin (Fig. S2) and used as cathode for the asymmetric carboxylation of different substrates with CO₂. A typical asymmetric carboxylation was carried out in a mixture of 0.05 M substrate, 0.1 M tetraethylammonium iodide (TEAI) in 20 mL CO₂-saturated MeCN in an undivided glass cell, with a [Co]@Ag composite cathode and sacrificial magnesium (Mg) anode, no additive chiral inducer was needed in reaction solution. Current density: 5 mA cm⁻², charge: 2 F mol⁻¹, CO₂ pressure: 1 atm, room temperature.

3. Differences between physical adsorption and entrapment

FT-IR further explored the difference between entrapment and adsorption. After physical adsorption in Co^{II}-(R, R) (salen) solution, FT-IR spectra of pure Ag NPs (d)

was almost identical to pure $\text{Co}^{\text{II}}\text{-(R, R) (salen)}$ (c). In $[\text{Co}]@\text{Ag}$ composite, $\text{Co}^{\text{II}}\text{-(R, R) (salen)}$ could not be detected by FT-IR spectra (a), but the presence of dopant could be confirmed by other characterization methods. If (d) was washed with MeCN, there was also no trace of $\text{Co}^{\text{II}}\text{-(R, R) (salen)}$ in FT-IR spectra (b). In summary, entrapment was fundamentally different from adsorption and much more stable.

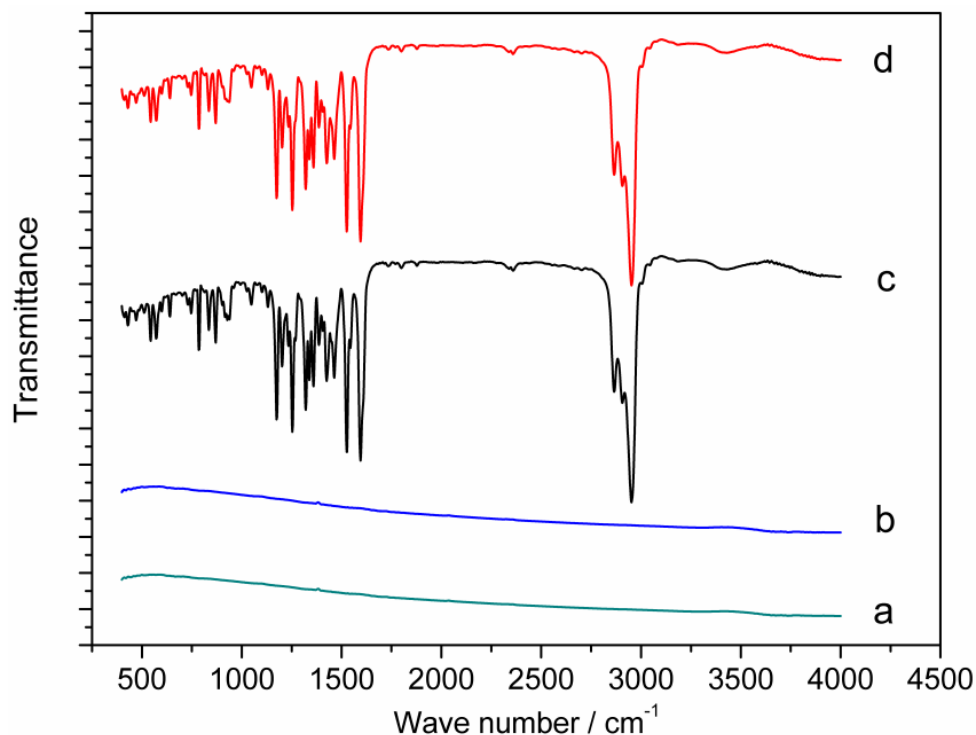


Fig. S4 FT-IR spectra of $[\text{Co}]@\text{Ag}$ after wash with MeCN (a), pure $\text{Co}^{\text{II}}\text{-(R, R) (salen)}$ (c), pure Ag NPs after physical adsorption (d), (d) after washed with MeCN (b).

4. Characterization of pure Ag NPs.

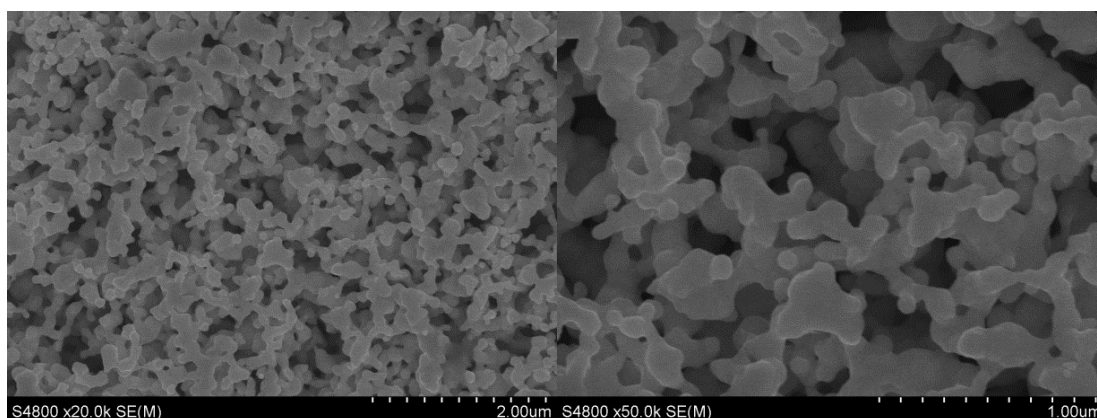


Fig. S5 FE-SEM patterns of pure Ag NPs with different magnification, A (20k), B (50k).

According to Fig. S5, pure Ag NPs are in the ~ 100 nm size range, which is obvious larger than $[\text{Co}]@\text{Ag}$.

5. EDAX spectrum of [Co]@Ag composite

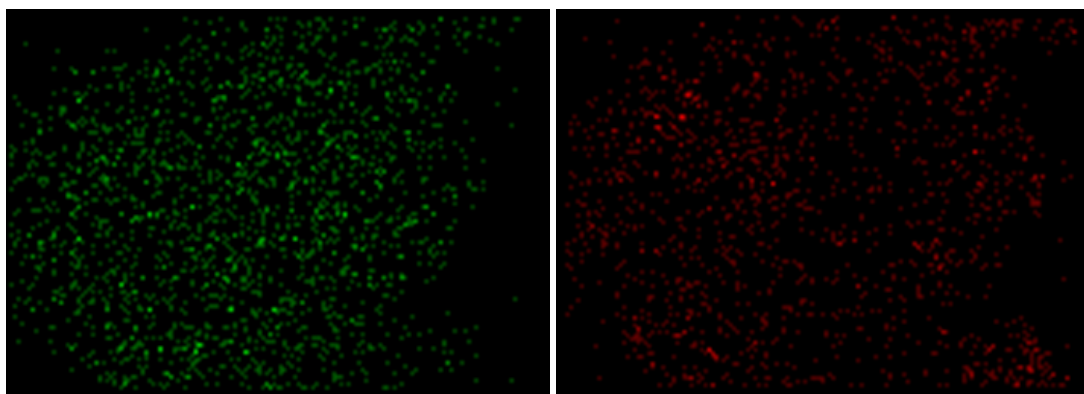
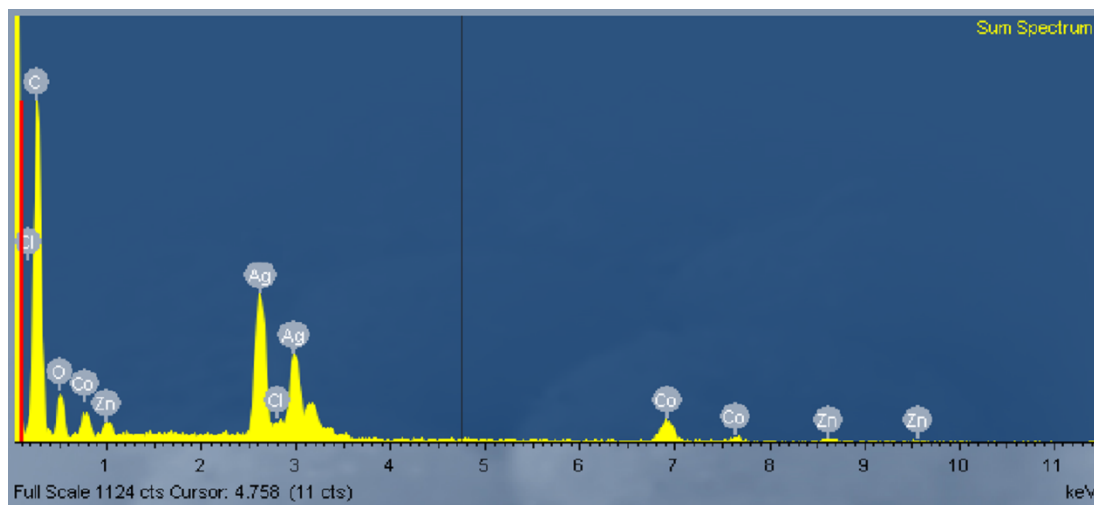


Fig. S6 EDAX spectrum of [Co]@Ag composite (up); X-ray atomic mapping of the elements of the [Co]@Ag composite (down), green and red colours represent silver and cobalt atoms, respectively.

6. Characterization of [Co]@Ag after using.

According to SEM patterns (Fig. S7), [Co]@Ag preserved its porous structure after using for 7 times, although the nanoparticles agglomerate into large ones to some extent. EDAX patterns reveal that chiral cobalt complex could also remain its homogenous dispersion in the composite (Fig. S8).

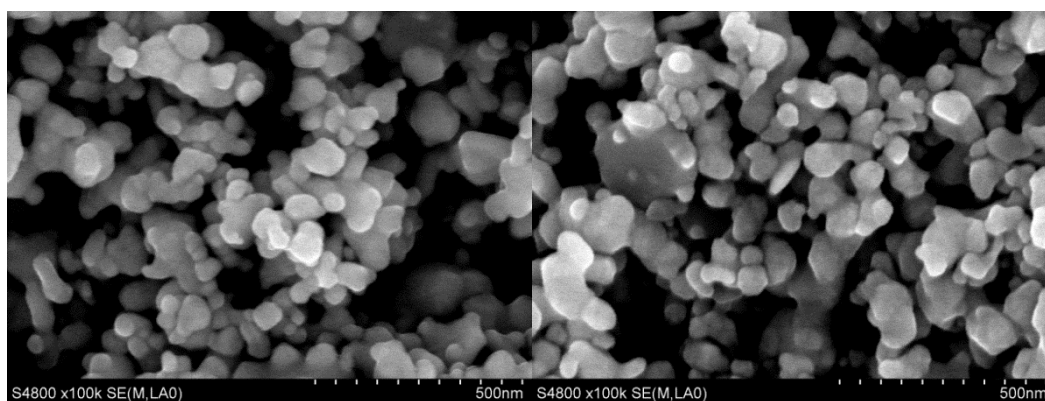


Fig. S7 FE-SEM patterns of [Co]@Ag before using (left) and after using for 7 times (right).

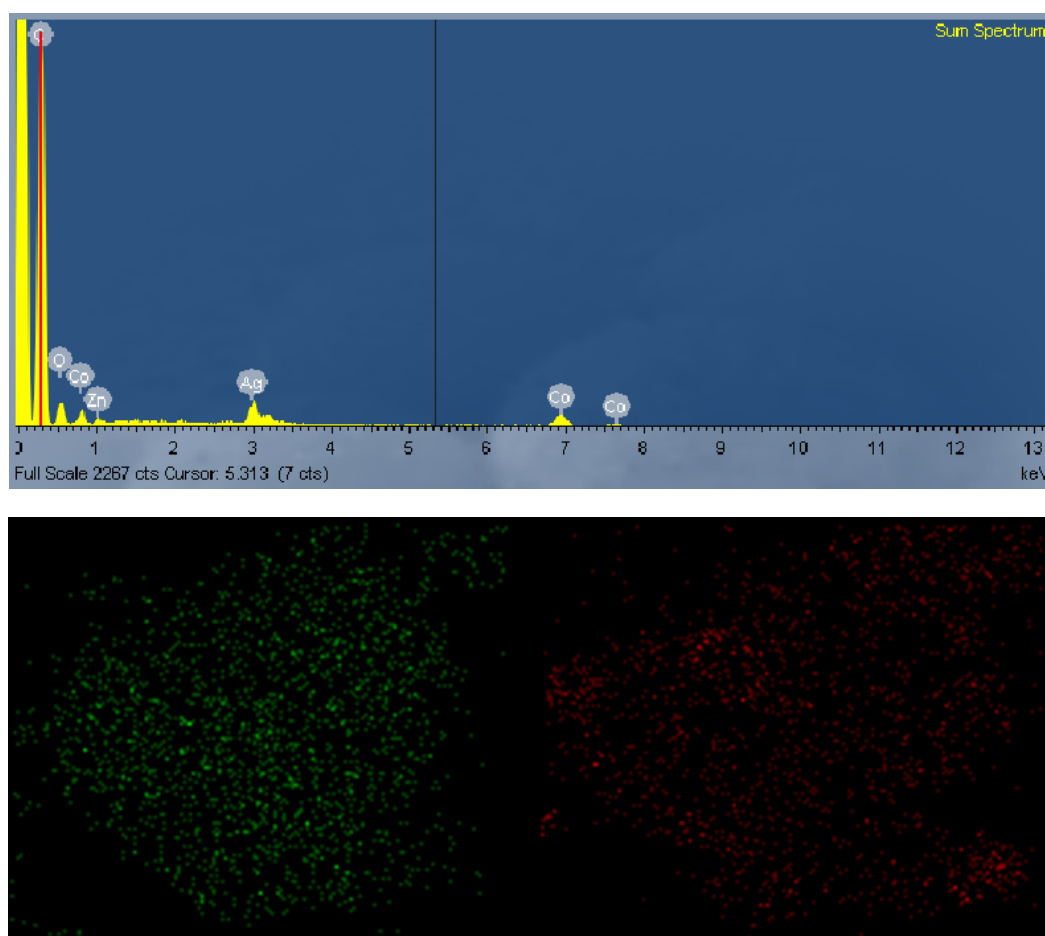


















Fig. S8 The EDAX spectrum of [Co]@Ag after using for 7 times (up); X-ray atomic mapping of the elements of the [Co]@Ag (down), green and red colours represent silver and cobalt atoms, respectively.

7. Expansion of substrates

Under same reaction conditions as Table 1, entry 3, certain ee value and yield could

also be achieved with these substrates. As is obvious from the results summarized in Table S1, [Co]@Ag composite could be applicable to the asymmetric carboxylation with wide range of substrates.

Table S1 Asymmetric carboxylation of different substrates with CO₂ on [Co]@Ag^a.

Entry	Substrate	Product	Yield ^b (%)	R-ee ^b (%)
1			58	73
2			62	58
3			64	51
4			68	66
5			57	49
6			76	47
7			61	33
8			70	20

^a Anode: Mg, 20 mL CO₂-saturated MeCN, 0.05 M substrate, supporting electrolyte: 0.1 M TEAI, current density: 5 mA cm⁻², charge: 2 F mol⁻¹, CO₂ pressure: 1 atm, room temperature. ^b Determined by HPLC with a chiral column.