Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Material Synthesis:

1. Synthesis of $AuPPh_3Cl$. $AuPPh_3Cl$ is synthesized from $HAuCl_4{\cdot}4H_2O$ and PPh_3 precursors. In a typical synthesis, 1 g of $HAuCl_4{\cdot}4H_2O$ is added into 35 mL of ethanol aqueous solvent ($V_{ethanol}$: V_{H2O}= 33:2). Meanwhile, 1.364 g of PPh_3 solid is added into 50 mL of ethanol aqueous solvent ($V_{ethanol}$: V_{H2O}= 48:2). The two solvents are then mixed together to afford a yellow suspension. After stirring for 2 min, the visual color of the suspension is changed from yellow to white, meaning $AuPPh_3Cl$ is formed. $AuPPh_3Cl$ solid is collected and preserved after washing with ethyl ether several times.

2. Synthesis of Supported AuNPs. A 100 mg portion of as-synthesized $AuPPh_3Cl$ was mixed with 400μL of dodecanethiol in 20 mL of benzene to form a clear solution, to which 84 mg of $NaBH_4$ was then added in one portion. The mixture was heated with stirring at 328 K for 6 h before the reaction system was cooled to room temperature. AuNPs were precipitated out from the reaction mixture as black solid powders by addition of 20 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol, and dried naturally. AuNPs was loaded into silica by a colloid deposition method. A desired amount of AuNPs was dissolved in 25 mL of chloroform. To this solution, a desired amount of supports was added. After 30 min of stirring, the solid product was centrifuged and dried in air. The supported AuNPs were calcined at 723 K for 5 h.

3. Synthesis of Supported AuCN. 60 mg 5.0 wt % AuNPs/SiO_2 and desired amount of $FeSO_4{\bullet}7H_2O$ were suspended in 4 mL acetonitrile solution containing 200 ul 30% H_2O_2 aqueous solution in air under stirring at 30°C. After 4 h of reaction, the solid product was obtained by centrifuging and washing twice with deionized water before drying in vacuum oven at 60°C overnight.

4. Synthesis of Supported $Cu_xAu_{1-x}CN$. 60 mg 5.0 wt % AuNPs/SiO_2 and desired ammount of $Cu(NO_3)_2{\bullet}3H_2O$ were suspended in 4 mL acetonitrile solution containing 200 ul 30% H_2O_2 aqueous solution in air under stirring at 30°C. After several hours of reaction, the solid product was collected by centrifuging, washing twice with deionized water and drying for characterization.

5. Synthesis $Au_xAg_{1-x}CN$ sample. desired ammount of $AgNO_3$ and AuNPs/SiO_2 were suspended in 4 mL acetonitrile solution containing 200 ul 30% H_2O_2 aqueous solution in air under stirring at 30°C. After 10 h of reaction, the solid product was collected by centrifuging, washing twice with deionized water and drying for characterization.

Measurement and Characterization:

X-ray diffraction patterns were recorded on a Ragaku Ultima IV diffractometer using Cu Kαradiation. UV/Vis adsorption spectra were measured with a Shimadzu UV-2450 spectrophotometer in the diffuse/reflectance mode. X-ray photoelectron spectrum were measured on an ESCA Lab250-Xispectrometer using using a monochromatic Al Kα X-ray source (1486.6 eV) with a 500 μm spot and an anode power of 150 W. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1230 operated at 100 kV. EXAFS data were measured at room temperature in transmission mode at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. X-band EPR signals were recorded at ambient temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10msec. FT-IR spectrum was recorded on a NICOLET NEXUS 470 FT/IR spectrometer using KBr pellets technique.

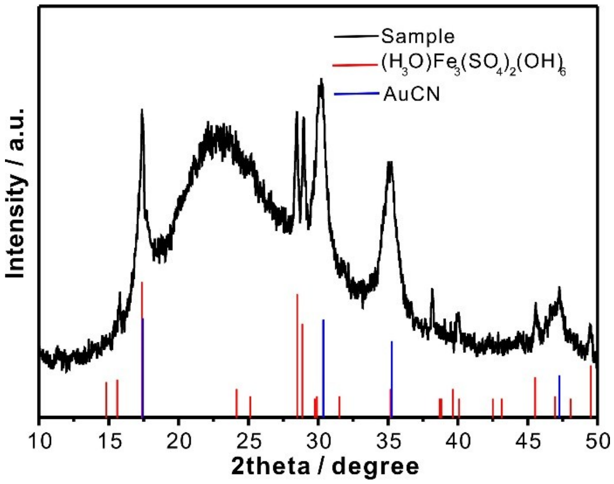

Fig. S1 XRD pattern of the sample obtained by FIC method without washing.

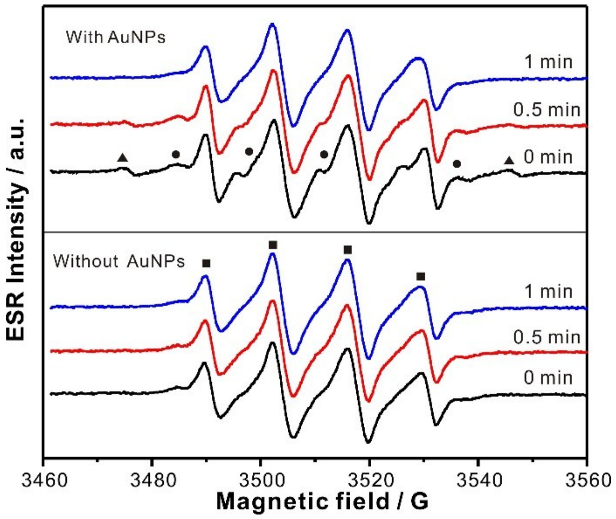

Fig.S2 In situ EPR spectra of DMPO adducts recorded FIC process. Signals are assigned to DMPO–▪OH (black squares), DMPO–▪CN (black dots), DMPO–▪H (black triangles).

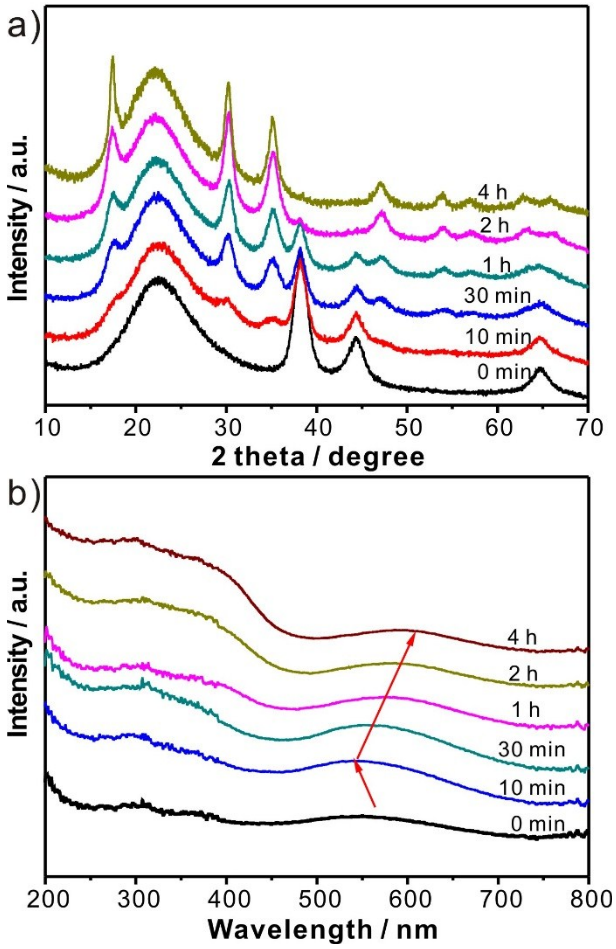

Fig. S3 a) XRD patterns and b) UV-vis spectra of solid products obtained by FIC method as time on stream.

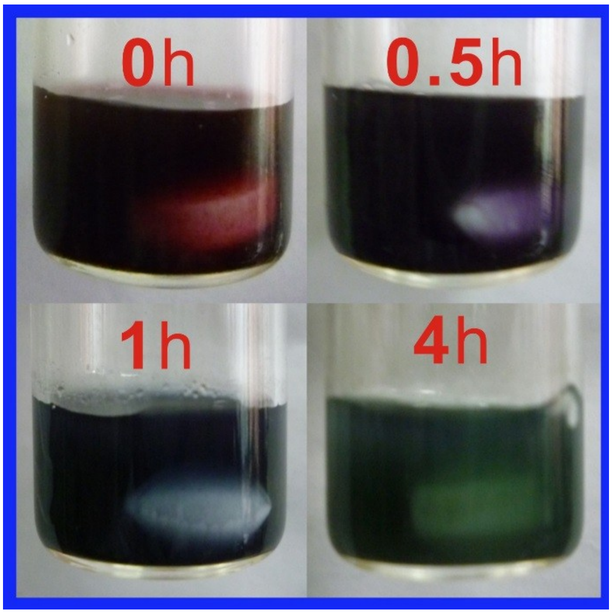

Fig. S4 photographs of the FIC system as time on stream.

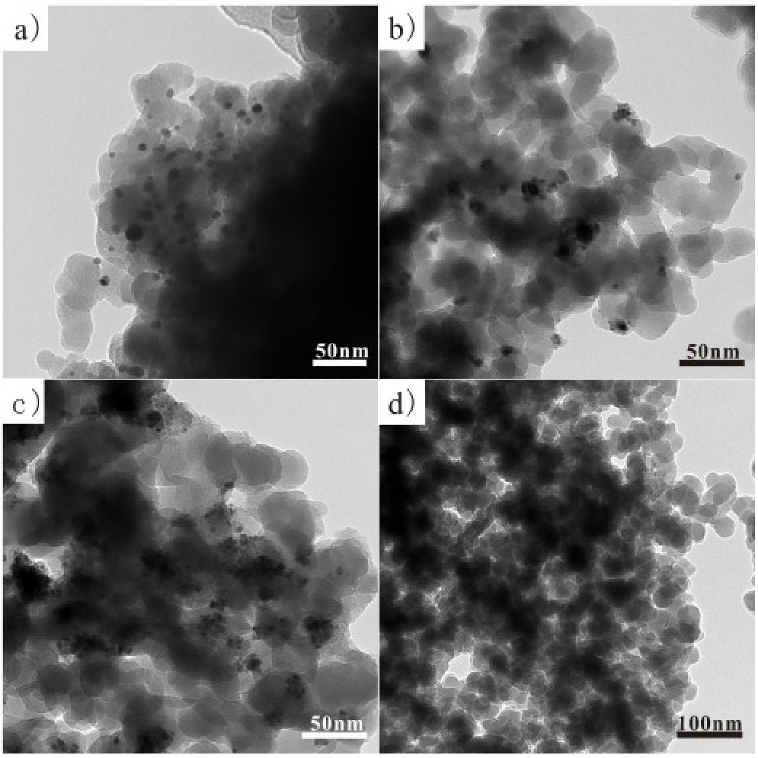

Fig.S5 TEM micrographs of solid products of different FIC time a) 0 h, b) 0.5 h, c) 1 h, d) 4 h.

Table S1. Extended X-ray absorption fine structure regression parameters for gold standard and AuCN (Au: S_0^2=0.9)

Sample	**shell**	***N***	***R*(Å)**	**σ^2(×10^{-3} Å^2)**	**ΔE_0(eV)**
Au foil	Au-Au	10.0 ± 0.4	2.851 ± 0.001	9.5 ± 0.3	2.8
AuCN	Au-C/N	2.4 ± 0.5	1.96 ± 0.01	3.1 ± 2.3	1.0
	Au-C-N OR Au-N-C	3.9 ± 1.0	3.14 ± 0.01	3.5 ± 3.0	5.1

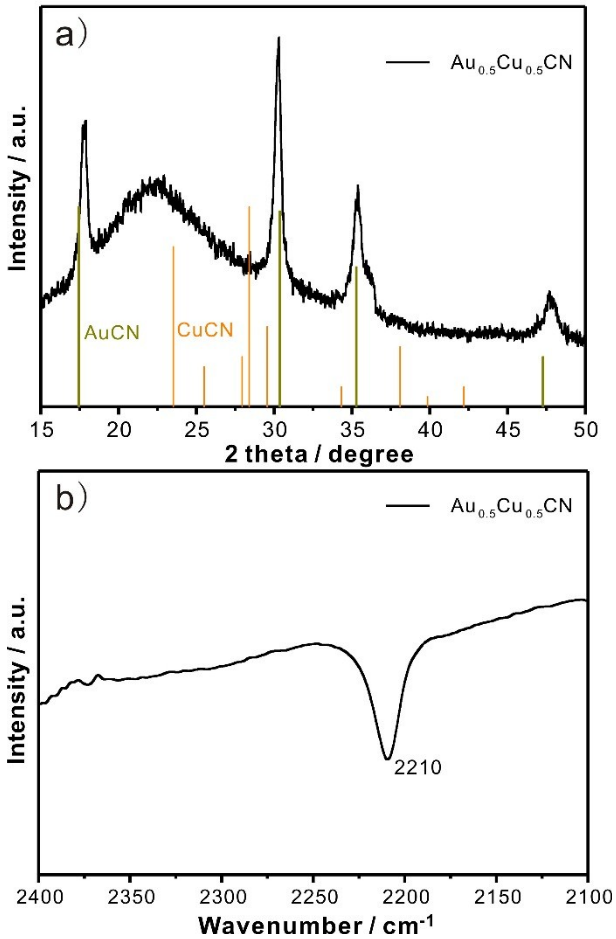

Fig.S6 a) XRD pattern and b) FT-IR spectra of as prapared Au$_{0.5}$Cu$_{0.5}$CN.

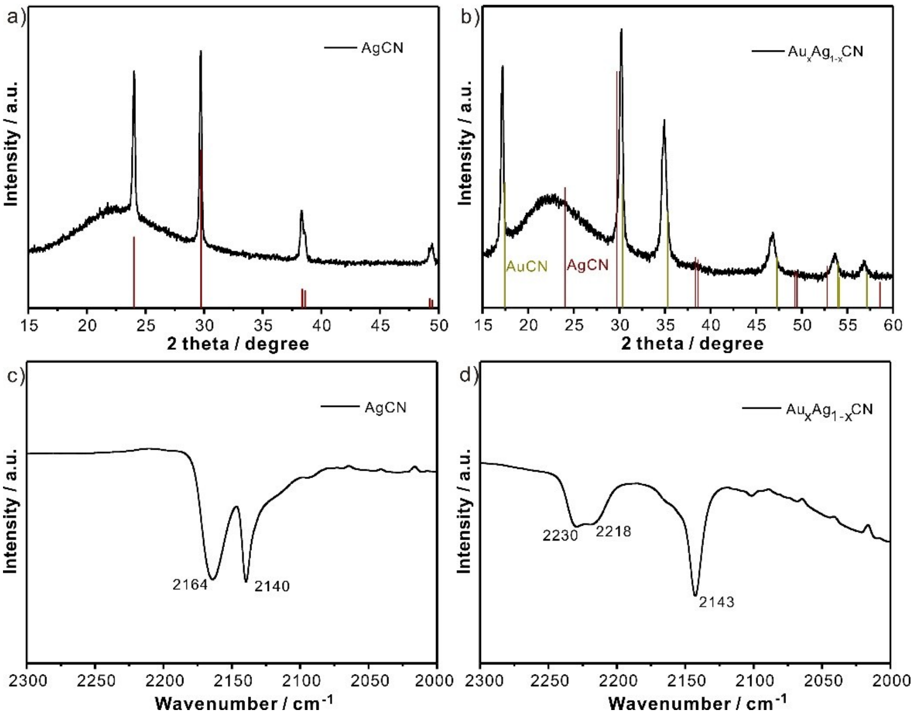

Fig.S7 XRD patterns and FT-IR spectras of as prapared AgCN and Au$_x$Ag$_{1-x}$CN.