Electronic Supplementary Information

Au Nanoparticles in Carbon Nanotubes with High Photocatalytic Activity for Hydrocarbon Selective Oxidation

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Preparation of short CNTs. 0.10 g CNTs were purified and shortened by refluxing the commercial CNTs in mixed solution of concentrated sulphuric (75 mL) and nitric acids (25 mL) (1 : 3 by volume) at 80 ℃ with constant refluxing for 12 h.[1] A centrifuge separates the CNTs at a speed of 20000 rpm. Precipitations are washed with 0.1 M NaOH aqueous solution till pH 7. Then washed with ultrapure water for five times. After that, the CNTs solution is dried at 50 ℃ to get purified short-CNTs powder.

Preparation of Au-in-CNTs. The purified short-CNTs 200 mg were homogeneously dispersed in 500 ml 0.002 mM $HAuCl_4$ aqueous solution stirring for 6 h. Aqueous $HAuCl_4$ solution was introduced into the CNT channels utilizing the capillary forces of CNTs aided by ultrasonication for 10 min and then followed by filtering and rinsing. Then the CNTs containing $HAuCl_4$ solution were dispersed in water (40 mL) with ultraviolet lamp radiation for 90 min. Au(Ⅲ) is in-situ reduced to Au (0) under ultraviolet irradiation. After drying in air at 50 ℃ for 12 h, Au-in-CNTs were prepared.

Preparation of Au-out-CNTs. Au-out-CNTs were synthesized by adding 200 mg untreated CNTs directly into 500 ml 0.002 mM $HAuCl_4$ solution stirring for 6 h. After 30 min standing, the precipitations were dispersed in water (40 mL) with ultraviolet lamp radiation for 90 min. After drying in air at 50 ℃ for 12 h, Au-out-CNTs were prepared.

Preparation of Au nanoparticles. 10-nm Au nanoparticles by adding 0.6 mL of icecooled $NaBH_4$ solution (10 mM) into a 10 mL aqueous solution containing $HAuCl_4$ (0.25 mM) and CTAB (100 mM), generating a brownish solution. The seed solution was kept undisturbed for 3 h at 27 °C to ensure complete decomposition of $NaBH_4$ remaining in the solution.[2] The TEM image of the Au nanoparticles is shown in Figure S5.

Photocatalytic reaction. The photocatalytic reactions were carried out in a quite mild condition with air used as oxidant. The reaction mixture of 50 mg catalyst, 10 ml cyclohexane and 0.5 ml tert-butyl hydroperoxide (TBHP) which using as initiating agent was magnetically stirred at 333 K in a round bottom flask with a condenser pipe in oil bath for 6-60 h. After reaction, the catalyst was centrifugation separated and products were directly analyzed by gas chromatography (GC).

Reactive species trapping experiments. Adding three kind of reactive species trapping agents directly into the photocatalysis reaction solution, the catalysis experiments were carried out under the same condition. The products were analyzed immidiately by HPLC.

Electrocatalytic ORR activity testing experiments. The steady-state hydrodynamic measurements were performed using a. The electrocatalytic activity of Au-in-CNTs and Au-out-CNTs for oxygen reduction reaction (ORR) was tested in a four-electrode electrochemical cell with a platinum wire as the auxiliary electrode and an SCE as the reference electrode. The working electrodes were prepared by

spreading catalysts dispersed in ethanol Pt disk (3.0 mm in diameter)-Pt ring rotating ring-disk electrodes (RRDE). The I-V curves of the electrodes were obtained in 0.1 M KOH solution at a scan rate of 20 mV/s. The current signal was recorded with a CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China). All electrochemical experiments were carried out at room temperature.

Scan Electrochemical Microscope (SECM) Measurements. A CHI model 900 scanning electrochemical microscope (CH Instruments, Austin, TX) was used to control the tip potentials, obtain the approach curves, and monitor the tip-to-substrate distance. The SECM tip made of a Pt disk (diameter = 25 μm) sealed in a glass capillary (Rg = 3.01), Ag/AgCl, and Pt wire were used as a working, reference, and counter electrodes, respectively. Prior to the experiments, the tip was manually polished with 0.05 μm alumina powder, and its surface quality was monitored under an optical microscope. The electrochemical performance of the tip was checked periodically with the help of steady-state voltammograms. All the electrochemical measurements were carried out in 3 mM α-methyl ferrocene methanol in phosphate buffer (pH = 7.4) solution. The tip was biased at +400 mV vs Ag/AgCl, and the probe approach curves were recorded on the SSCF along the Z direction.

Au-in-CNTs spot was deposited on a watch glass. Briefly, 0.1 (a single drop of near 1 mm diameter) of an aqueous solution of Au-in-CNTs was deposited on a watch glass using a micropipet. The drop was dried at 45 ℃ in the air for 1 h.

Hydrogen peroxide yield (%H_2O_2) calculation. The hydrogen peroxide yield in

the catalyzed ORR is calculated as equation 1 as follow:

where N is the RRDE collection efficiency, which is determined as shown in Fig. S4.

Here, N is determined to be 0.24.

1 U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé, E. L. Pires, *Appl. Catal. A* 2001, **211**, 1.

2 Yanyun Ma, Weiyang Li, Eun Chul Cho, Zhiyuan Li, Taekyung Yu, Jie Zeng, Zhaoxiong Xie, Younan Xia, *ACS Nano.*, 2010, **4**, 6725.

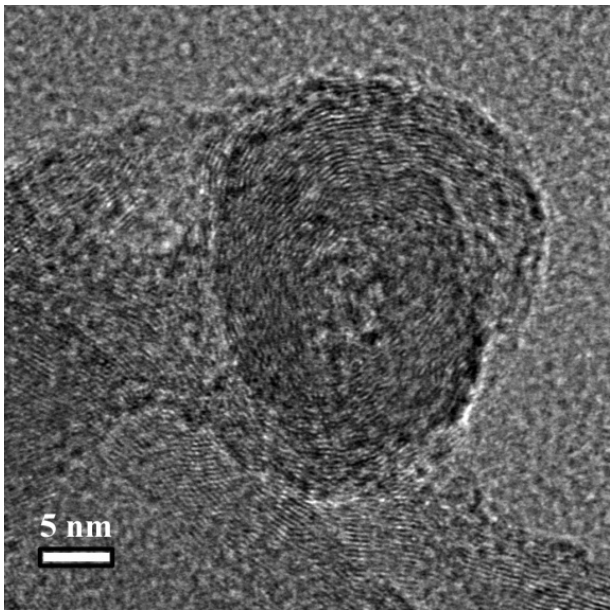

Figure S1. TEM images of a shortened CNT with an open end.

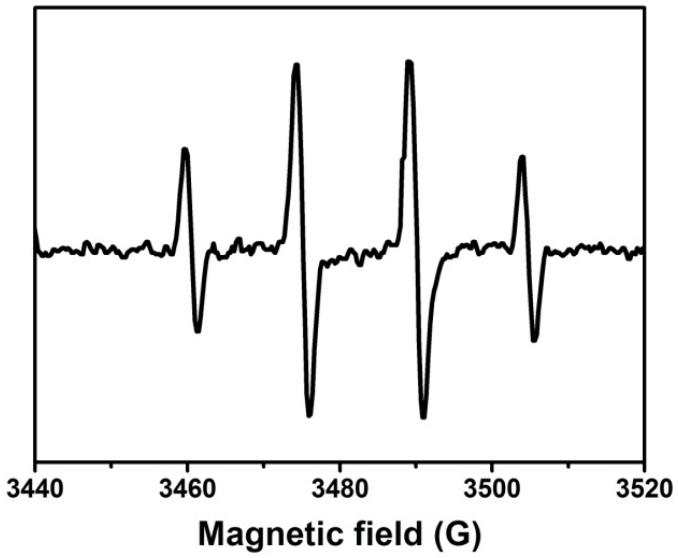

Figure S2. The ESR signals of the DMPO-•OH (aqueous solution) adducts for Au-in-CNTs-H_2O system under visible light irradiation. [Au-in-CNTs] = 5 mg/50 mL; H_2O = 10 mL; [DMPO] = 40 mM.

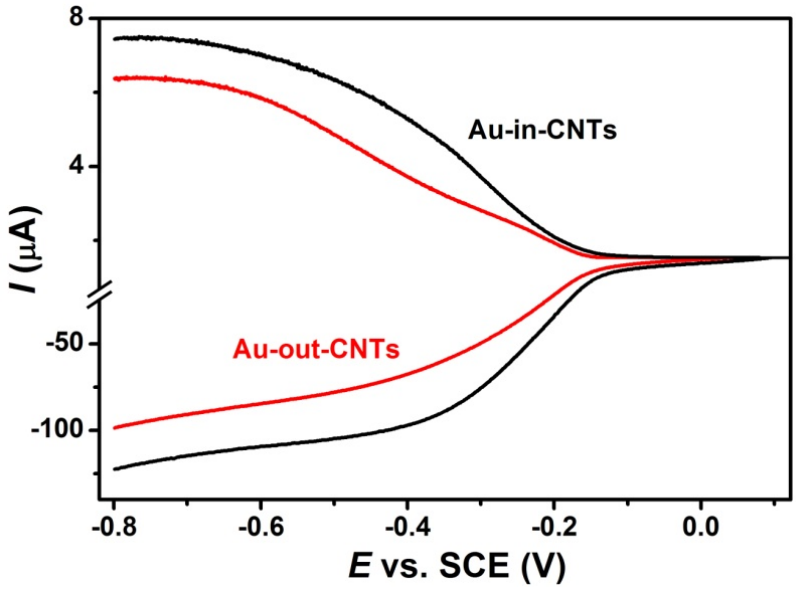

Figure S3. RRDE voltammograms for the ORR, in air-saturated 0.1 M KOH, at Au-in-CNTs (black trace) and Au-out-CNTs (red trace) modified Pt disk electrodes. The top curves are measured at Pt-disk. The bottom curves represent the corresponding Pt-ring currents (polarized at +0.5 V). Rotation rate: 1600 rpm. Potential scan rate of the disk electrode: 20 mV s^{-1}

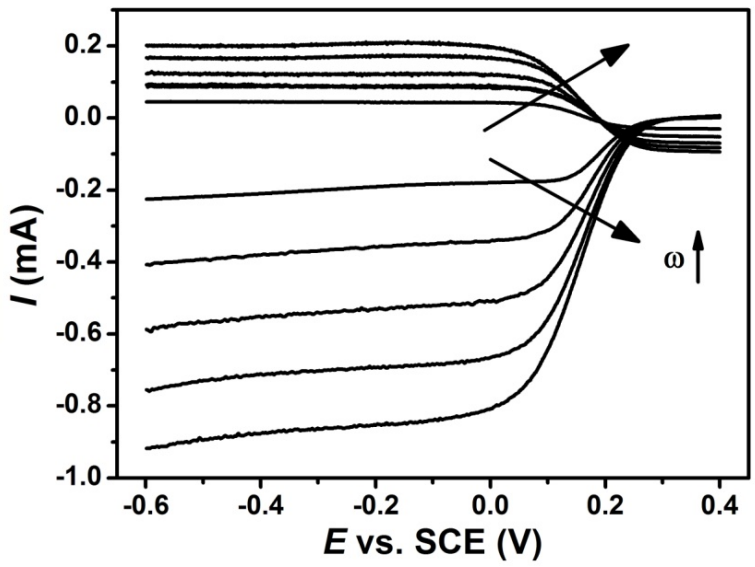

Figure S4. I-V curves of bare RRDE in 0.1 M KCl containing 0.01 M $K_3Fe(CN)_6$ under rotation rates: 100, 400, 900, 1600, 2500 rpm (from inner to outer).

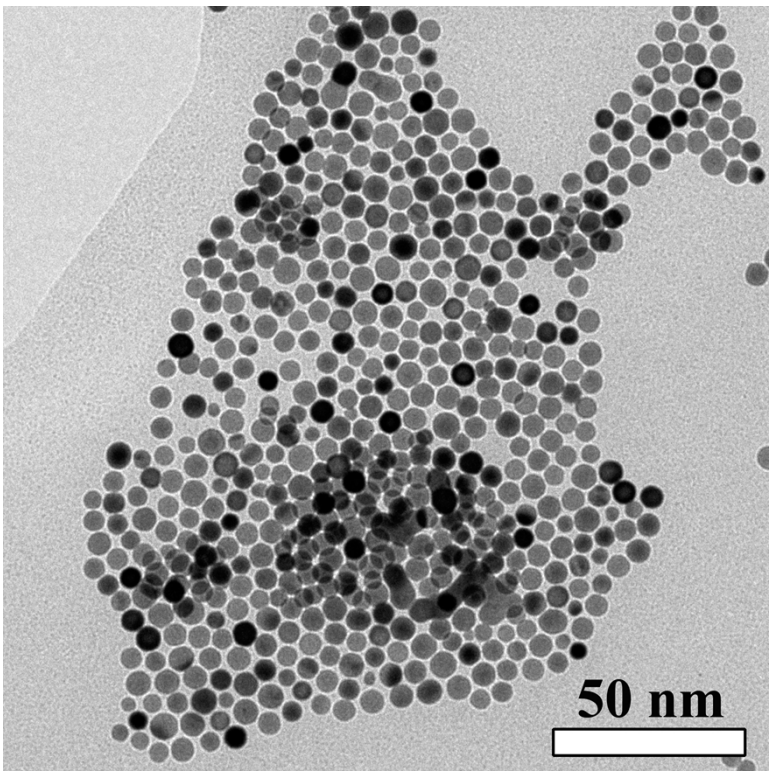

Figure S5. TEM images of the Au nanoparticles. $NaBH_4$ served as the reduction agent.

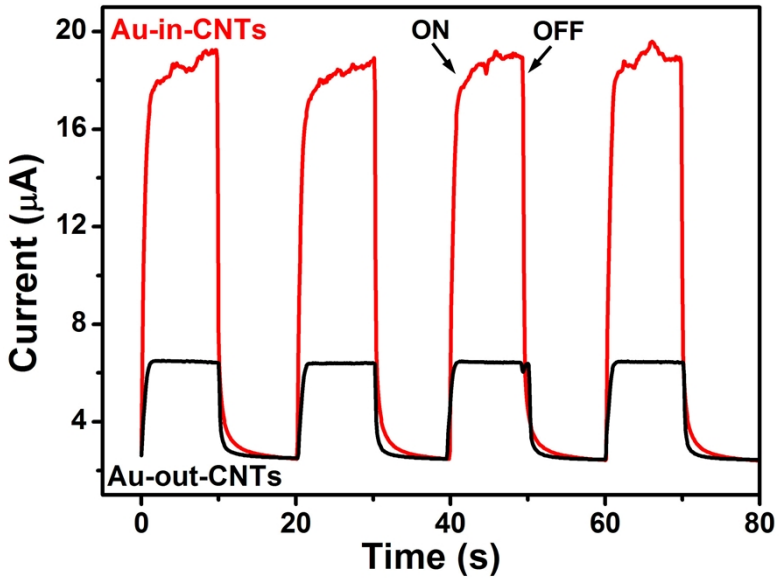

Figure S6. Transient photocurrent responses of Au-in-CNTs and Au-out-CNTs under radiation.