

Electronic Supplemental Information

Metal nanoparticle catalyzed cyclobutane cleavage reaction

Dengtai Chen, Xijiang Han,* Wen Jin, and Bin Zhang*

Department of Chemistry, Harbin Institute of Technology, Harbin, 150001, China.

Email: zhangbin_hit@aliyun.com; hanxijiang@hit.edu.cn

Experimental Section:

General Information

All reactions were monitored by TLC and visualized by UV lamp (254 nm). Column chromatography was performed using 200-400 mesh silica gel. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ¹H NMR spectra were reported in parts per million relative to the signal of CDCl₃ at 7.26 ppm. Chemical shifts for ¹³C NMR spectra were reported in parts per million relative to the center line signal of the CDCl₃ triplet at 77.0 ppm. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, and doublet of doublets, triplet, quartet and multiplet, respectively.

The **Raman spectra** were recorded on Renishaw inVia Raman microscope system with spatial resolution 2 μm. Wavelength 632.8 nm laser was used for all experiments. The laser power was adjusted through the WiRE 3.4 software, and four laser power grades 100%, 50%, 10%, 5% were used.

The **crystalline sample** was placed between two glass slides and crushed into small particles, then the crystalline samples were mounted on the Renishaw inVia Raman system. The sample images were taken on Leica camera. In order to get the reliable spectrum results, all experiments with certain laser powers were carried out on the same sample and repeated at least three times.

Thin layer chromatography was used to develop and distribute the dimer/monomer on the TLC plate. The dimer/monomer distributed TLC plates were used to record the Raman spectra, after the silver gel was sprayed on and dried. The same procedure was repeated three times to get reliable results. Randomly three different points were collected. **Time-resolved *in situ* Raman spectra** were collected with time-step 1 second, during which silver gel was dropped on TLC plates. **Raman mapping** was carried out within the randomly selected area, more than 200 spectra were collected to give **reliable results**.

The *trans*-1,2-bis(4-pyridyl)-ethylene (**bpe**), resorcinol (**res**) and (E)-methyl-3-(pyridin-4-yl)acrylate (**PMA**) were purchased from the Energy Chemical Co. Ltd.

Dimers, 1,2,3,4-tetra(pyridin-4-yl)cyclobutane (**TPCB**), dimethyl 3,4-di(pyridin-4-yl)cyclobutane-1,2-dicarboxylate (**DMCB**), were obtained through UV irradiation cocrystals in solid-state.

1,2,3,4-tetra(pyridin-4-yl)cyclobutane (TPCB)

TPCB was obtained through [BPE]₂[RES]₂ co-crystal in solid with UV irradiation for long enough time (35 hours).^{1, 2} Dimer TPCB was purified with column chromatography, firstly Ethyl Acetate to remove the residual BPE and RES, then methanol to elute dimer TPCB. ¹H NMR: (400 MHz, CDCl₃, ppm); δ 8.335 (d, 8H, J=6Hz, pyridine αH), 7.213 (d, 8H, J=6Hz, pyridine βH), 4.660 (s, 4H, cyclobutane H).

Dimethyl 3,4-di(pyridin-4-yl)cyclobutane-1,2-dicarboxylate (DMCB)

DMCB was obtained through PMA with silver trifluoroacetate (AgTFA) crystal in solid state [Ag₂(PMA)₄][TFA]₂ with UV irradiation for long enough time (30 hours). The dimer DMCB was purified with column chromatography, the eluent was firstly Ethyl Acetate (EA) mixed with n-hexane (1:1 v/v) to remove the residual PMA, then methanol to elute DMCB. ¹H NMR: (400 MHz, CDCl₃, ppm); δ 8.363 (d, 4H, J=4.4Hz, pyridine αH), 6.976 (d, 4H, J=5Hz, pyridine βH), 4.479 (d, 2H, J=6Hz, Py-cyclobutane H), 3.920 (d, 2H, 4Hz, carboxymethyl-cyclobutane H) 3.791 (s, 6H, -CH₃).

Synthesis of Ag sol and Au sol

The silver sol was prepared according to the literature method.³ In detail, 40 mg AgNO₃ was dissolved in 200 mL H₂O and brought to boiling. 4 mL of 1% sodium citrate were added. The solution was kept on boiling for ca.1 h, and was then left to be cooled down in the open air.

Gold sol was also prepared according to the literature method.³ 6.4 mL HAuCl₄ (0.1 M) was dissolved in 500 mL water and the solution was brought to boiling. A solution of 1% sodium citrate (50 mL) was added. Boiling was continued for ca. 1 h, and was then left to be cooled down in the open air.

Additional Figures:

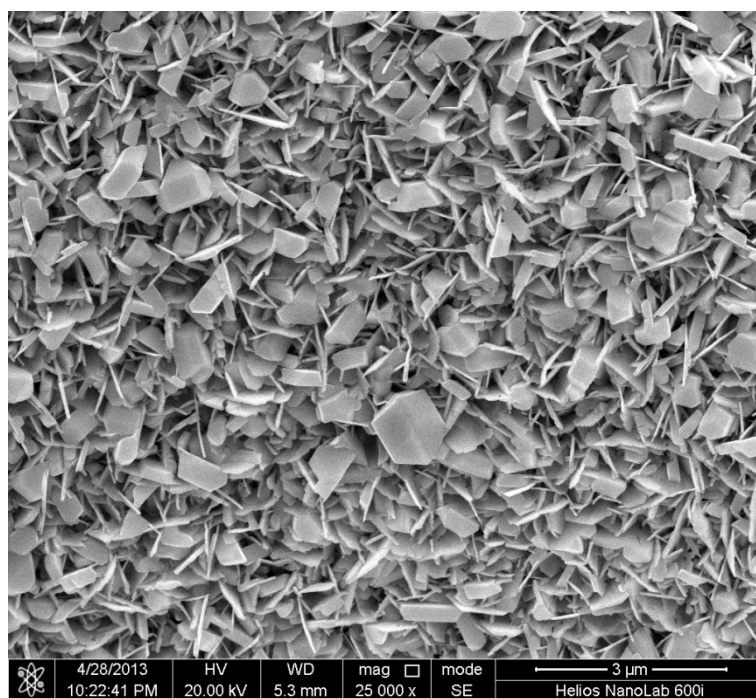


Fig. S1 SEM image of Ag nanostructures supported on PANI substrate

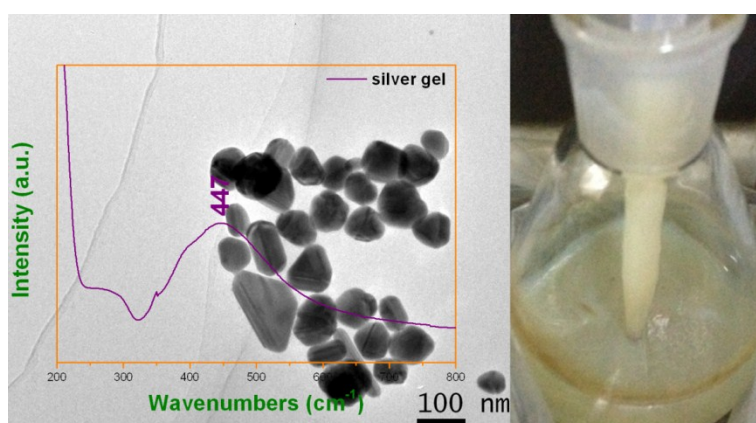


Fig. S2 the pale silver gel prepared according to the literature method. Average diameter is 50-100 nm; the max UV-vis absorption located at 447 cm⁻¹

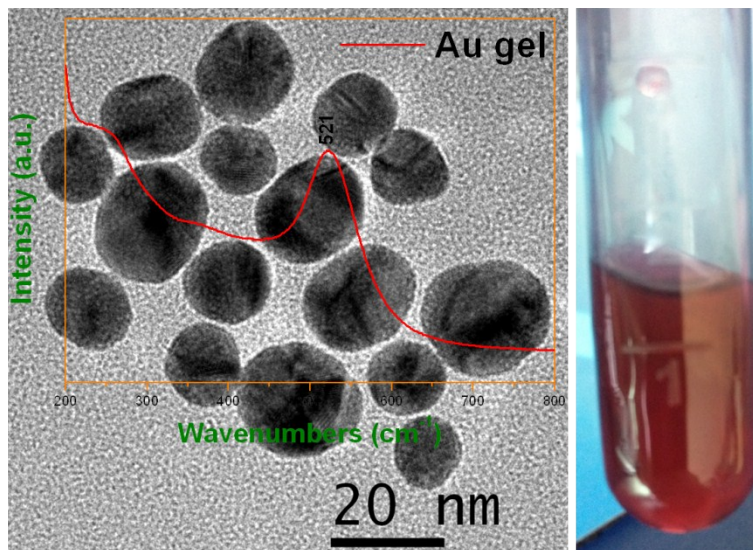


Fig. S3 the wine red gold gel with average diameter 20 nm, the max UV-vis absorption is located at 521 cm^{-1}

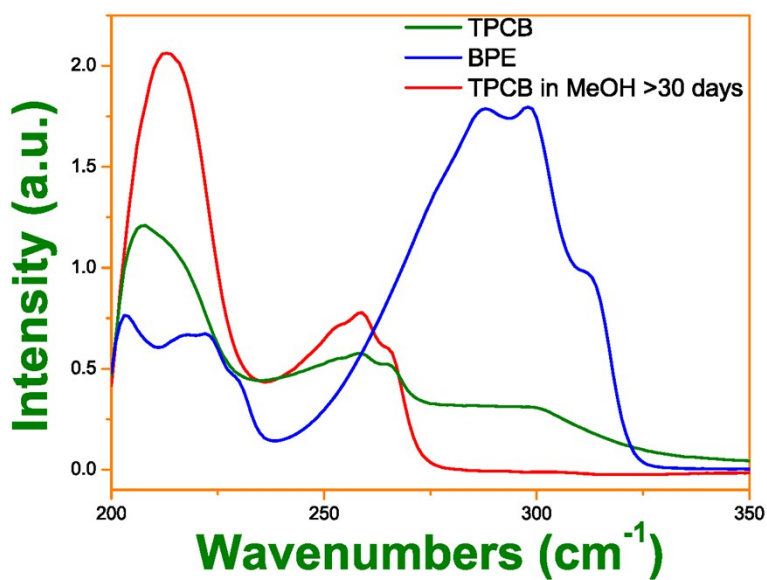


Fig. S4 the UV-vis spectrum of TPCB (blue line), BPE (green line) in methanol solution with 0.5 mM; To test TPCB stability, it is stored in open air > 30 days at room temperatures (red line)

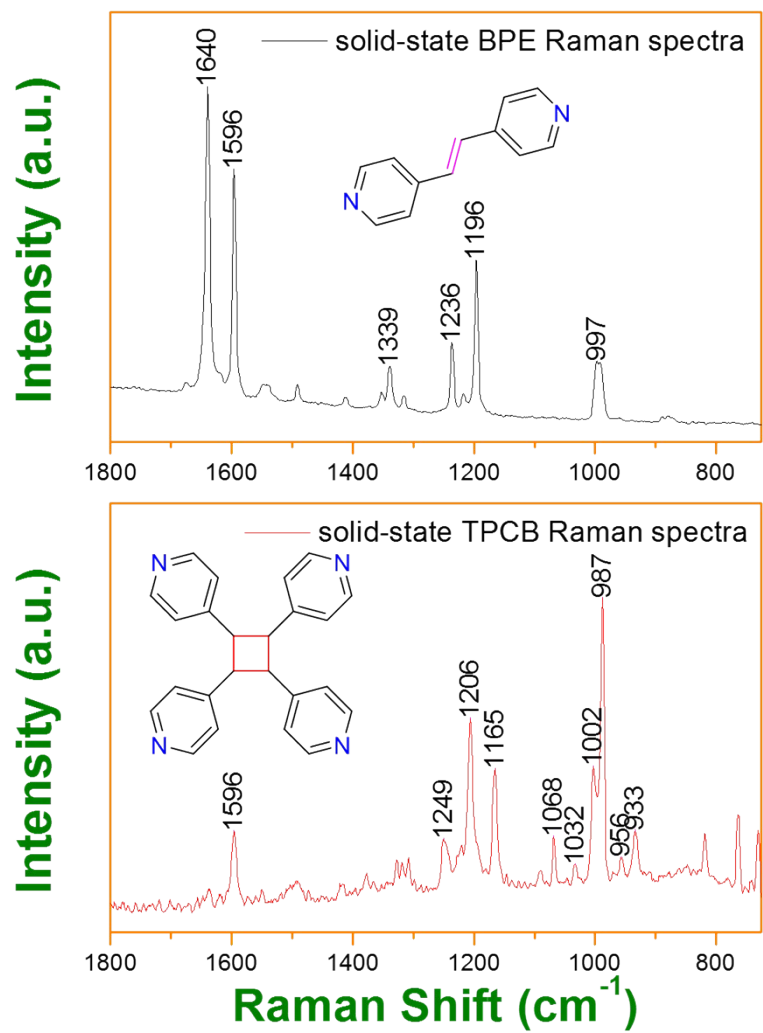


Fig. S5 solid-state BPE & TPCB standard Raman spectra

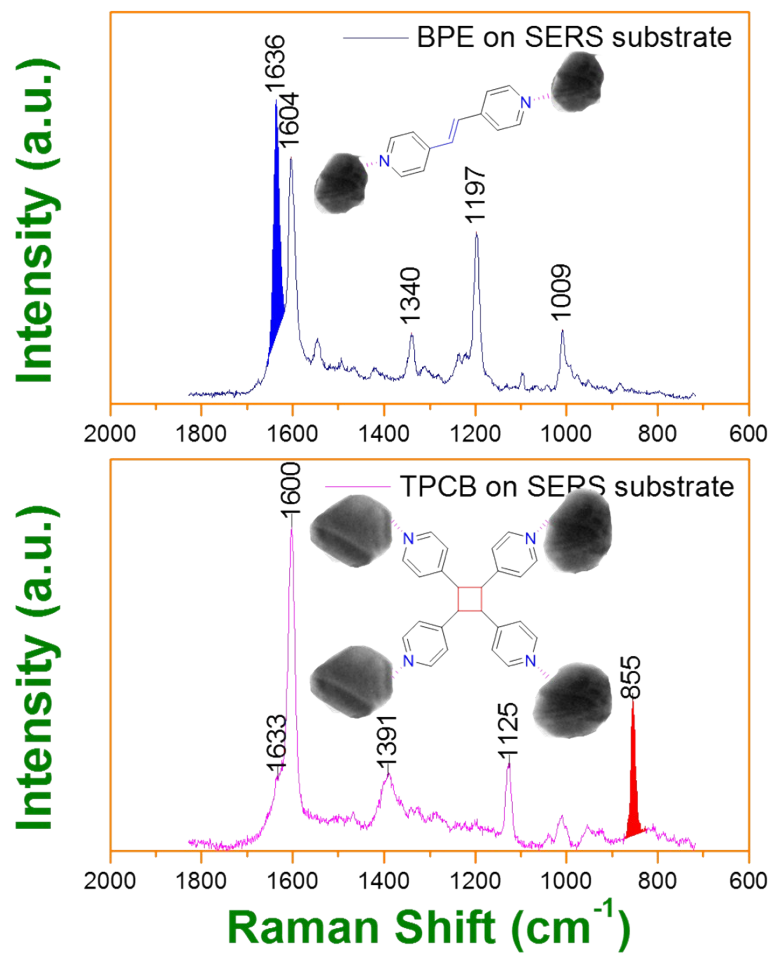


Fig. S6 the standard BPE & TPCB SERS spectra on PANI-Ag NSs composite film

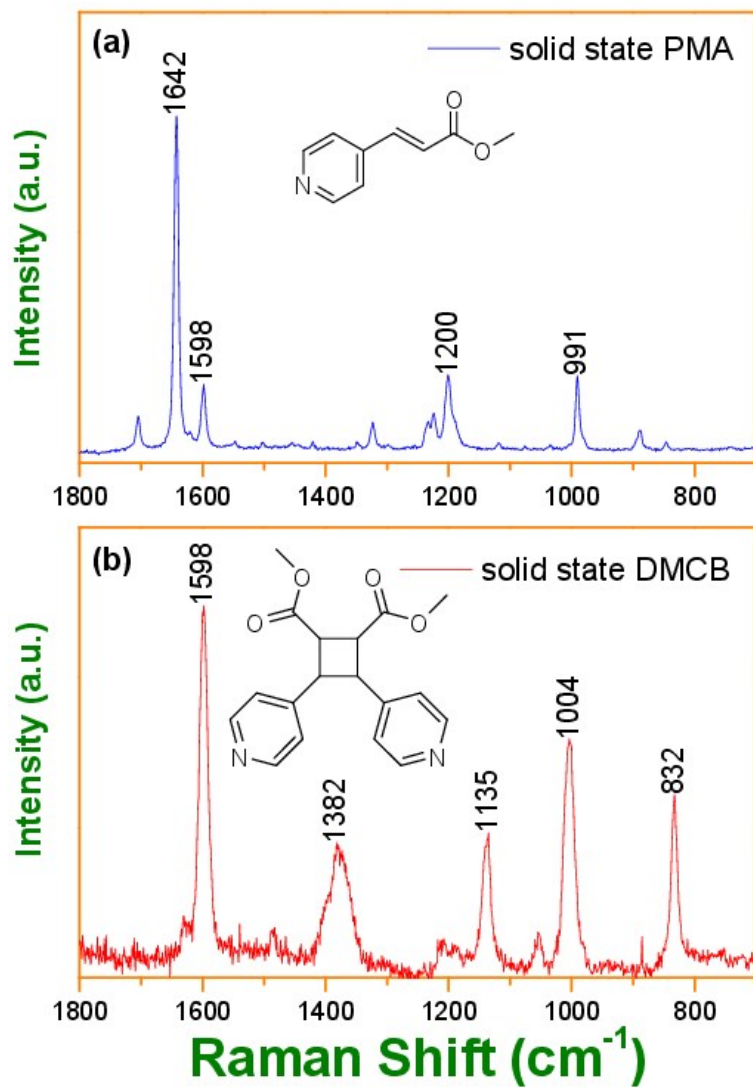


Fig. S7 (a), (b) solid-state PMA & DMCB Raman spectra, cyclobutane were confirmed with the peaks at 832 & 1135 cm^{-1} .

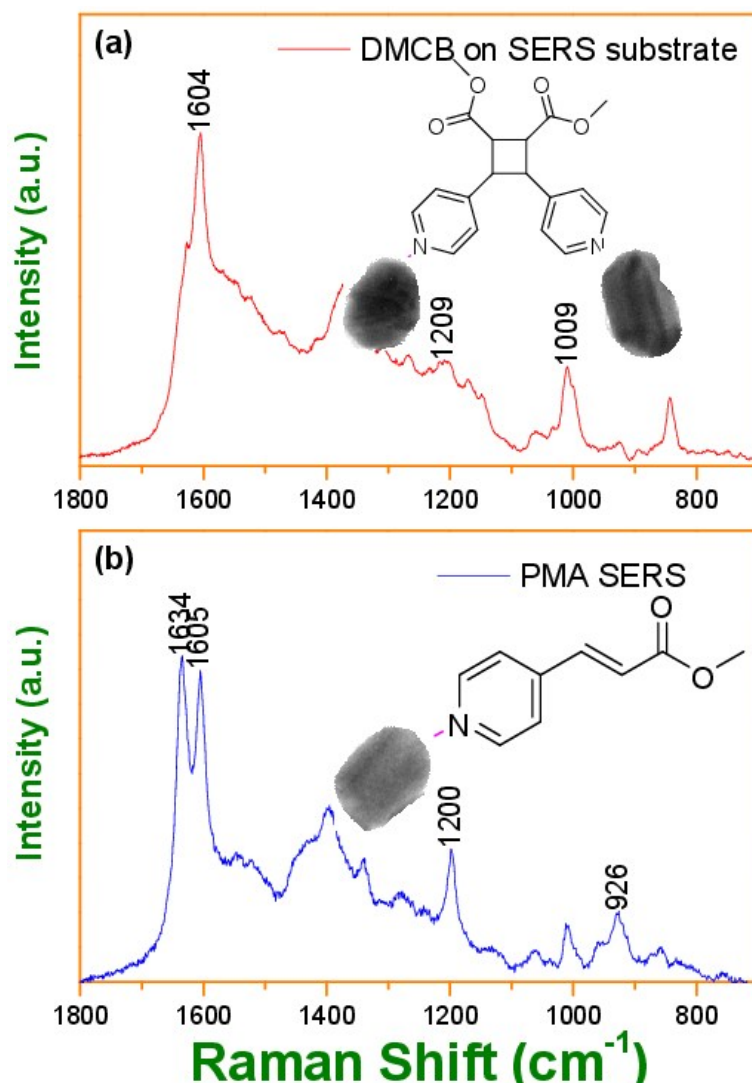


Fig. S8 SERS spectra of PMA & DMCB

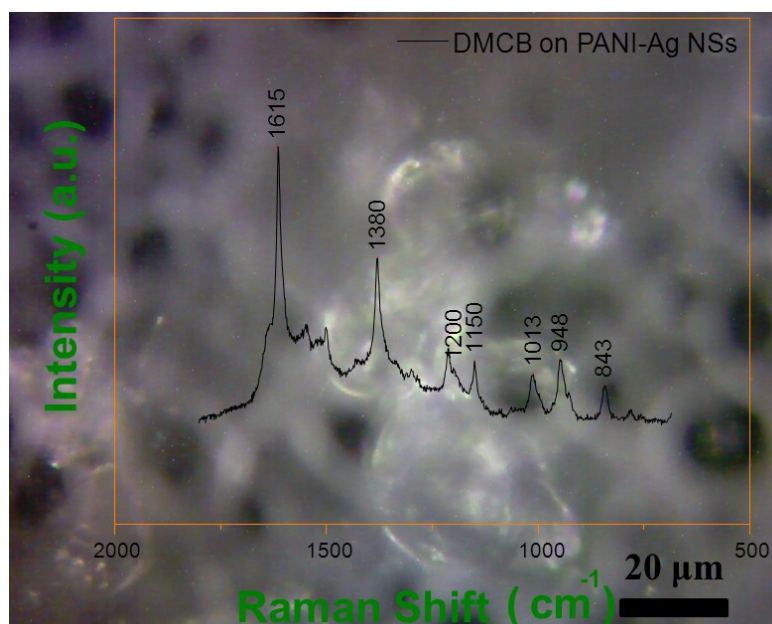


Fig. S9 PANI-Ag NSs composite film was immersed in DMCB 0.5 mM methanol water mixed solution for 30 minutes. Sharp Raman peaks confirmed crystalline DMCB existence

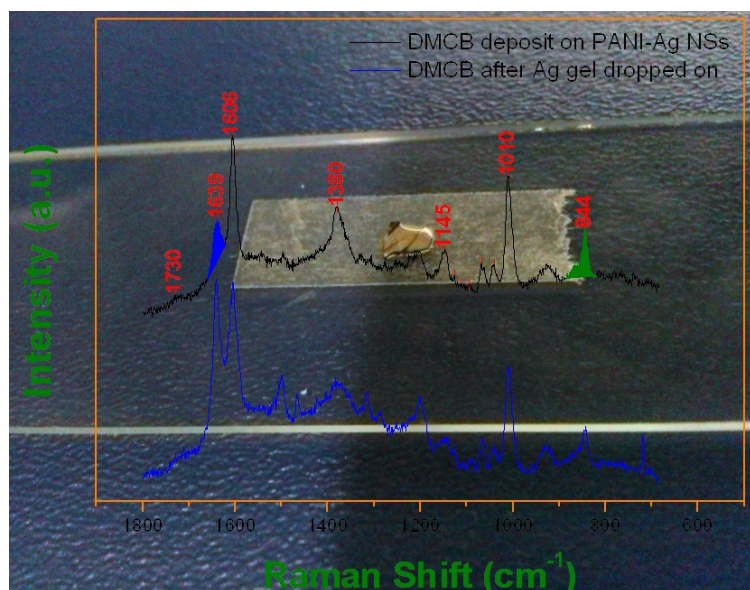


Fig. S10 Firstly, the TLC plate was immersed in DMCB methanol solution, SERS spectra confirmed the dimers' existence from the peaks at 842, 1145 cm^{-1} , while 1730 cm^{-1} was assigned to carboxyethyl (-COOMe) vibration. Then silver gel was dropped on PANI-Ag NSs composite films, in some points, however, there are still monomer SERS spectra

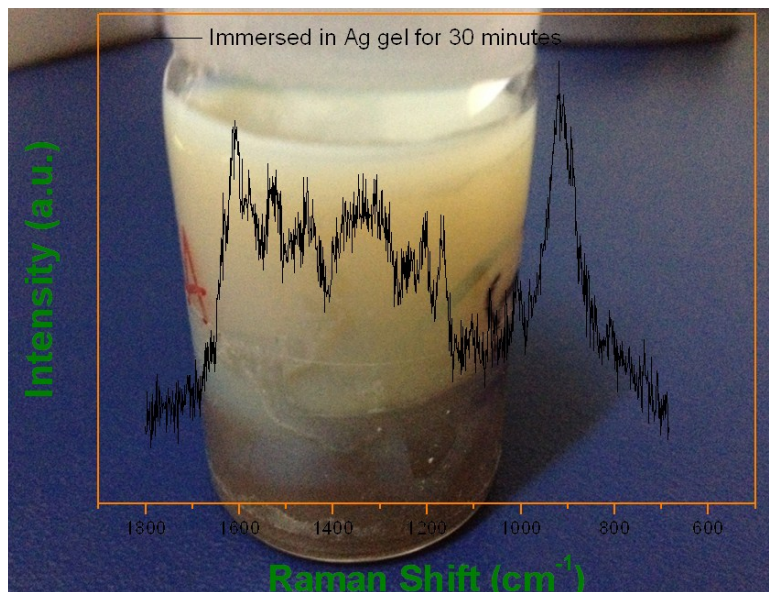
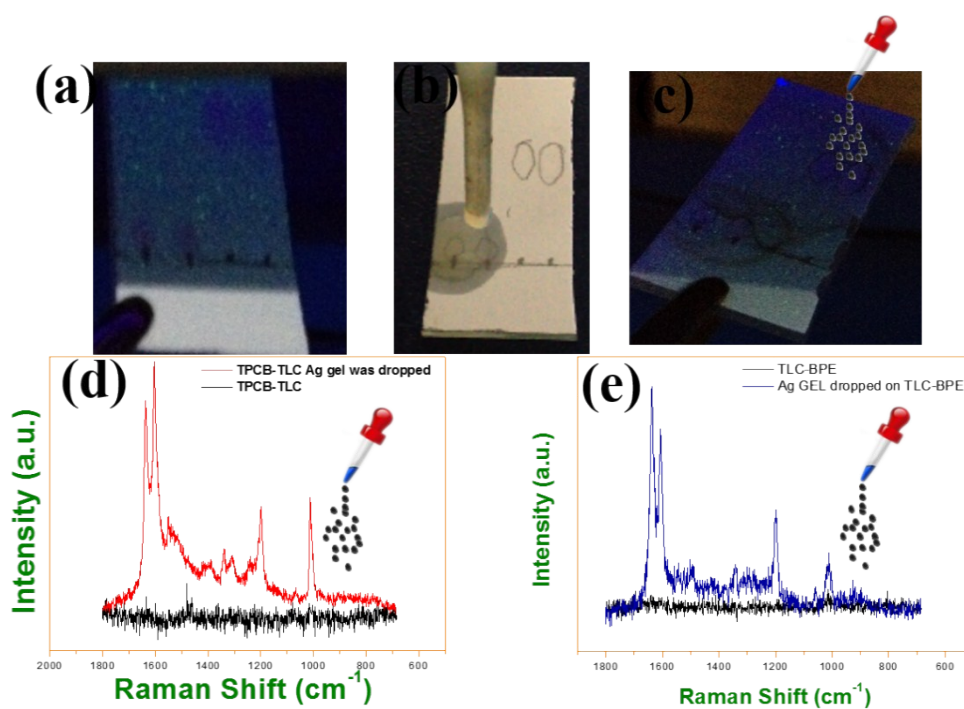


Fig. S11 TLC plate was immersed in the silver gel for 30 minutes. This treatment made the SERS spectra worse. The over-deposition of silver gel on TLC plate made the Raman no signal



TPCB SERS spectra, developed on TLC plate.

Ag gel was dropped on TLC plate BPE SERS spectra.

Fig. S12 so the optimized conditions were as following, (a) TPCB & BPE were developed on TLC plate; (b) & (c) silver gel was dropped on the TPCB spot area; (d) & (e) Raman spectra were collected firstly, then SERS spectra were collected after silver gel dropped.

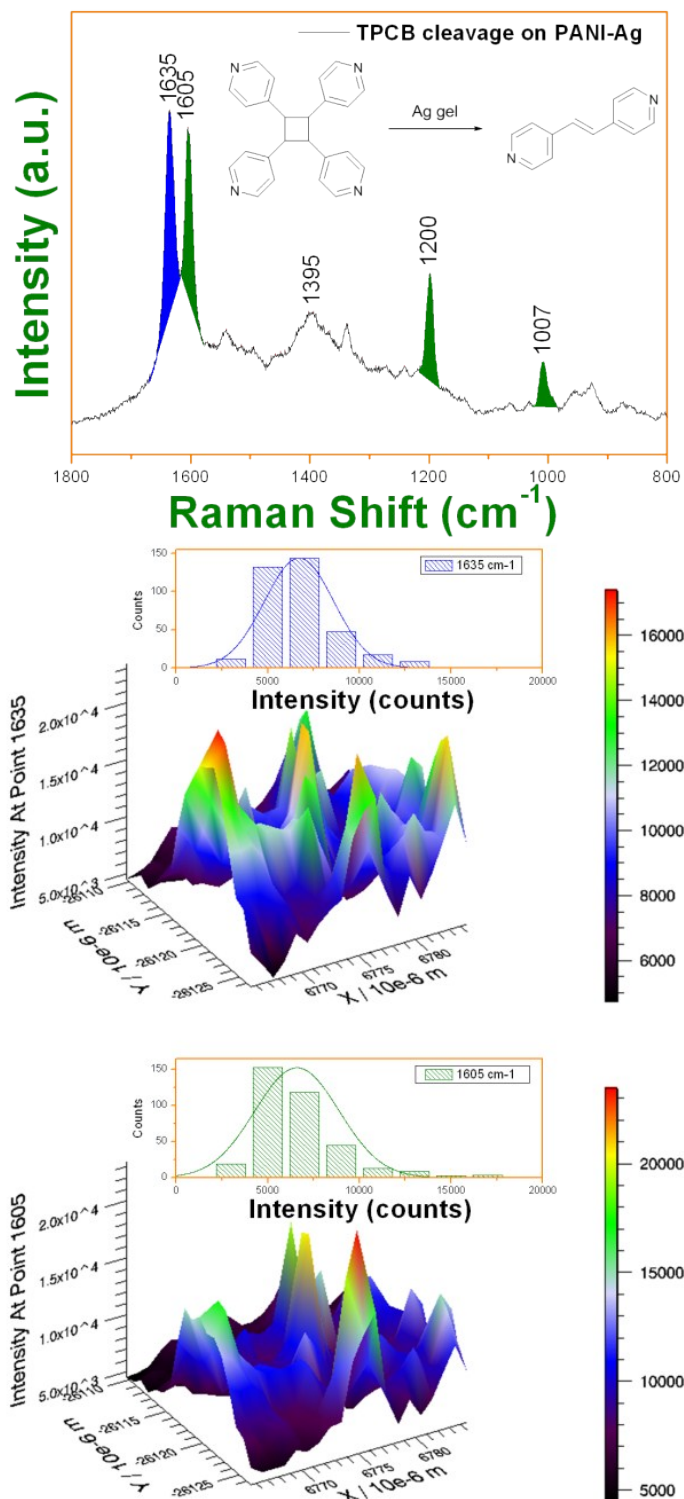


Fig. S13 (a) TPCB cleavage was confirmed with Raman spectra on TLC plate after silver gel dropped on; (b) The peak intensity of 1637 cm^{-1} , 1605 cm^{-1} on the selected TLC plate area was illustrated as colored surface image, and the inset in each image is the corresponding intensity distribution statistical curves

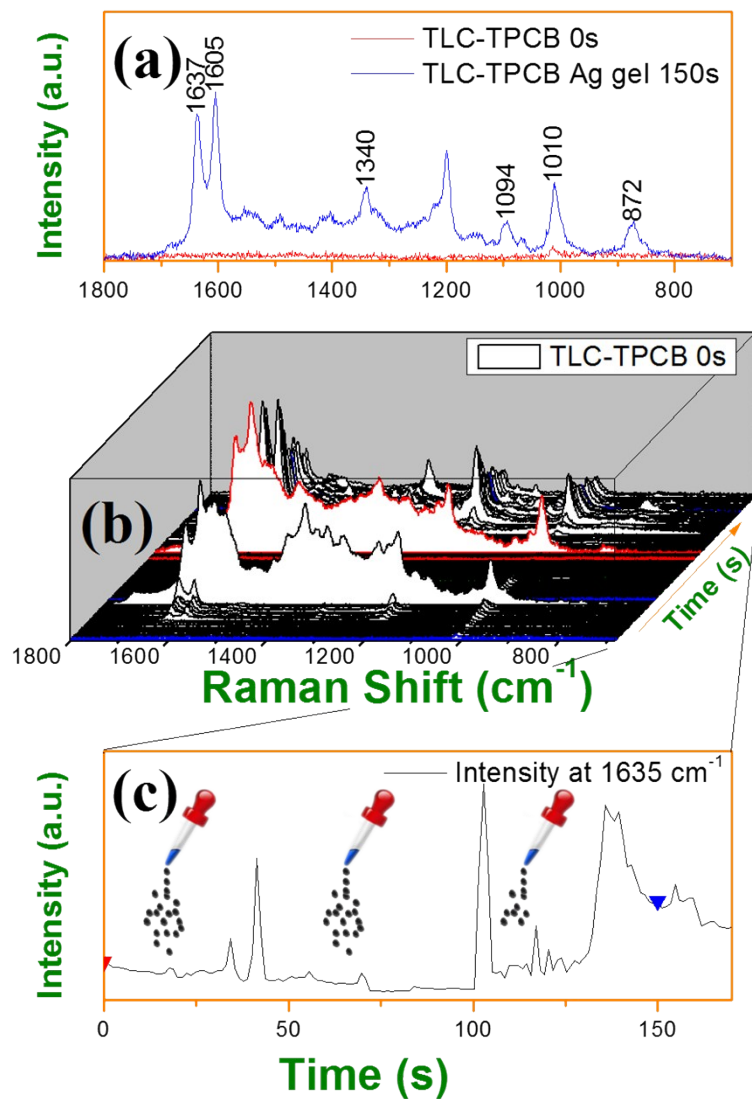


Fig. S14 (a) TPCB Raman spectra changed on TLC plate before and after silver gel was dropped on; (b) DPCB time-resolved *in-situ* SERS spectra were obtained; (c) the peak intensity at 1635 cm^{-1} changed during the silver gel was dropped on

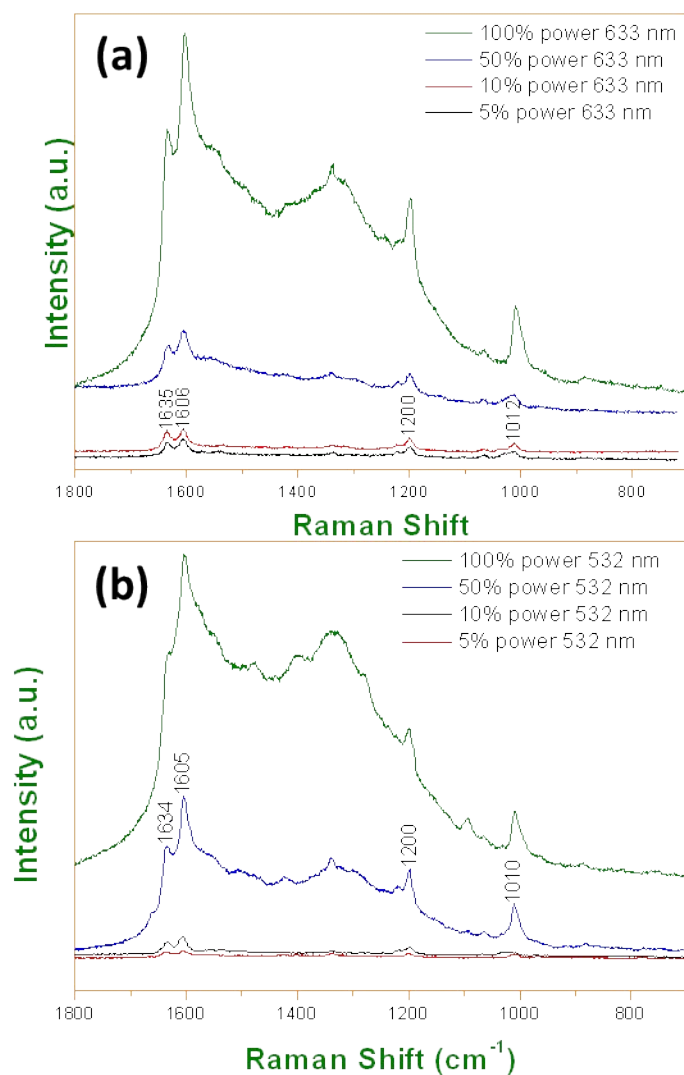


Fig. S15 (a) 633 nm laser power-dependent Raman spectra were recorded with 5%, 10%, 50%, 100%, when the power increased up to 50%, carbonization can be observed from the 1380 cm⁻¹, and the 1635 cm⁻¹ decreased; (b) 532 nm laser power-dependent Raman spectra with 5%, 10%, 50%, 100% power were recorded, even 50% can caused carbonization

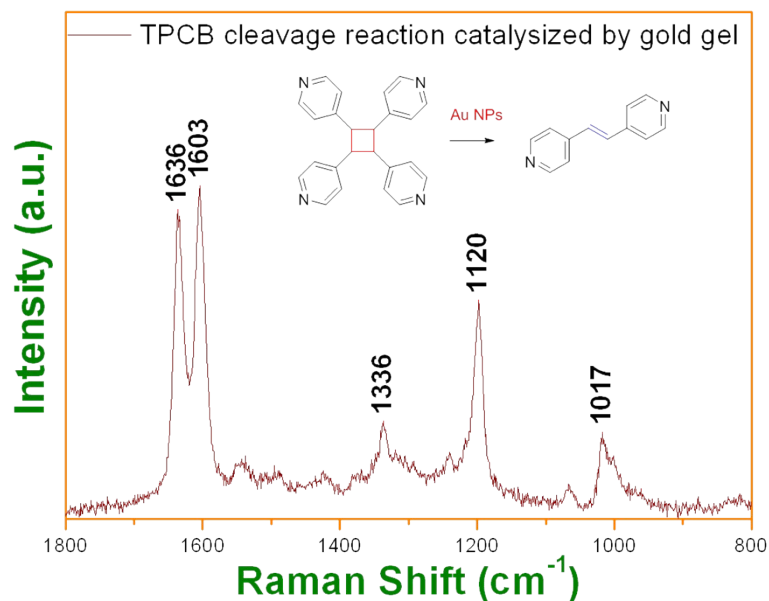


Fig. S16 TPCB cleavage reaction catalyzed with gold NPs

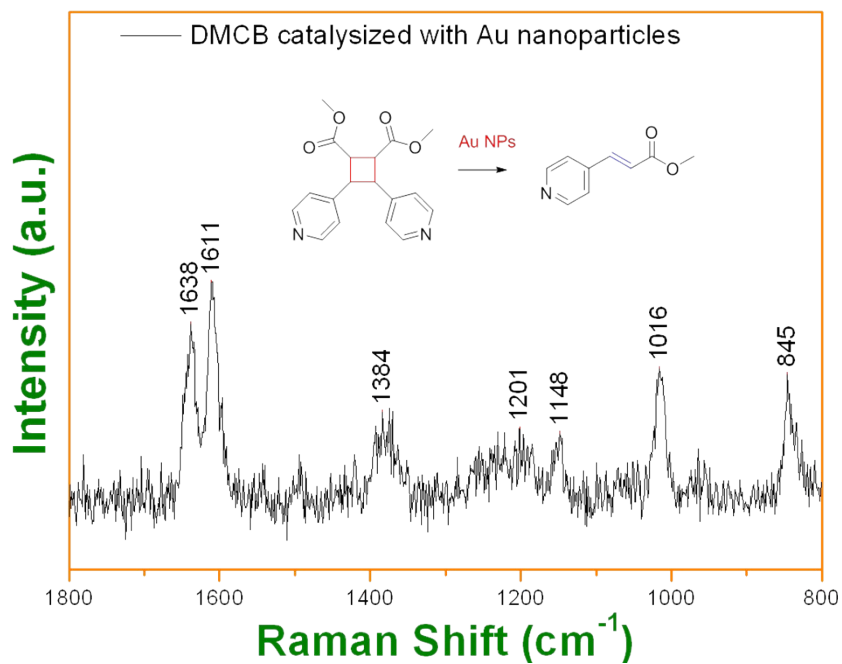


Fig. S17 DMCB cleavage reaction catalyzed with gold NPs, the unreacted DMCB can be certificated with the 844 cm^{-1} and 1148 cm^{-1}

References:

1. S. Ghorai, J. C. Sumrak, K. M. Hutchins, D. K. Bucar, A. V. Tivanski and L. R. MacGillivray, *Chem Sci*, 2013, **4**, 4304-4308.
2. L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *Journal of the American Chemical Society*, 2000, **122**, 7817-7818.
3. P. C. Lee and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391-3395.