

## Supporting Information

# **A new cobalt(II) complex nanosheet as an electroactive medium for plasmonic switching on Au nanoparticles**

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## **Content**

1. Experimental Section
2. Repairability of **Co-nanosheet**
3. TGA result of **Co-nanosheet**
4. Wide scan XP spectra of **L, Co-nanosheet, and R**
5. FT-IR spectra of **L, Co-nanosheet, and R**
6. SEM image of Au NPs deposited onto **Co-nanosheet**
7. Time-current curves of **Au@Co-nanosheet** under different applied voltages

## 1. Experimental section

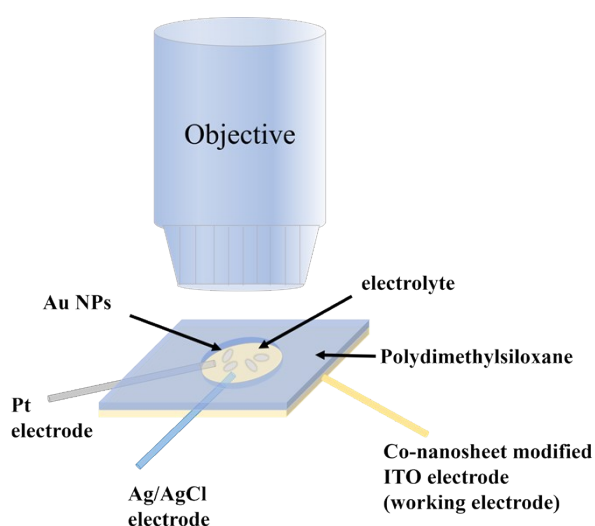
### Materials

All commercial chemical reagents were directly used as received unless otherwise stated. Analytical pure grade solvents were used for the ligands synthesis while high-performance liquid chromatography grade solvents were used for nanosheet preparation. The  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was recrystallized from D.I. water before use. All chemically synthetic reactions were monitored by silica gel thin-layer chromatography (TCL) with pre-coated aluminum plates from Merck. The starting material trimethyl-1,3,5-benzenetricarboxylate, gold chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\geq 99.9\%$ ), cetyltrimethylammonium bromide (CTAB,  $\geq 98\%$ ), sodium borohydride ( $\text{NaBH}_4$ , 98%) and L-ascorbic acid (AA,  $\geq 99\%$ ), were all purchased from Sigma-Aldrich. Deionized water with a resistivity of 18.2 M $\Omega$  was used throughout the experiments.

### Apparatus

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured in deuterated reagents on a Bruker Ultrashield Plus 400 MHz FT-NMR or Bruker Ascend 400 MHz FT-NMR spectrometer with chemical shifts ( $\delta$  in ppm) quoted with tetramethylsilane as the internal standard. Mass spectrometry was carried out on a Bruker Autoflex matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). Optical microscope image was collected on Fluorescence Stereomicroscopy with Digital Camera-Olympus. SEM and EDX were conducted with LEO 1530 Field

Emission Scanning Electron Microscope mounted with an Energy Dispersive X-ray Spectrometer. TEM image was obtained by FEI Tecnai G2 20 S-TWIN Transmission Electron Microscope mounted with an Energy Dispersive X-ray Spectrometer. AFM images and the cross-sectional analysis results were recorded by Digital Instruments NanoScope IV atomic force microscope. XPS measurement was taken with Sengyang SKL-12 electron spectrometer assisted with VG-CLAM-4 multichannel hemispherical analyzer. The spectra were analyzed with CasaXPS Software and the  $C_{1s}$  peaking at 284.6 eV was used as the standard. Fourier transform infrared (FTIR) spectrometry was conducted on a Nicolet Magna 550 Series II FTIR spectrometer by using KBr pellets. TGA was performed using a Perkin-Elmer TGA6 thermal analyzer under nitrogen.

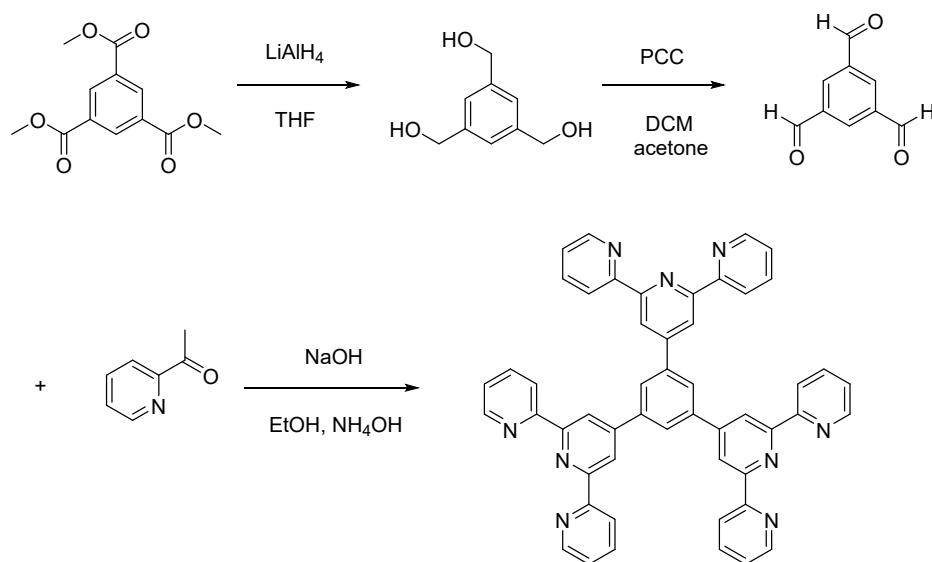


**Scheme S1.** The schematic diagram for electrochemical plasmonic switching measurement in single-particle level.

## Pretreatment of Substrates

The vacuum-packed ITO glasses were directly used without further treatments. Both Si(111) and quartz substrates were cut into 1 cm x 1 cm pieces and then washed by solvents and detergents. The clean substrates were stored in D.I water and dried in vacuum overnight just before use.

## Synthesis of ligand



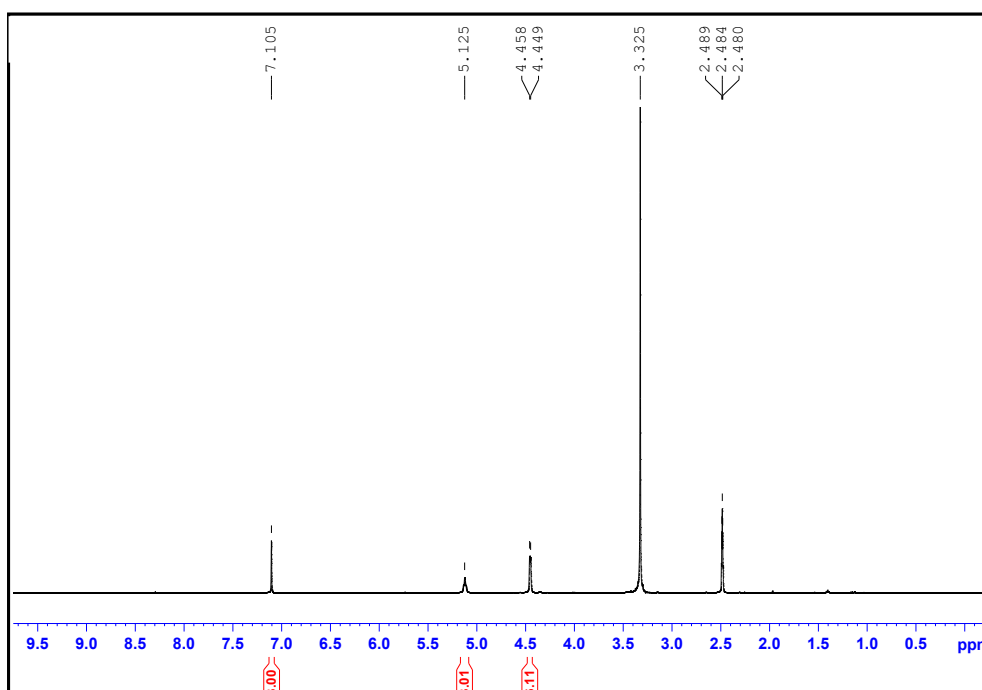
**Scheme S2.** Synthetic route for **L** (PCC stands for pyridinium chlorochromate).

## Synthesis of L

### *Synthesis of 1,3,5-tris(hydroxymethyl)benzene*

1,3,5-Tris(hydroxymethyl)benzene was prepared according to the reported procedure.<sup>[1]</sup>  $\text{LiAlH}_4$  (0.45 g, 11.8 mmol) was suspended in 35 mL anhydrous THF before the slow addition of trimethyl-1,3,5-benzenetricarboxylate (1.0 g, 3.95 mmol) in 15 mL anhydrous THF through a pressure-equalized addition funnel under a  $\text{N}_2$

atmosphere in an ice-bath. Then the mixture was allowed to warm to room temperature (r.t.). After stirring for 4 h, the reaction was quenched with a 1:1 mixture of  $\text{KHSO}_4$  and Celite. Then the sediment was filtered off and washed with methanol. The solvent was vaporized by reduced pressure to afford a white solid of 465 mg in 70% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ,  $\delta$ ): 7.14 (s, 3H, Ar-H), 5.15 (t, 3H, -OH), 4.49 (d, 6H,  $-\text{CH}_2-$ ).

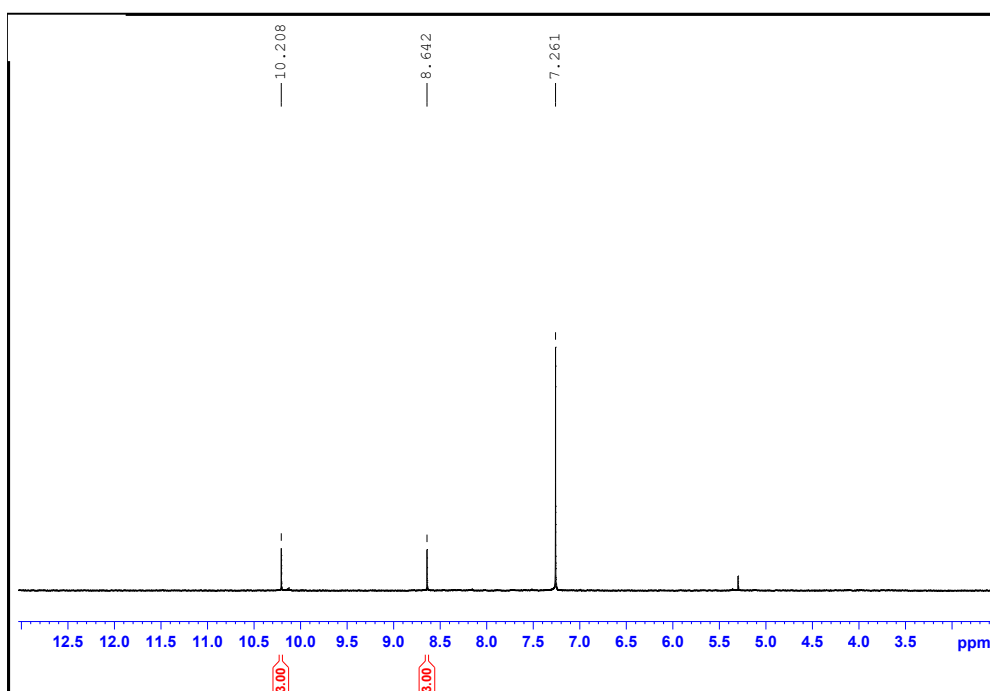


**Figure S1.** The  $^1\text{H}$  NMR spectrum of 1,3,5-tris(hydroxymethyl)benzene in  $\text{DMSO-}d_6$ .

#### *Synthesis of 1,3,5-triformylbenzene*

1,3,5-Triformylbenzene was synthesized through the reported procedure.<sup>[1]</sup> To a suspension of 1,3,5-tris(hydroxymethyl)benzene (0.5 g, 3.0 mmol) in 15 mL DCM, pyridinium chlorochromate (PCC, 2.8 g, 13.1 mmol) was added and the mixture was

stirred for 0.5 h. After dilution of the system with 5 mL acetone, a further 3 h of stirring was continued. After being conformed by TLC, the insoluble salt was filtered off and washed with DCM. The organic layer was washed with saturated aqueous  $\text{Na}_2\text{CO}_3$  solution three times. After separation, the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and vacuum system. Purification was conducted through silica column chromatography (DCM/EA, 4:1) to obtain a white solid of 145.9 mg in 30% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 10.21 (s, 3H,  $-\text{CHO}$ ), 8.64 (s, 3H, Ar- $H$ ).

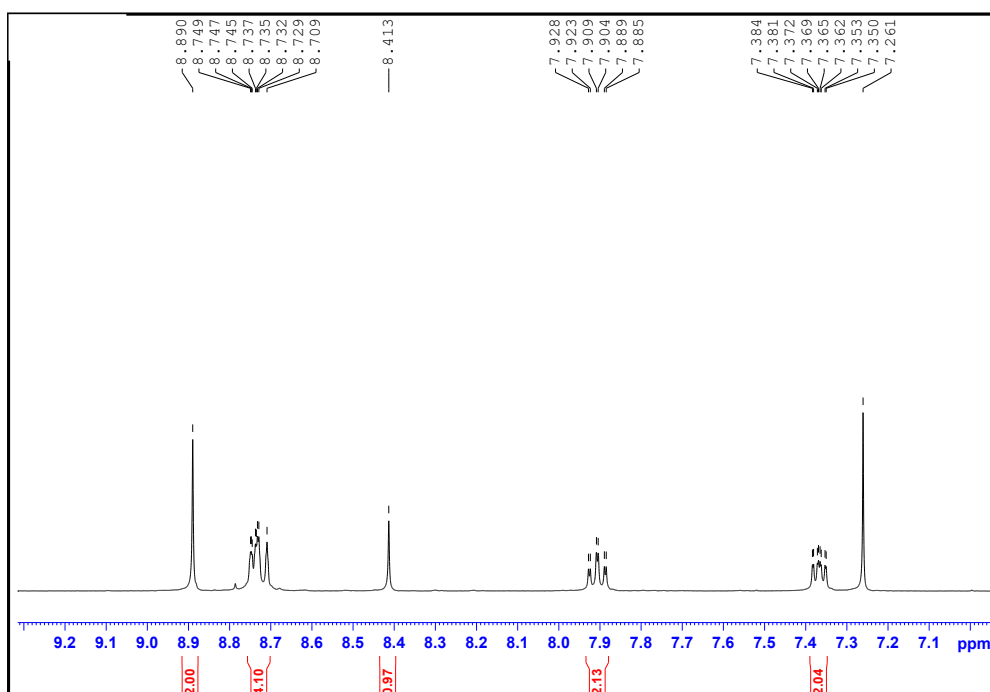


**Figure S2.** The  $^1\text{H}$  NMR spectrum of 1,3,5-triformylbenzene in  $\text{CDCl}_3$ .

### *Synthesis of L*

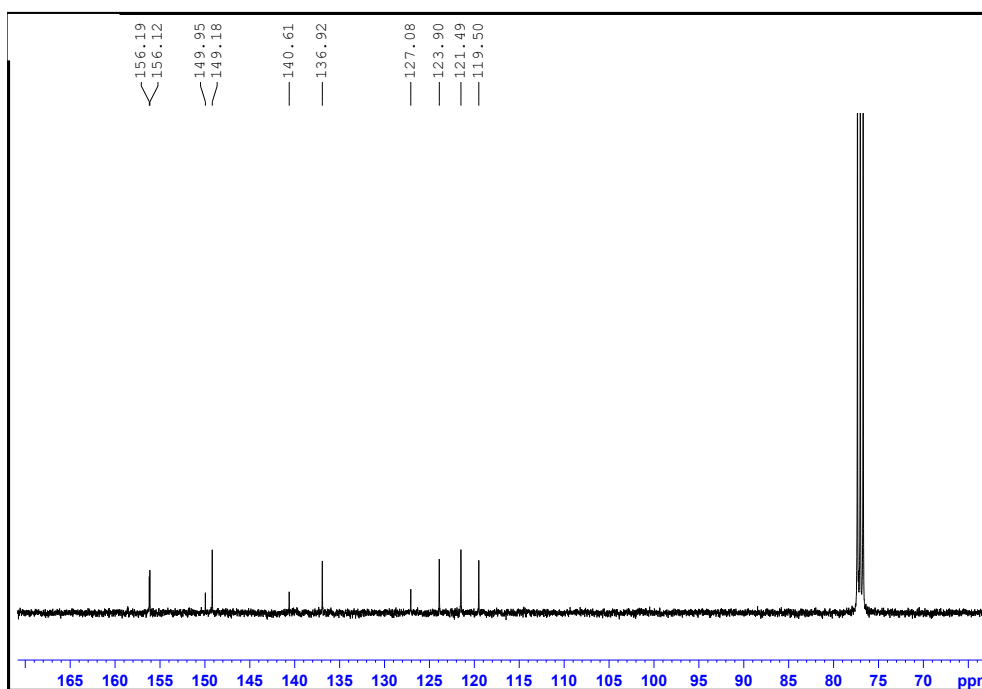
**L** was synthesized according to the modified procedure.<sup>[2]</sup> 1,3,5-Triformylbenzene (0.3 g, 1.9 mmol), 2-acetylpyridine (1.5 g, 12.2 mmol), NaOH (0.6 g, 14.8 mmol), 40

mL aqueous  $\text{NH}_3\cdot\text{H}_2\text{O}$  and 40 mL ethanol were used to afford a white solid. Yield 357 mg, 25%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.90 (s, 6H, Py- $H^{3',5'}$ ), 8.74 (d, 6H, Py- $H^{6,6''}$ ), 8.72 (d, 6H, Py- $H^{3,3''}$ ), 8.42 (s, 3H, Ar- $H$ ), 7.90 (dt, 6H, Py- $H^{4,4'}$ ), 7.37 (m, 6H, Py- $H^{5,5''}$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 156.2, 156.1, 150.0, 149.2, 140.6, 136.9, 127.1, 123.9, 121.5, 119.5; MALDI-TOF-MS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{51}\text{H}_{34}\text{N}_9$ , 772.293; found, 772.293.



**Figure S3.** The  $^1\text{H}$  NMR spectrum of **L** in  $\text{CDCl}_3$ .





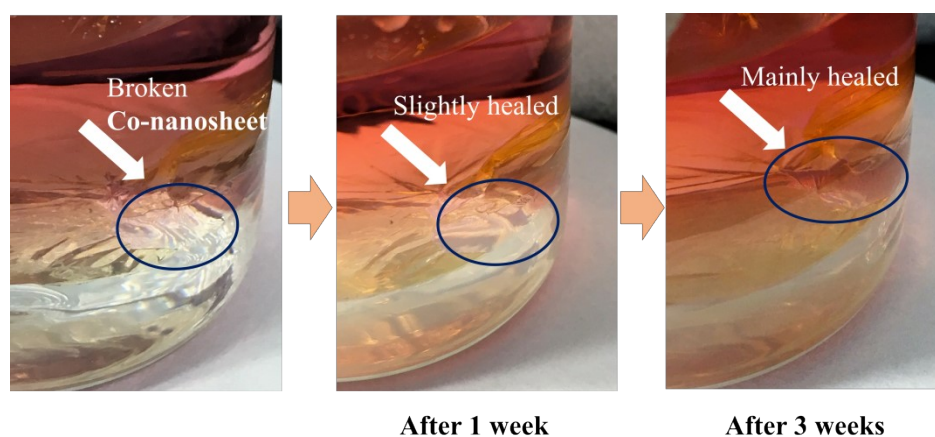
**Figure S4.** The  $^{13}\text{C}$  NMR spectrum of **L** in  $\text{CDCl}_3$ .

### Synthesis of Au NPs and Au@Co-nanosheet composite

The Au NPs were synthesized according to the reported procedures.<sup>[3]</sup> The preparation of Au NPs was conducted in aqueous solution by a seed-mediated growth method. On the one hand, the seed solution was prepared by adding a freshly prepared  $\text{NaBH}_4$  solution (0.01 M, 0.6 mL) into a mixture solution of  $\text{HAuCl}_4$  (0.01 M, 0.25 mL) and CTAB (0.1M, 9.75 mL) with stirring for 1 min and then was kept undisturbed at room temperature (r.t.) for 2 h. On the other hand, the mixture of CTAB (0.1 M, 9.75 mL),  $\text{HAuCl}_4$  (0.01 M, 4.0 mL), water (190 mL) and AA (0.1 M, 15 mL) made up the growth solution. Then, under gentle stirring, the seed solution (0.12 mL) was injected into the growth solution, and the mixture was kept undisturbed overnight at r.t. to obtain a colloidal solution, followed by washing with water for three times by

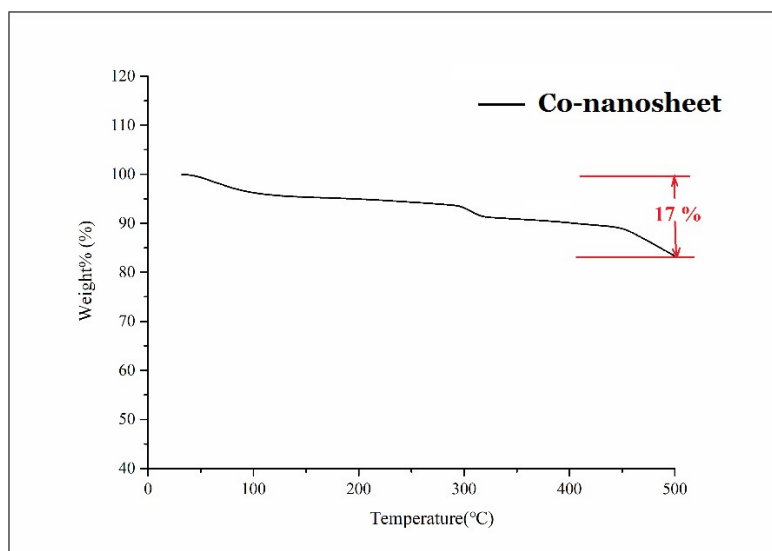
centrifugation. The acquired nanoparticles were redispersed into 200 mL water. 4 mL of this solution was mixed with CTAC (0.025 M, 30 mL), HAuCl<sub>4</sub> (0.01 M, 2 mL) and AA (0.1 M, 0.75 mL) solution in sequence. After that, the mixed solution was heated in an isothermal oven at 50 °C for 3 h, synthesizing the Au NPs which were centrifuged and redispersed in CTAB solution (0.02 M, 30 mL) for storage. The preparation of the composite Au@Co-nanosheet was carried out by drop-casting of the Au NPs solution onto ITO-supported Co-nanosheet.

## 2. Repairability of Co-nanosheet



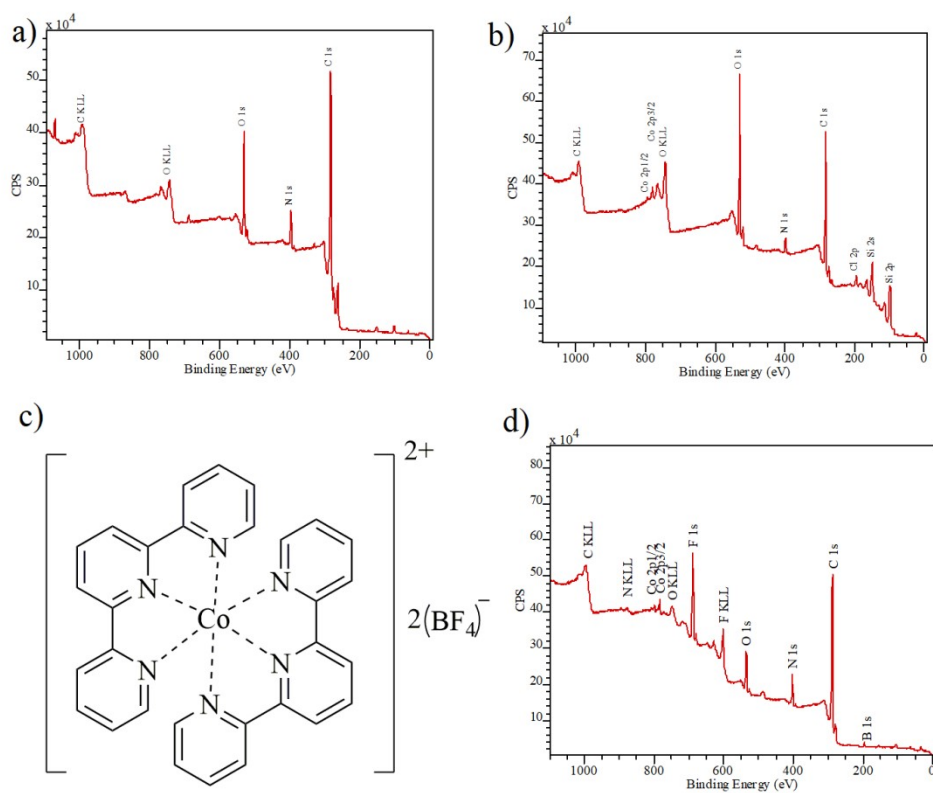
**Figure S5.** The photographs of the broken Co-nanosheet at the interface across three weeks.

### 3. TGA result of Co-nanosheet



**Figure S6.** TGA result of Co-nanosheet.

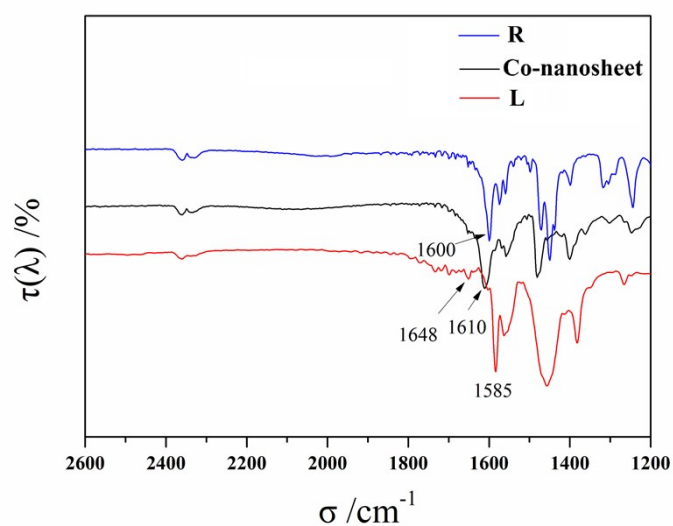
### 4. Wide scan XP spectra of L, Co-nanosheet, and R



**Figure S7.** Wide scan XP spectra of a) L, b) Co-nanosheet. c) The chemical structure

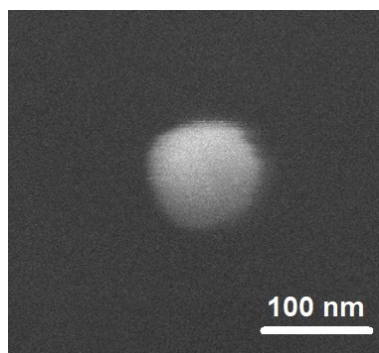
of **R**. d) The wide scan spectrum of **R**.

#### 5. FT-IR spectra of **L**, **Co-nanosheet** and **R**



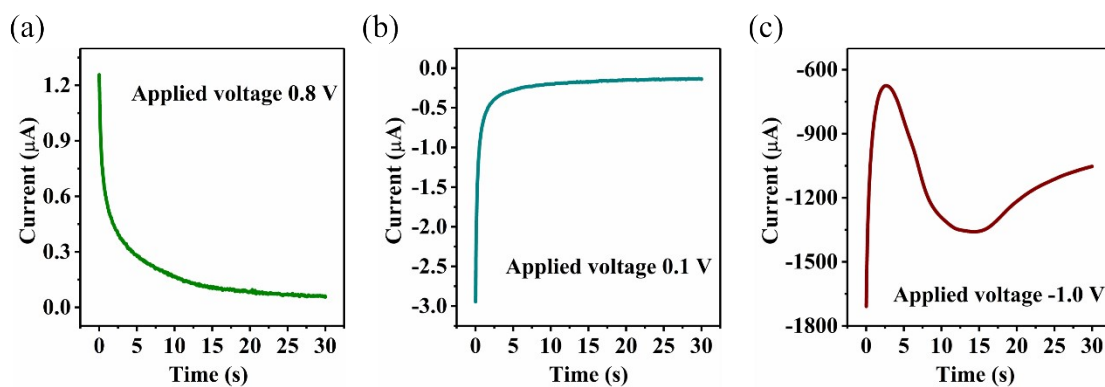
**Figure S8.** The FT-IR spectra of **L**, **Co-nanosheet** and **R**.

#### 6. SEM image of Au NPs deposited onto **Co-nanosheet**



**Figure S9.** SEM image of the individual Au NPs deposited onto **Co-nanosheet**.

#### 7. Time-current curves of Au@**Co-nanosheet** under different applied voltages



**Figure S10** Switching current curves ( $i-t$  curve) of Au@Co-nanosheet under different applied potentials.

## References

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- [3] W. Lu, N. Jiang, J. Wang, *Adv. Mater.* **2016**, 1604862.