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The Role of Adsorbed Oleylamine on Gold Catalysts During Synthesis for High Selective Electrocatalytic Reduction of CO₂ to CO

Experimental section

Chemicals: Oleylamine (90%), multi-walled carbon nanotube, tert-butylamine borane, HAuCl₄ and potassium bicarbonate were purchased from Aladdin. Carbon Paper (HCP120) were from Shanghai Hesun Electric Co., Ltd. All reagents were of analytical grade and used without further purification. Carbon dioxide (99.999%) and Argon (99.999%) gas was purchased from Hengyuan Gas Co., Ltd.

Synthesis of catalysts: Preparation of multi-walled carbon nanotubes: 6 mg of commercially available multi-walled carbon nanotubes were refluxed at 60 °C for 4 h in an acetone solution to remove organic impurities on the surface of the carbon nanotubes. It was washed by ethanol and water then dried at 80 °C. Then, it was immersed in a mixture of concentrated nitric acid and concentrated sulfuric acid at a volume ratio of 3:1 for 24 hours. Lastly, multi-walled carbon nanotubes were washed with ethanol and water until the filtrate was neutral, followed by drying overnight under vacuum.

Synthesis of Au/CNT NP: 0.0243 mmol HAuCl₄ was add to 10 ml oleylamine solution, the it was stirred vigorously at 60 °C for 15 min. Heating up to 90 °C, quickly borane tert-butylamine complex was add, and the solution kept reacting for half an hour. Then, ultrasonic uniform carbon nanotubes were added to the above solution. Stir at constant temperature for 3 h. The reaction was stopped when it cooled down to room temperature. The free oleylamine on the surface of the catalyst was washed with an appropriate amount of glacial acetic acid. The particles were then centrifuged (9000 rpm, 10 min) and washed with a mixed solution of n-hexane and ethanol (3:1). Au-OAM/CNT NP was then obtained by vacuum drying at 60 °C for 12 h. The Au-OAM/CNT NP was annealed at 185 °C for 500 minutes to obtain Au-Air/CNT NP without oleylamine ligands on the surface. The Au-N₂/CNT NP is obtained by

annealing Au-OAM/CNT NP at 185 °C for 500 minutes in nitrogen atmosphere. Immerse the Au-Air/CNT NP in 6 ml of oleylamine solution, ultrasonic for 4 h, wash and dry to obtain the Au-Air/CNT-OAM.

Characterizations: The morphology of the samples was observed by high resolution transmission electron microscopy (HRTEM) (JEM-2100F). HRTEM images were recorded with an accelerating voltage of 200 kV. The surface element type and valence bond structure of the sample were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250XI). XRD patterns of the catalysts were collected on a DX2700 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Analysis of organic compounds on Catalyst Surface by in-situ diffuse reflectance FTIR (NICOLET IS50) and by STA449F5 thermogravimetric mass spectrometry (TG-MS). In the atmosphere of N₂ or O₂, the catalyst was heated from 30 °C to 350 °C, and the heating rate was 5 °C/min, then TG curve was obtained. Then, the decomposition products were analyzed by mass spectrometry. The molar content of nano-gold in the catalyst is determined by inductively coupled plasma mass spectrometry (ICP-MS)(Optima 7000DV).

Electrochemical and catalysts characterization:

Firstly, 5 mg of the catalyst and 10 μL of Nafion (5 wt%) were dispersed in a mixed solution of 0.5 mL deionized water and 1.5 mL ethanol. The catalyst inks ultrasonicated for 30 minutes to make it uniformly disperse. Then, 40 μL of the above mixed solution was coated to $1 \times 1 \text{ cm}^2$ carbon paper electrode. The electrode is dried at room temperature for later use. The reaction is carried out in an H-type electrolytic cell at room temperature. A three-electrode system is used, the counter electrode is a platinum plate electrode, and the reference electrode is an Ag/AgCl electrode. The working electrode was a carbon paper electrode. The electrode chamber was separated by a Nafion 117 cation exchange membrane, and 40 mL of a 0.5 mol/L KHCO₃ solution was added to each half of the electrolytic cell. Before the test, N₂ is purged into the electrolyte for 30 min to ensure that there is no oxygen in the electrolyte. Then, CO₂ is purged into the electrolyte for 30 min to ensure that the electrolyte reach a constant pH value. The CO₂ reduction reaction measured by using linear sweep voltammetry and chronoamperometry at each fixed potential.

Electrochemical active surface area (ECSA): The ECSA of the nano-Au electrode was determined by measuring the reduction peak area obtained from a cyclic voltammogram (CV) in 50 mM H₂SO₄ continuously purged with N₂ in electrochemical cell. The CV curve scanning was conducted in the range of 0 - 1.5 V (versus Ag/AgCl)

with a scan rate of 50 mV s⁻¹. A monolayer of chemisorption oxygen is formed in the forward scanning and reduced in the reverse scanning. The ECSA was obtained by calculating integration of the monolayer chemisorbed oxygen reduction peak (0.9 V versus Ag/AgCl) area and the experimentally determined reduction charge per geometric unit area (448 μC cm⁻²).

Reversible hydrogen electrode (RHE) is a common standard to convert the Ag/AgCl electrode potential into a reversible hydrogen potential. The conversion formula is:

$$E(\text{vs RHE}) = E(\text{vs Ag/AgCl}) + 0.201 + 0.0591 \times \text{pH}$$

0.5 M KHCO₃ solution pH 7.2.

Gas phase and liquid phase products were detected using gas chromatography (SHIMADZU GC-2014). The H₂ was detected by a thermal conductivity detector (TCD) and the CO was analyzed by a methane reformer and a flame ionization detector (FID). The liquid phase product formic acid was pretreated and converted to ethyl formate by gasification through a headspace sampler and analyzed by a flame ionization detector (FID).

Calculation of Turnover Frequency (TOF, S⁻¹). The TOF for CO was calculated as:

$$TOF = \frac{i_{CO}/zF}{n_{tot} * f}$$

i_{CO} : partial current for CO;

z : the number of electron transferred for product formation, which is 2 for CO;

F : Faradaic constant, 96485 C mol⁻¹;

n_{tot} : the molar amount of Au on the working electrode, calculated according to ICP-MS results;

f : the surface fraction of electrochemically active Au sites.

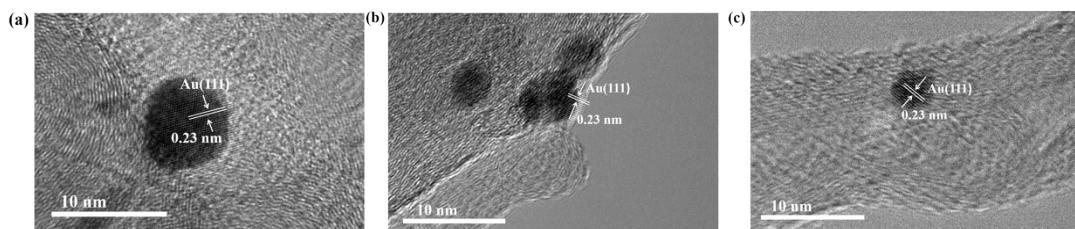


Fig. S1 HRTEM images of the Au-OAM/CNT, Au-N₂/CNT and Au-Air/CNT.

To clarify the effect of heat treatment on the adsorbed oleylamine molecules of Au surfaces, the diffuse reflectance FTIR spectroscopy (DRIFTS) was performed. The DRIFT spectrum of the Au-OAM/CNT (Fig. S2) showed peaks at 2922 and 2853 cm⁻¹, which correspond to the alkyl C-H stretching vibrations originating from the surface oleylamine ligands. The significantly reduced signal of C-H stretching vibration for the Au-N₂/CNT indicated the loss of oleylamine after annealing. The alkyl C-H stretching peak disappeared on Au-Air/CNT, indicating that the oleylamine molecules on the surface of the catalyst completely decomposed. The oleylamine on the surface of Au-OAM/CNT was tested by thermogravimetric mass spectrometry (TG-MS) under the air atmosphere (Fig. S3). The TG curve begins to drop at 175 °C and the MS spectrum shows a characteristic ion peak of CO₂ with a m/z of 44. CO₂ is one of the main products of the combustion and decomposition of oleylamine in the air, which proves that oleylamine decomposed under air conditions at 175 °C. Gold valence state was determined by X-ray photoelectron spectroscopy (XPS), which showed only the characteristic Au 4f contributions of the Au⁰ species (Fig. S4). The valence state of Au NPs did not change before and after annealing treatment, which proves that there is no oxidation state on the surface. The appearance of N 1s peaks at 399.5 eV in the XPS profiles of Au-OAM/CNT and Au-N₂/CNT proves the existence of oleylamine as surface ligand. And the disappearance of N 1s peaks from Au-Air/CNT proves that annealing treatment can remove oleylamine from the catalyst surface.

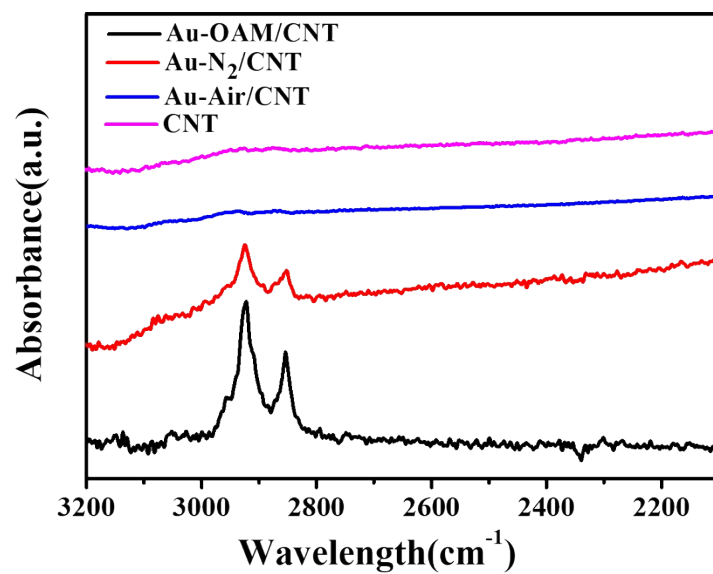


Fig. S2 DRIFTS of CNT, Au-OAM/CNT, Au-N₂/CNT and Au-Air/CNT NP.

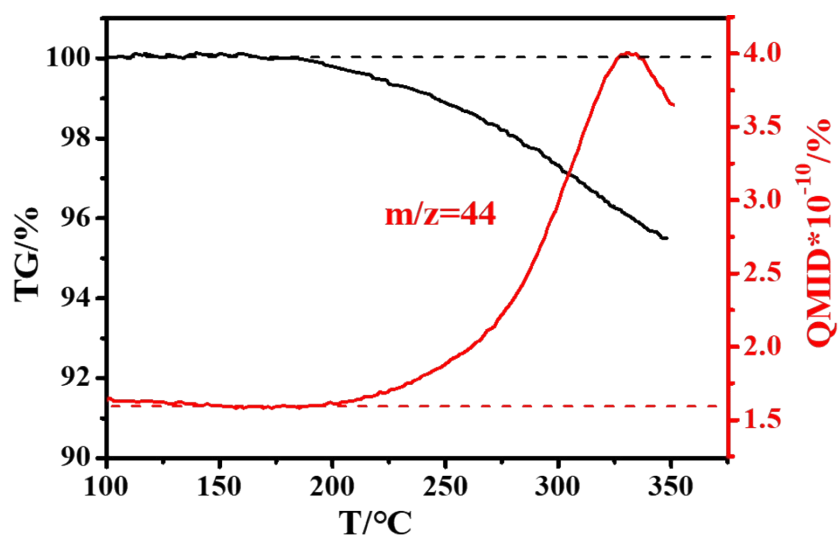


Fig. S3 TG-MS spectrum of Au-OAM/CNT NP under air.

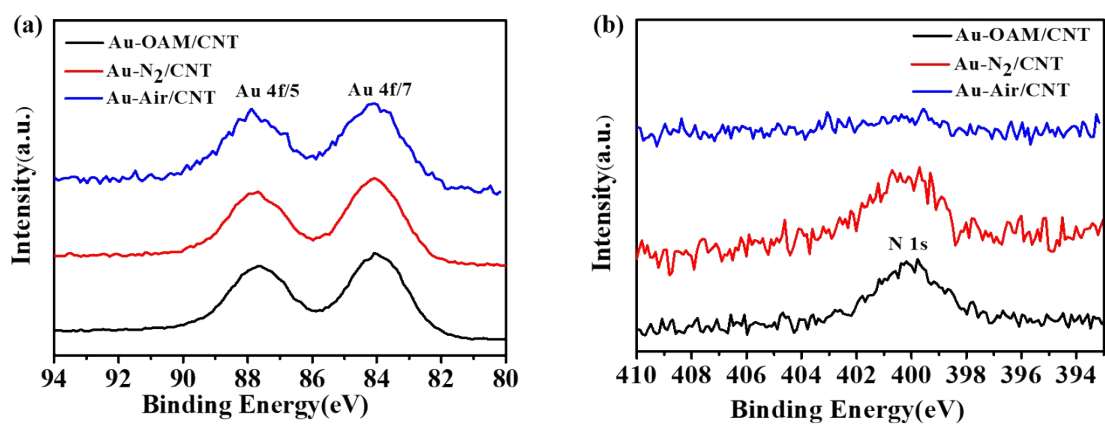


Fig. S4 High-resolution XPS spectrum of (a) the Au 4f region and (b) the N 1s region of Au-OAM/CNT, Au-N₂/CNT and Au-Air/CNT NP

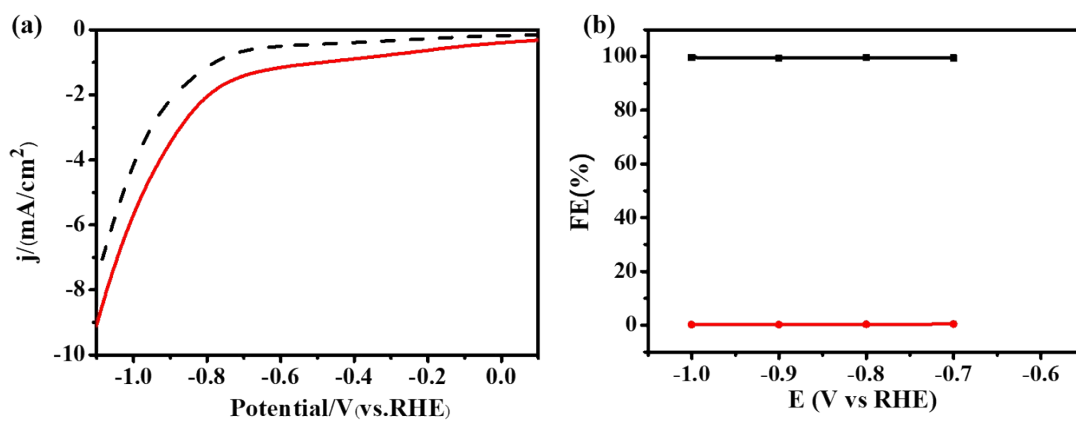


Fig. S5 (a) LSV scans of CNTs electrodes under CO₂-saturated (red line) and N₂-saturated (black line) 0.5 M KHCO₃ at pH 7.2; (b) FEs of CO (red line) and H₂ (black line) produced by CNTs NPs electrodes.

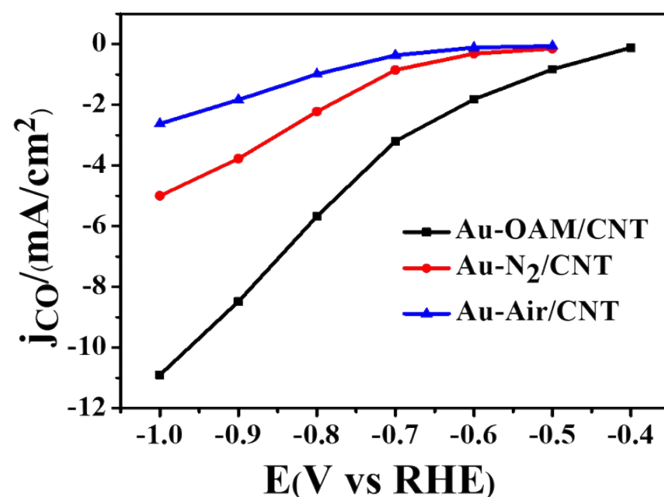


Fig. S6 Specific current densities of CO generated by Au-OAM/CNT, Au-N₂/CNT and Au-Air/CNT NP electrodes

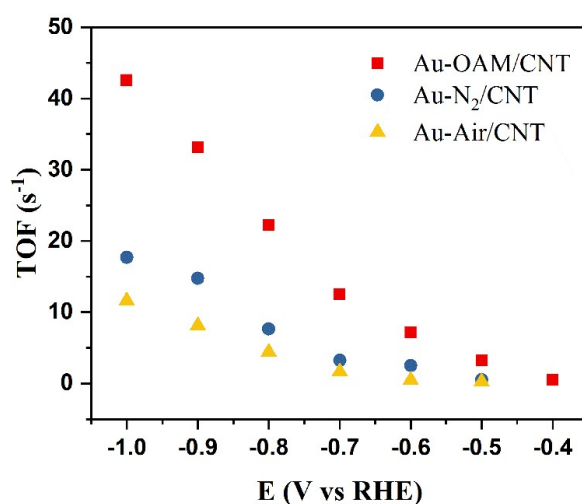


Fig. S7 TOF versus the applied potentials (TOF-E) of Au-OAM/CNT, Au-N₂/CNT and Au-Air/CNT

To exclude the influence of heat treatment of the catalysts, the Au-Air/CNT was re-wrapped with oleylamine to obtain the Au-Air/CNT-OAM, then the only difference between these two catalysts is the presence of oleylamine. From XRD patterns, TEM and HRTEM images we can see the crystal structure of the catalyst is unchanged and its average particle size is consistent with that of Au-Air/CNT.

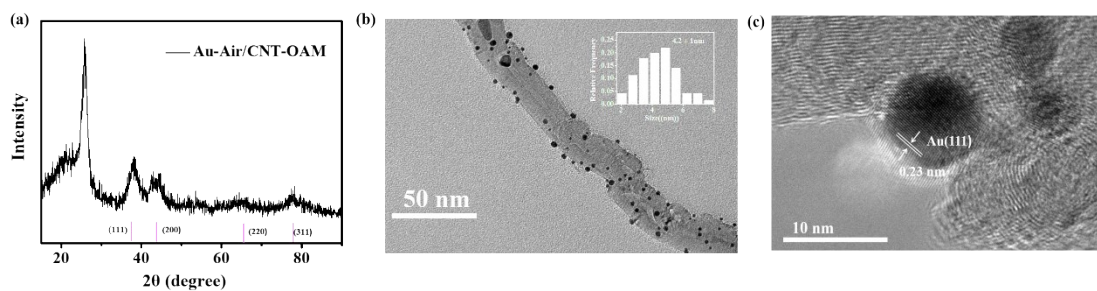


Fig. S8 (a) XRD diffraction patterns of the Au-Air/CNT-OAM; (b) and (c) TEM and HRTEM the Au-Air/CNT-OAM.

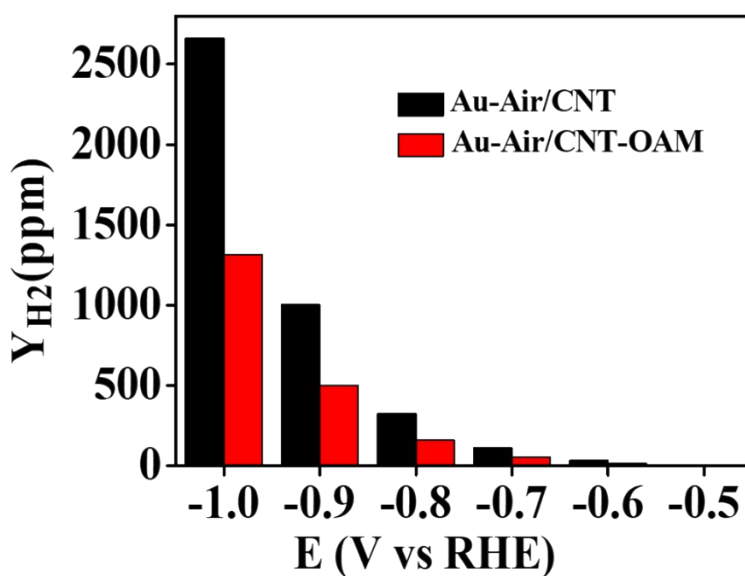


Fig. S9 H₂ production distribution of Au-Air/CNT-OAM and Au-Air/CNT electrodes.

A catalyst with 7.3 nm Au NPs was prepared for the size of Au NPs can affect the performances of catalysts. This catalyst showed a distinct decrease in FE_{CO} when the surface oleylamine were removed by heat treatment, which is the same as that of 3.1 nm Au NPs (Fig. S10). The control experiments prove that the absorbed oleylamine is the main factor leading to the change of catalytic performance of nano-gold catalyst in the present work.

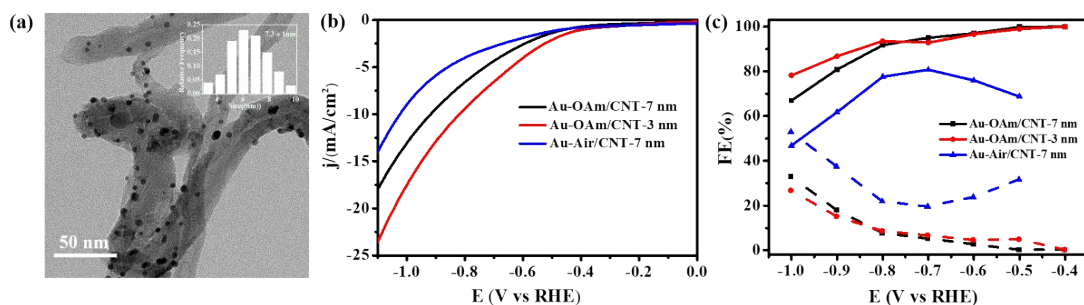


Fig. S10 (a) TEM images of the Au-OAM/CNT-7; (b) LSV scans of Au-OAM/CNT-7 nm and Au-OAM/CNT-3 nm electrodes under CO_2 -saturated 0.5 M KHCO_3 at pH 7.2; (c) FEs of CO (solid line) and H_2 (dotted line) produced by Au-OAM/CNT-7 nm and Au-OAM/CNT-3 nm NPs electrodes.

The ECSA of Au-OAM/CNT and Au-Air/CNT catalysts for long-term potentiostatic electrolysis were tested, as shown in Fig. S11. The ECSA of Au-OAM/CNT before electrolysis is 1.3 times of that after electrolysis. The ECSA of Au-OAM/CNT before and after electrolysis did not change much. According to TEM images (Fig. S12a), the Au NPs of Au-OAM/CNT was stable, which is benefit from the protection effect of oleylamine on catalyst surfaces to inhibits the agglomeration of Au NPs during the electrolysis process. While the ECSA of Au-Air/CNT before electrolysis is 14.7 times of that after electrolysis. The dramatic loss of ECSA for Au-Air/CNT is mainly due to the agglomeration of Au nanoparticles during the electrolysis process (Fig. S12b).

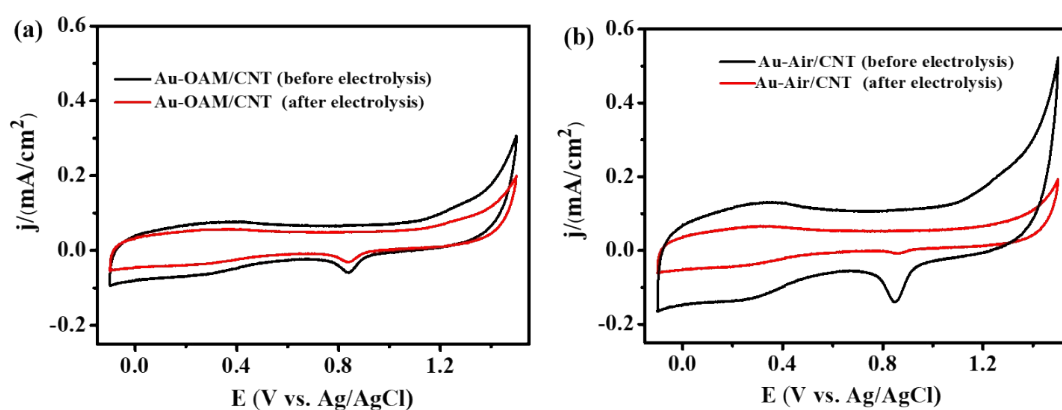


Fig. S11 Cyclic voltammograms in 50 mM H_2SO_4 of the Au-OAM/CNT and Au-Air/CNT before and after electrolysis at scan rate $50 \text{ mV} \cdot \text{s}^{-1}$.

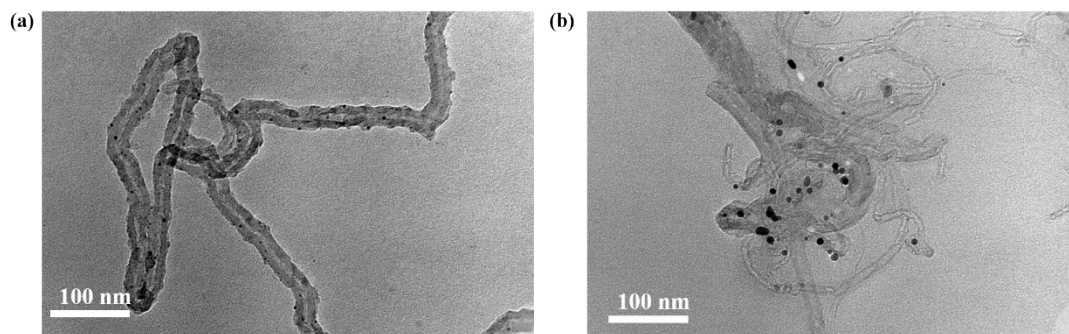


Fig. S12 TEM images of the (a) Au-OAM/CNT and (b) Au-Air/CNT after electrolysis.