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Supplementary Information

Development of Highly Efficient Resin-Based Ag-π Nanocatalysts via In-Situ Catalytic Strategy for Selective Cinnamaldehyde Hydrogenation

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Experimental Section

1. Materials

Weak acid cation exchange resin (D113) was obtained from Langfang Ruixi Auxiliaries Co., Ltd. Sodium hydroxide (NaOH) was bought from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. Silver nitrate ($AgNO_3$, ≥99%) and sodium borohydride ($NaBH_4$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Cinnamaldehyde was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2. Pretreatment experiment of cation exchange resin

First, fresh resin (1 g) was soaked in saturated NaCl aqueous solution (50 g) for 24 h, and the resin was filtered and washed with deionized water for 3 times. Then, the resin was soaked in NaOH aqueous solution (100 g, 2 wt.%) for 4 h. Finally, The Na^+ exchanged resin was washed with deionized water for 3 times and vacuum-dried.

3. Synthesis of Ag/RS nanocomposite catalyst

First, $AgNO_3$ (0.157 g) was dissolved in deionized water (20 g) to prepare $AgNO_3$ solution. Pre-RS (1 g) was dispersed in the above $AgNO_3$ solution, stirred for 6 h in dark, and filtered. The obtained Ag^+ exchanged resin (Ag^+/RS) was washed with deionized water for 3 times, and dried in an 80℃ vacuum oven. Finally, Ag^+/RS sample was heated at 300℃ in air for different time to obtain the Ag/RS-X sample (X represents heat treatment time, unit is minute). For comparison, Ag/RS-180-N_2 was prepared by the similar procedure except that the heat treatment was under N_2 atmosphere.

4. Catalytic activities

The hydrogenation of cinnamaldehyde was performed as follows: 5 mg of catalyst and 5 mL of 20 $mmol \cdot L^{-1}$ cinnamaldehyde ethanol solution were placed in a glass cuvette. The mixture was stirred and purged with argon for 30 min to eliminate oxygen from the solution.

The reaction was then initiated by adding 0.06 mol·L^{-1} $NaBH_4$. The reaction mixture was continuously stirred and bubbled in the dark for 20 min. Afterward, the product was separated and analyzed using gas chromatography (GC7820A, Agilent) equipped with a flame ionization detector (FID), with O-xylene used as an internal standard.

5. Characterization

Scanning electron microscopy (SEM) studies were carried out on S-4800 (Hitachi Ltd., Japan) with accelerating voltage and electricity of 5 kV and 10 mA. Transmission electron microscopy (TEM) measurements were conducted on JEM-2100 (JEOL, Japan) operated at an acceleration voltage of 200 kV. The solid-state ^{13}C nuclear magnetic resonance spectra (^{13}C NMR) were recorded on an Agilent 600M spectrometer. X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu Kα radiation (λ= 0.15406 Å) at 40 kV and 150 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out on AXIS SUPRA spectrometer (Kratos Analytical Ltd.) equipped with an Al Kα monochromated X-ray source (hv = 1486.69 eV). The X-ray anode was run at 250 W, and the high voltage was kept at 15.0 kV with the beam 10 mA. The FT-IR spectra were recorded from 500 to 4000 cm^{-1} on a Shimadzu IR Prestige21 FT-IR spectrophotometer (Japan). The mechanical strength of resins and resin-based composites is evaluated according to the Chinese national standard GB/T 12598-2001 "Determination of Penetration Sphericity and Post-Grinding Sphericity of Ion Exchange Resins". A ball mill is used to test the post-grinding sphericity.

6. Charging and discharging experiment

In a typical charging and discharging process,[s1] 0.2 mL of ice-cold $NaBH_4$ solution was added into 2 mL of catalyst suspension. After injection of $NaBH_4$ solution, spectroscopic measurements were initiated and absorption spectra were recorded continuously.

7. Computational methods

Density functional theory (DFT) calculations were performed using the first principle code VASP,[s2,s3] and the projector-augmented wave (PAW) method was used with a plane wave cutoff energy of 500 eV.[s4,s5] The electron exchange correlation functional was performed by the Perdew-Burke-Ernzerhoff (PBE) approximation.[s6] A fixed supercell of 15 Å×15 Å×20 Å was used for all the calculation systems and a gamma-centered k-point mesh of (1 × 1 × 1) was used during calculations. The electronic energy convergence and residual forces were set at 10^{-5} eV and 0.02 eV/Å, respectively. The Bader charge analysis was carried out to determine the transferred charges on each atom.[s7] DFT-D3 method with Becke-Jonson damping was used to treat the van der Waals interaction.[s8,s9] The adsorption energies were calculated by $E_{ads\text{-}Ag} = E_{adsorbate/Ag} - E_{adsorbate} - E_{Ag}$; $E_{ads\text{-}4np} = E_{adsorbate/4np} - E_{adsorbate} - E_{4np}$.

Reference:

(s1) T. Ung, L. M. Liz-Marzán, P. Mulvaney, *J. Phys. Chem. B*, 1999, 103(32), 6770-6773.

(s2) G. Kresse, J. J. C. m. s. Furthmüller, *Comput. Mater. Sci.*, 1996, 6(1), 15-50.

(s3) G. Kresse, J. Furthmüller, *Phys. Rev. B.*, 1996, 54(16), 11169-11186.

(s4) G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, 59(3), 1758-1775.

(s5) J. P. Perdew, Burke, K.; Ernzerhof, M., *Phys. Rev. Lett.*, 1996, 77(18), 3865-3868.

(s6) P. E. Blöchl, *Phys. Rev. B*, 1994, 50(24), 17953-17979.

(s7) W. Tang, E. Sanville, G. Henkelman, *J. Phys.: Condens. Matter*, 2009, 21(8), 084204.

(s8) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comb. Chem.*, 2011, 32(7), 1456-1465.

(s9) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, 132(15), 154104.

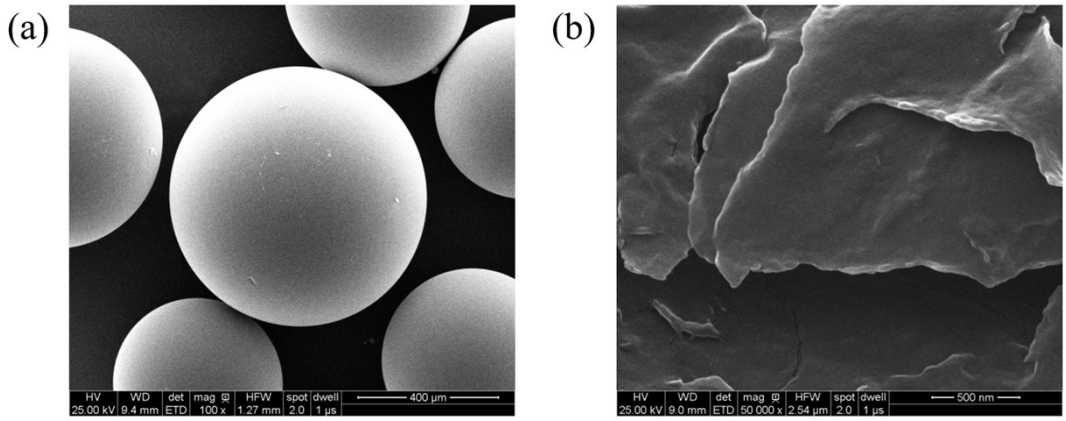


Figure S1. SEM images of the pre-treated RS obtained with different magnification.

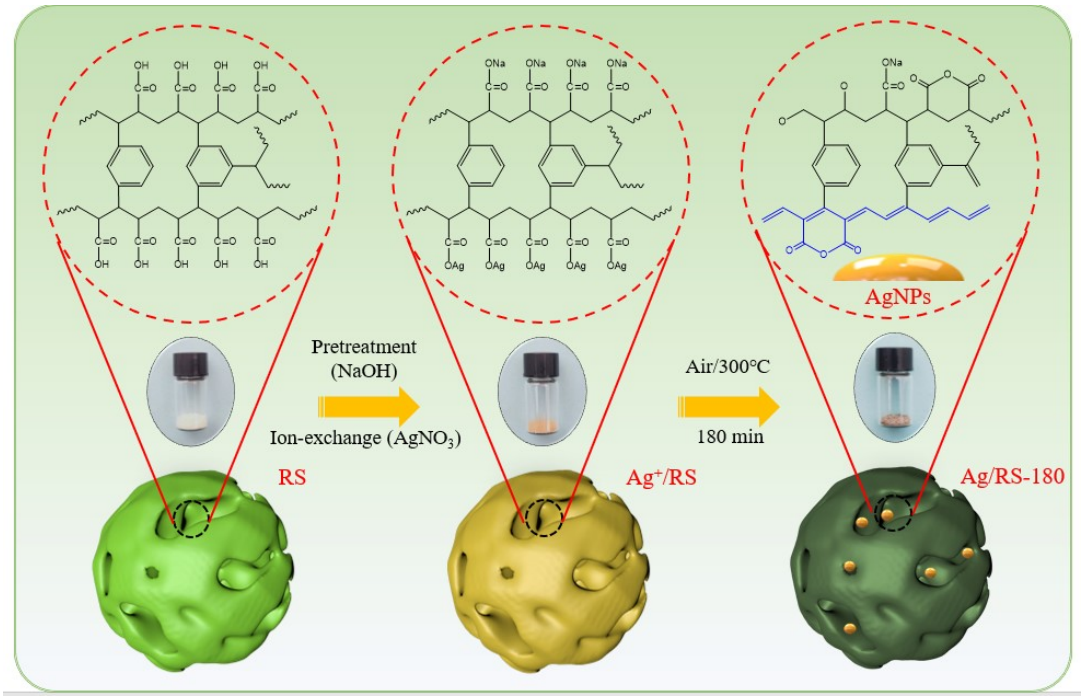


Figure S2. Schematic illustration of catalyst fabricating process.

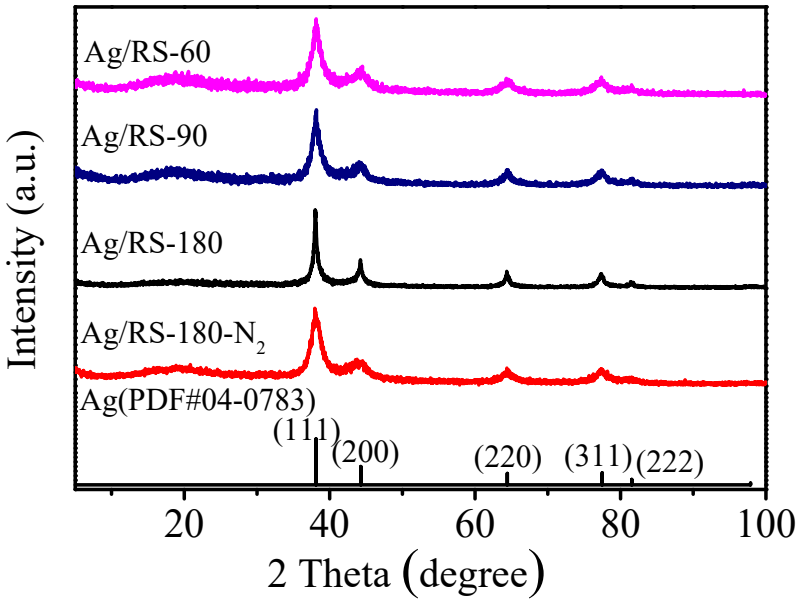


Figure S3. XRD patterns of typical catalyst samples.

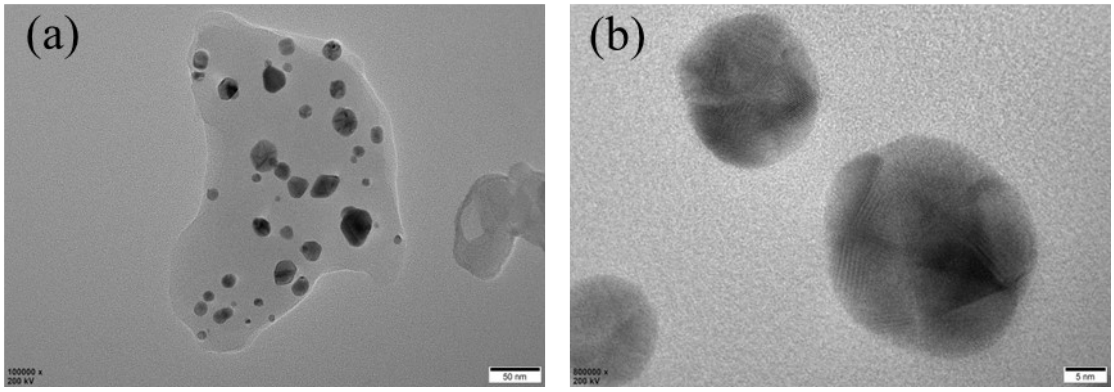


Figure S4. TEM image of Ag/RS-180.

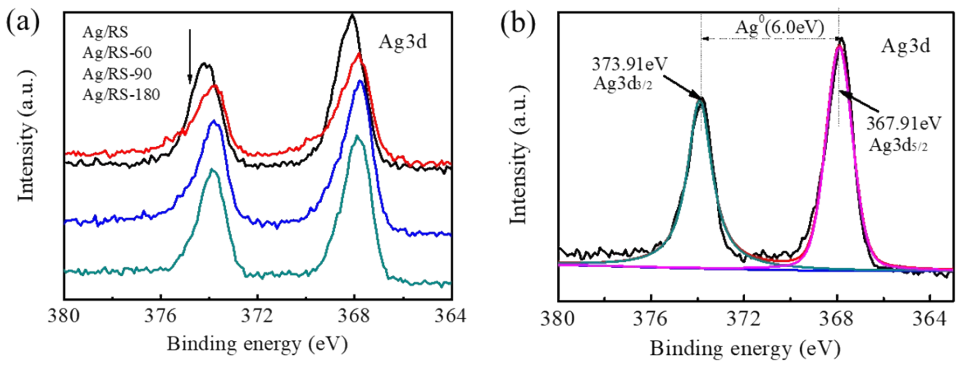


Figure S5. (a) Ag 3d XPS spectra of the RS in different treatment time. (b) XPS spectra of Ag 3d for the sample Ag/RS-180-N_2.

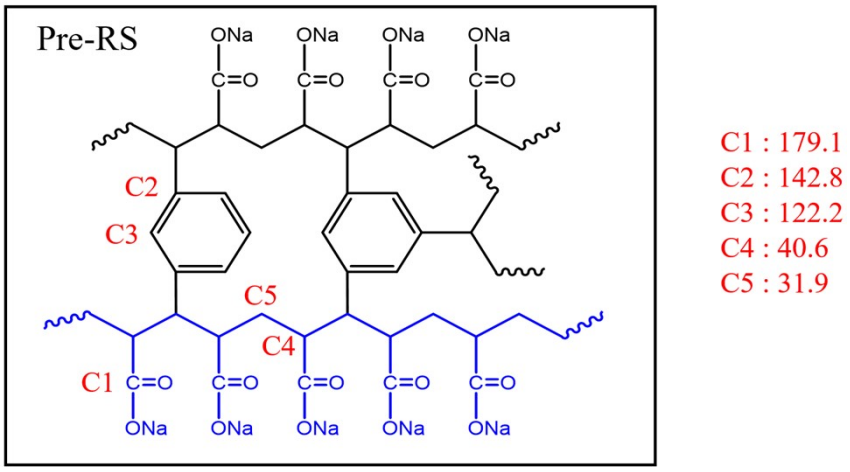


Figure S6. The structure of Pre-RS.

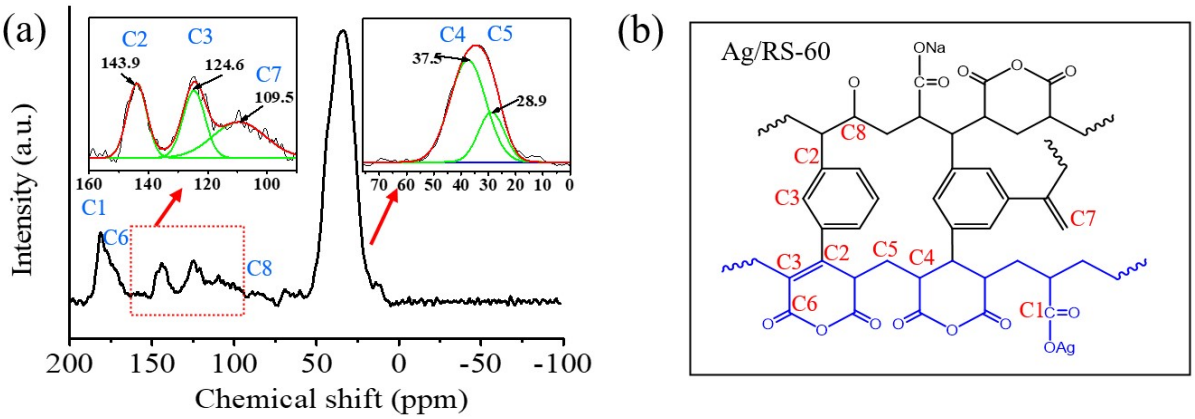
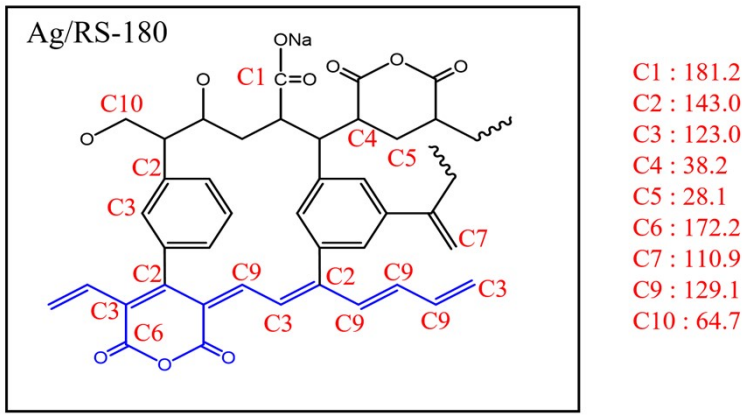


Figure S7. Local fitted NMR spectra and corresponding structure of Ag/RS-60.



C1 : 181.2
C2 : 143.0
C3 : 123.0
C4 : 38.2
C5 : 28.1
C6 : 172.2
C7 : 110.9
C9 : 129.1
C10 : 64.7

Figure S8. The structure of Ag/RS-180.

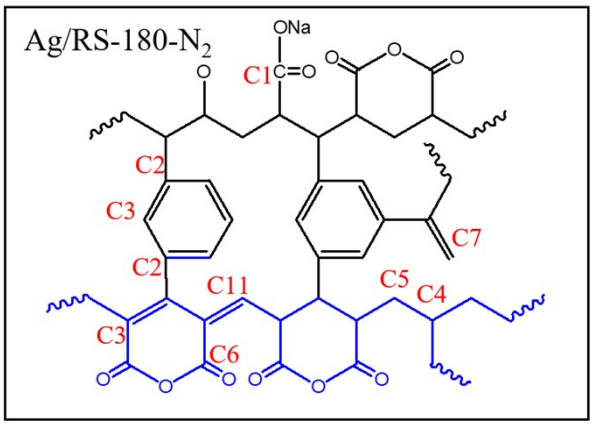


Figure S9. The structure of Ag/RS-180-N_2.

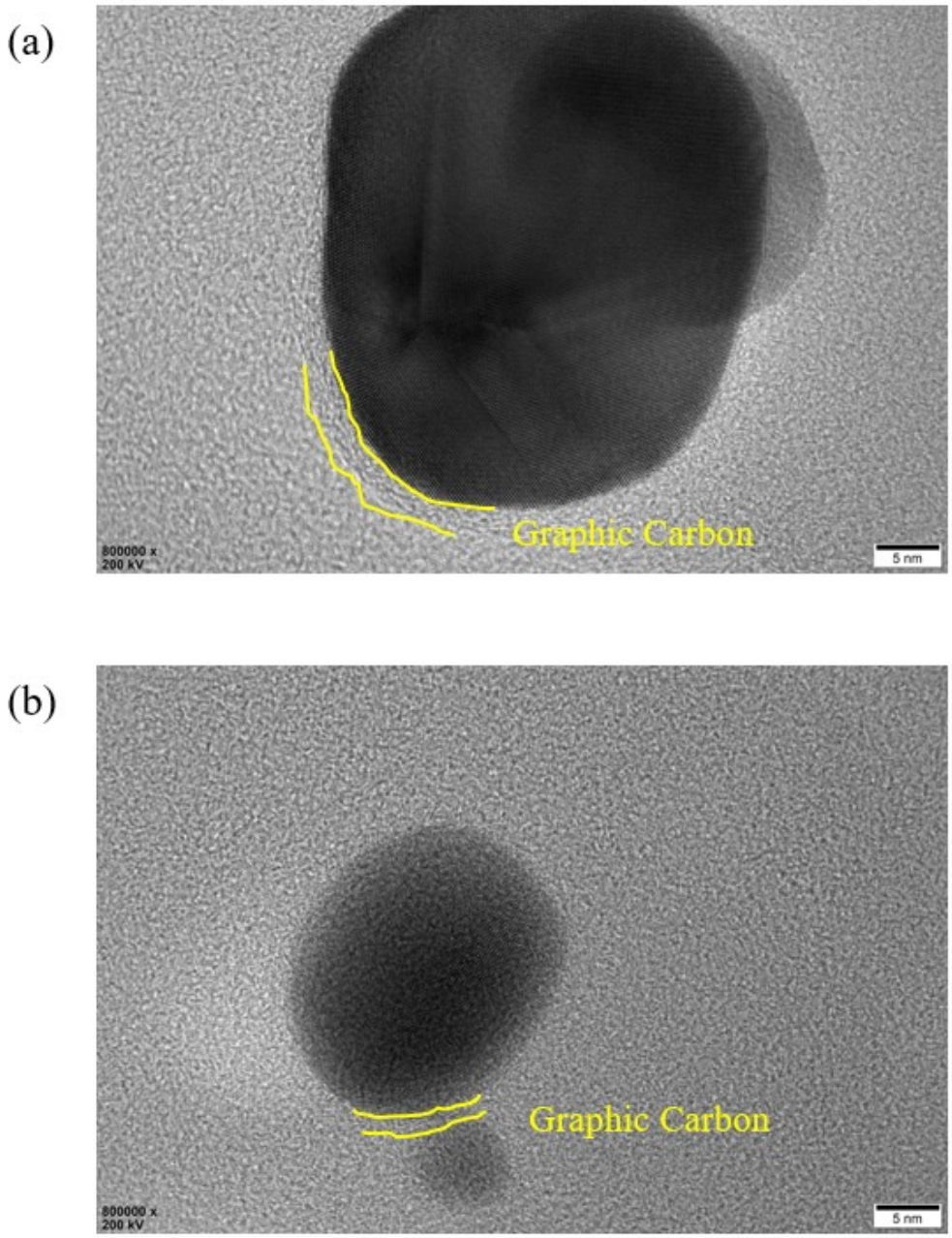


Figure S10. High-resolution TEM images of the Ag/RS-180 sample at the Ag-resin interface.

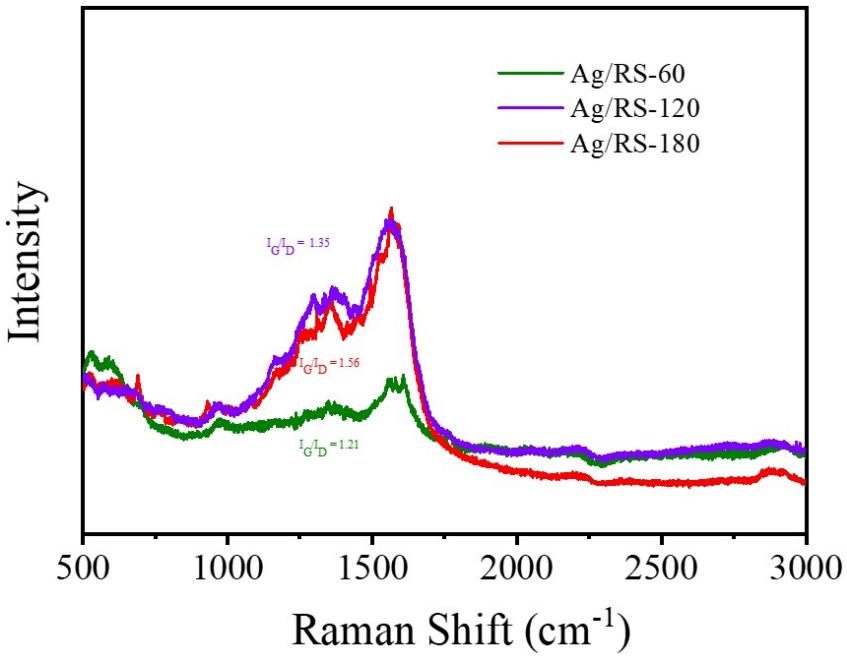


Figure S11. Raman spectra of Ag/RS-60, Ag/RS-120 and Ag/RS-180.

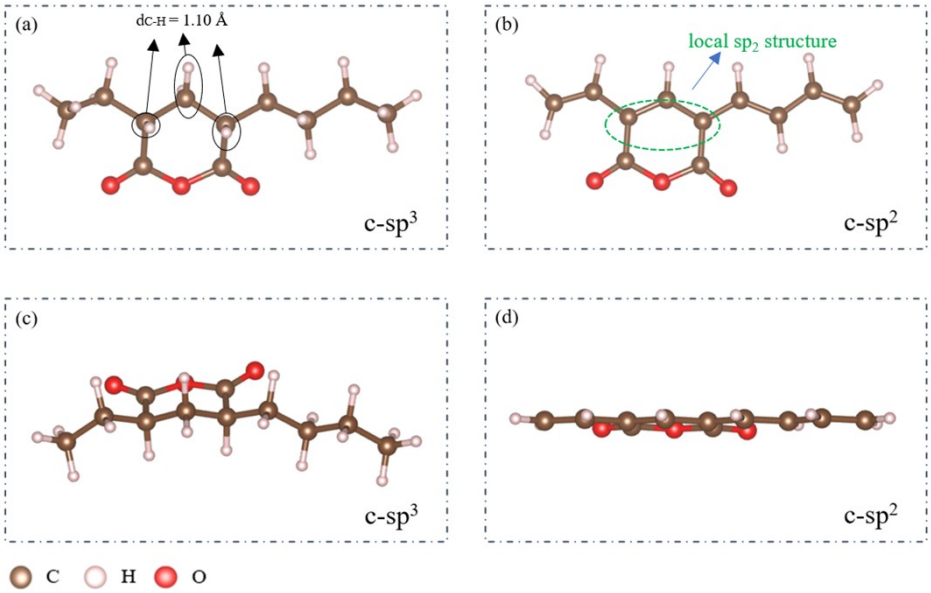


Figure S12. Schematic optimal structures of c-sp^3 and c-sp^2: top view (a) and (b); side view (c) and (d).

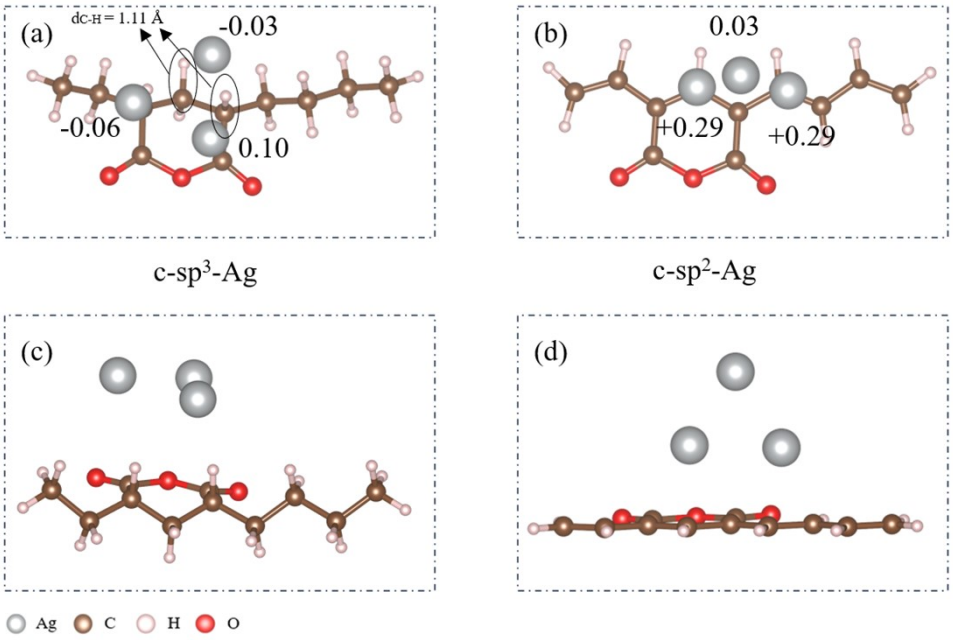


Figure S13. Schematic optimal structures and Bader charges (Ag atom) of c-sp^3-Ag and c-sp^2-Ag: top view (a) and (b); side view (c) and (d)

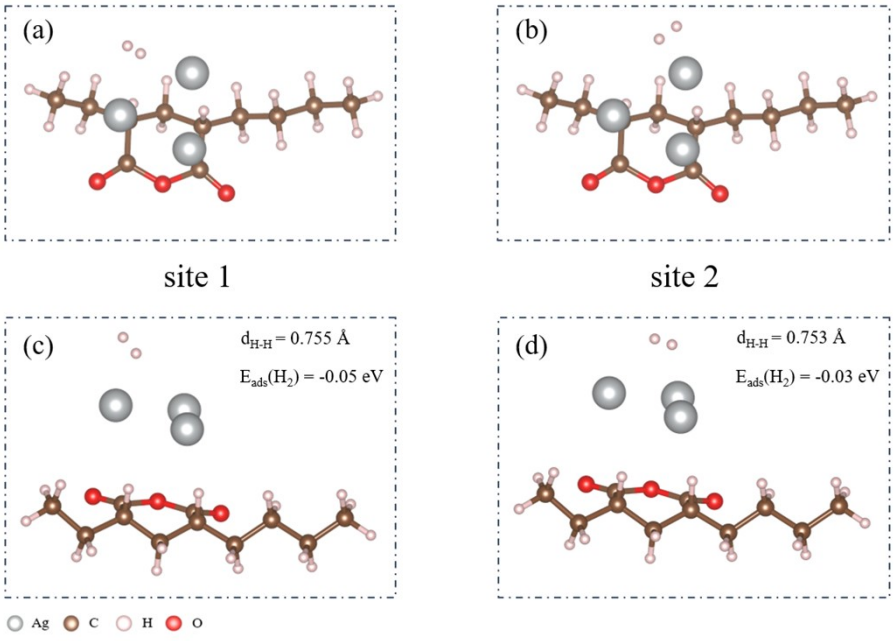


Figure S14. Schematic optimal structures of H_2 adsorbed on different site of c-sp^3-Ag: top view (a) and (b); side view (c) and (d)

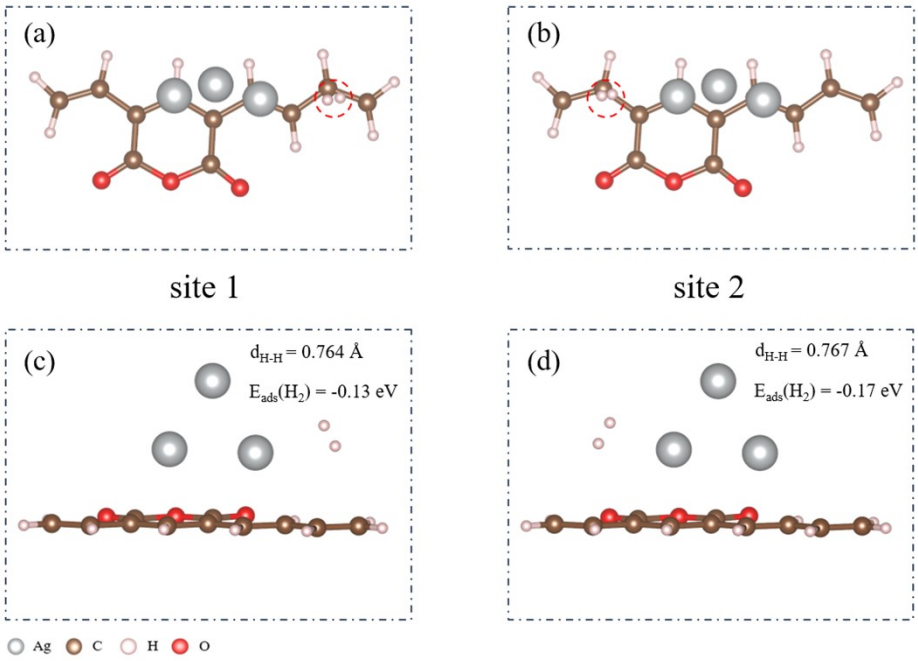


Figure S15. Schematic optimal structures of H_2 adsorbed on different site of c-sp^3-Ag: top view (a) and (b); side view (c) and (d).

Table S1. The post-grinding sphericity of the samples.

RS	Ag/RS-180
92.3%	79.5%