

## Electronic Supplementary Information

### Preparation of catalytic films of the Au nanoparticles-carbon composite tubular arrays

Wei Gong,<sup>a</sup> Lei Su,<sup>\*,a</sup> and Xueji Zhang<sup>\*,a</sup>

<sup>a</sup> Research Center for Bioengineering and Sensing Technology, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China

\* Corresponding authors.

E-mail addresses: [sulei@ustb.edu.cn](mailto:sulei@ustb.edu.cn) (L.S.); [zhangxueji@ustb.edu.cn](mailto:zhangxueji@ustb.edu.cn) (X.J.Z.).

## Experimental

*Materials:* Zinc acetate dehydrate ( $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ), sodium acetate trihydrate ( $\text{NaAc} \cdot 3\text{H}_2\text{O}$ ), 4-nitrophenol, sodium borohydride ( $\text{NaBH}_4$ ), dopamine chloride, and ammonium persulfate (AP) were purchased from Sigma. All other chemicals of at least analytical reagent were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Aqueous solutions were prepared using deionized water (Milli-Q system).

*Preparation of ZnO NRs, deposition of Au NPs and PDA coating:* ZnO NRs were prepared electrochemically, as follows. Fluorine-doped tin oxide (FTO) slides with the dimensions of  $2.5 \text{ cm} \times 0.8 \text{ cm}$  were used as the substrates. Electrochemical deposition was performed in 0.1 M NaAc solution containing 1 mM  $\text{Zn}(\text{Ac})_2$  at 85 °C under constant potential condition (-0.85 V vs Ag/AgCl) for 15 min. Then, the substrates were rinsed with deionized water and dried overnight at 60 °C.

Au NPs were deposited onto the ZnO NRs using an Au sputtering deposition system (SBC-12,  $P_{\text{Ar}} = 3 \text{ Pa}$ , 1000 V) at a constant current of 6 mA for 10 s. The ZnO NRs substrates were placed 40 mm below the Au target (99.99% purity) with 58 mm in diameter and 0.5 mm in thickness.

Due to the amphoteric property of ZnO NRs, the coating of the AuNPs-decorated ZnO NRs with PDA film at alkaline pH risks decomposing ZnO. The coating process was carried out in a freshly prepared AP-containing dopamine neutral solution, as described previously by us.<sup>[1]</sup> In brief, the as-prepared Au NPs-decorated ZnO NRs were dipped into 40 mL of freshly prepared 0.1 M phosphate buffer solution (pH 7.0) containing 1 mg mL<sup>-1</sup> dopamine and 1.71 mg mL<sup>-1</sup> AP for 1 h under moderate magnetic stirring for PDA coating. Afterwards, they were rinsed with deionized water and then dried at 60 °C overnight.

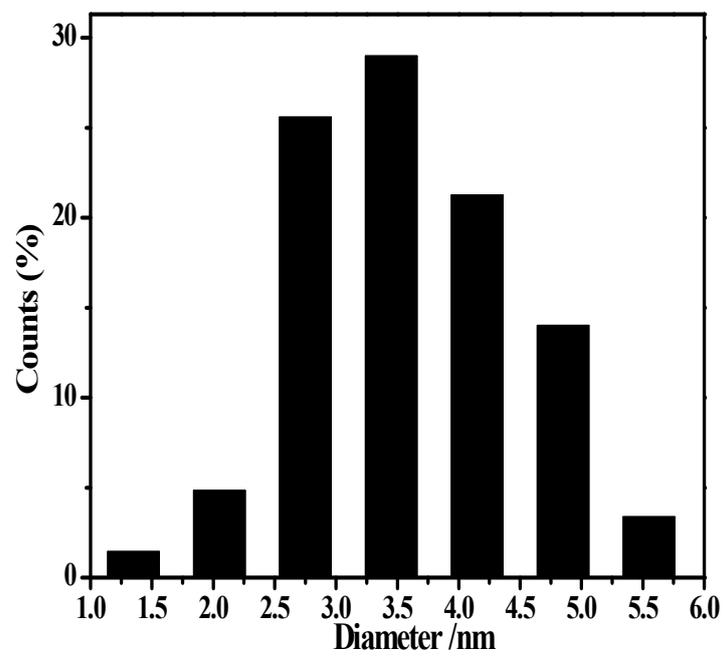
*Carbonization and removal of ZnO NRs:* The Au NPs-decorated ZnO NRs coated with PDA films were carbonized under N<sub>2</sub> atmosphere at 500 °C for 3 h with a heating rate of 5 °C min<sup>-1</sup>, then cooled to room temperature. After immersing in 0.24 M hydrochloric acid solution for 10 min to remove ZnO, the Au NPs-embedded pBIDI-CNTs were obtained.

*Catalytic reduction of 4-NP:* 4-NP aqueous solution (0.5 mL, 0.1 mM) was mixed with freshly prepared NaBH<sub>4</sub> solution (17 μL, 0.3 M) to reach final concentrations of 0.097 mM 4-nitrophenol and 9.9 mM NaBH<sub>4</sub>. The Au NPs-embedded pBIDI-CNTs films (total surface area = 1.6 cm<sup>2</sup>) were then immersed in the mixture solution. The

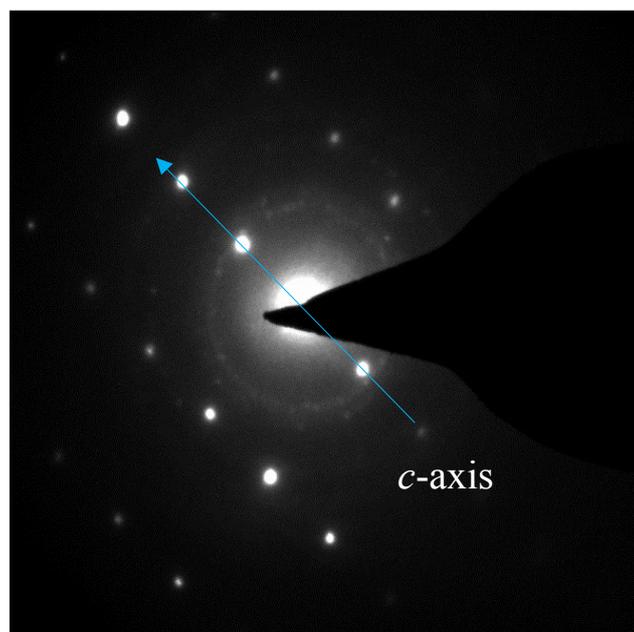
solution was shaken at 200 rpm at room temperature for a certain time. UV-vis absorption spectra were recorded to monitor the change in the reaction mixture.

*Characterizations:* The morphologies and chemical compositions of the samples were observed using a field emission scanning electron microscopy (SEM, Zeiss Supra 55) and a field emission transmission electron microscopy (TEM, JEM-2100F) equipped with energy-dispersive X-ray spectroscopy (EDS), respectively. For TEM characterization, the samples were firstly scraped carefully from the substrates with a blade, and then dispersed in ethanol; 5  $\mu$ L of the dispersion was drop-casted on a lacey carbon TEM grid. For UV-vis measurements, quartz micro cuvettes with 10 mm path lengths and 1 mm window widths were used on a UV-vis spectrophotometer (UV-1800, SHIMADZU, Tokyo, Japan).

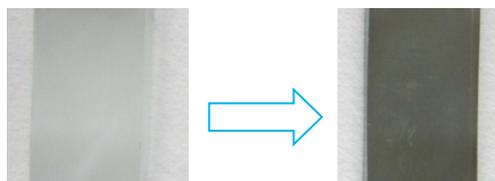
- 1 a) W. Gong, W.S. Chen, J.P. He, Y. Tong, C. Liu, L. Su, B.W. Gao, H.K. Yang, Y. Zhang, X.J. Zhang, *Carbon* 2015, 83, 275-281; b) B. W. Gao, L. Su, Y. Tong, M. Guan, X. J. Zhang, *J Phys Chem B* 2014, 118, 12781-12787.



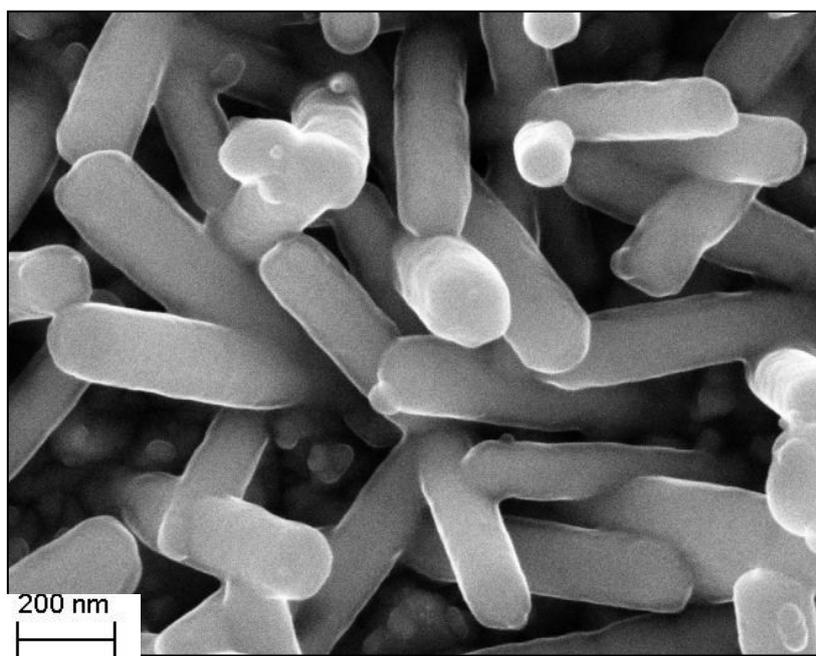
**Fig. S1** Histogram of size distribution of the AuNPs deposited on the ZnO NRs.



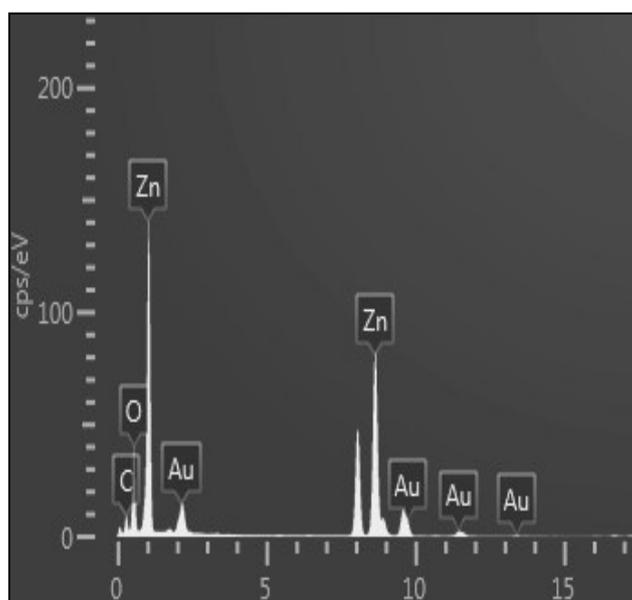
**Fig. S2** SAED pattern of the AuNPs deposited on the ZnO NRs.



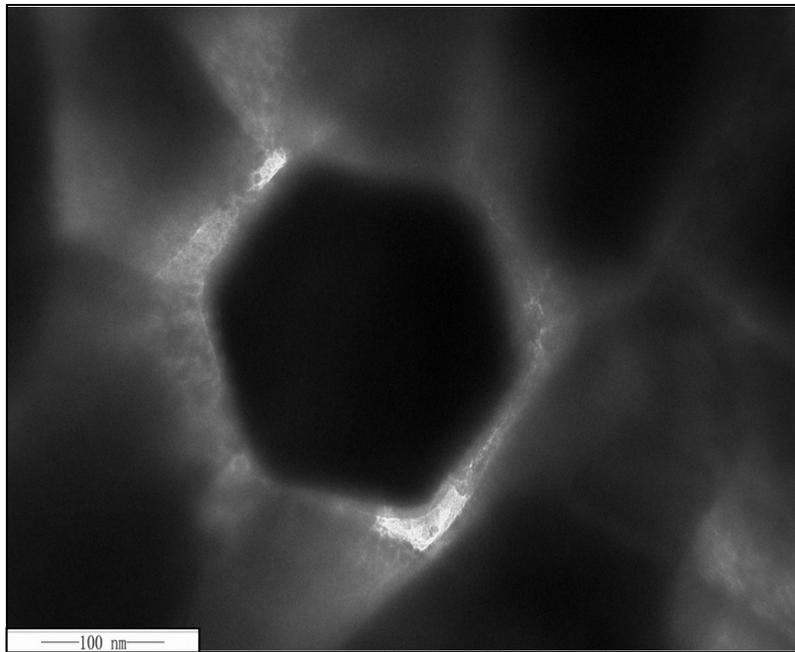
**Fig. S3** Photographs of the color change in the AuNPs-decorated ZnO NRs array film after PDA coating.



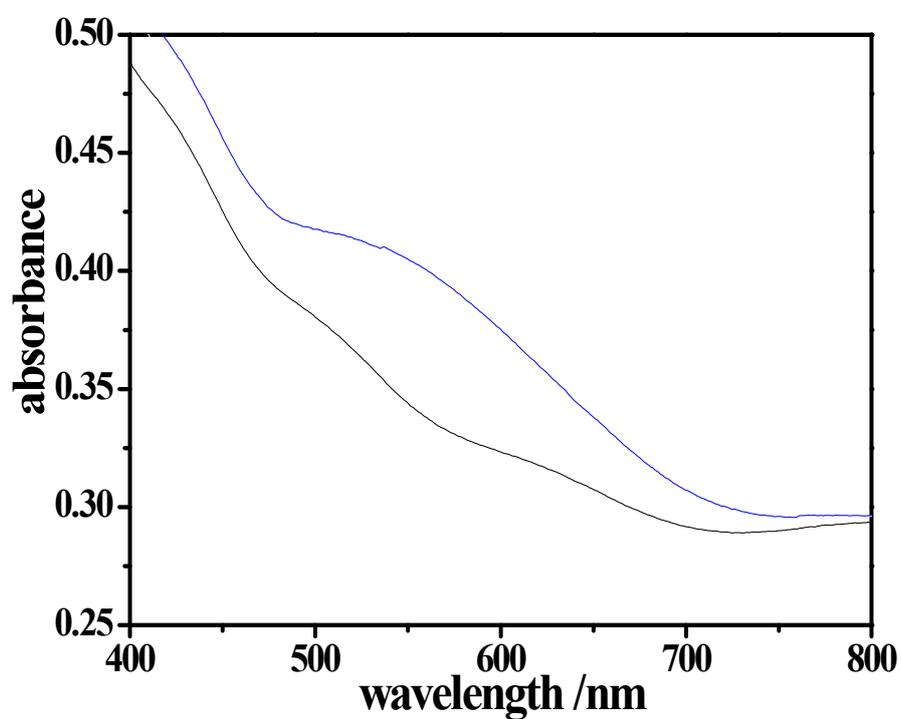
**Fig. S4** SEM image of the ZnO/AuNPs/PDA composite films.



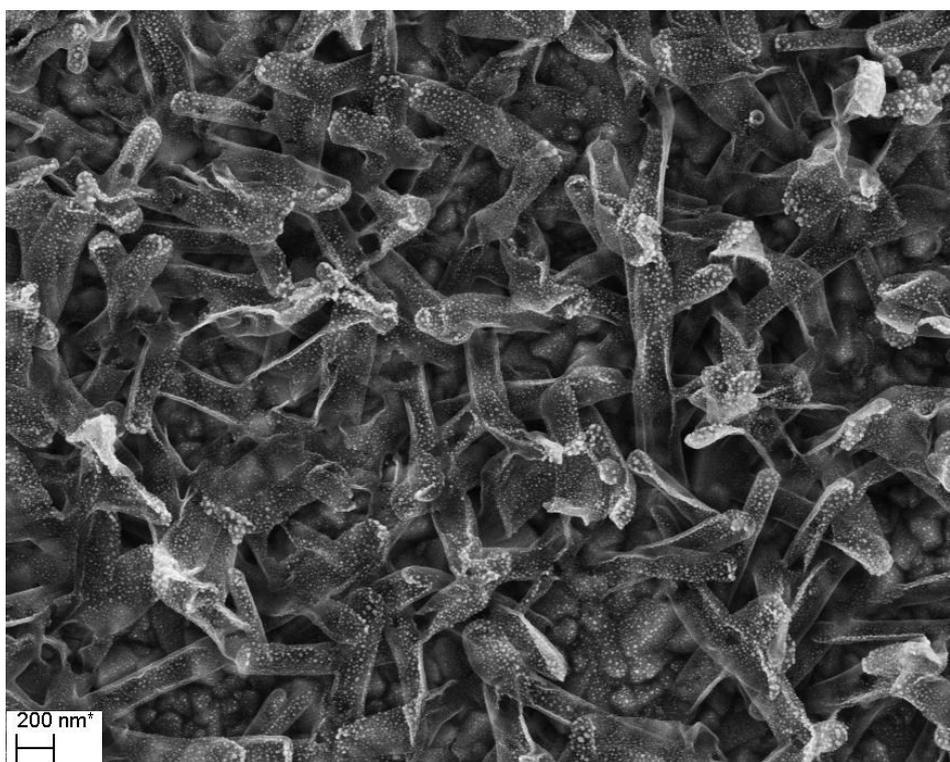
**Fig. S5** EDS spectrum of the ZnO/AuNPs/PDA composite films.



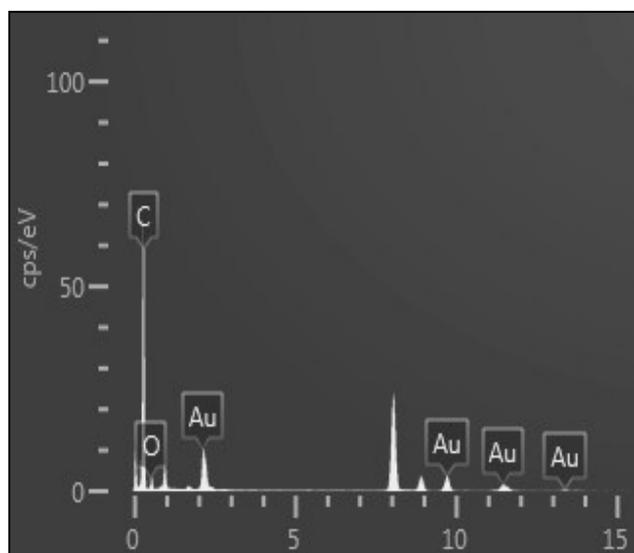
**Fig. S6** Plan-view TEM image of the Au NPs-decorated ZnO NR coated with PDA films.



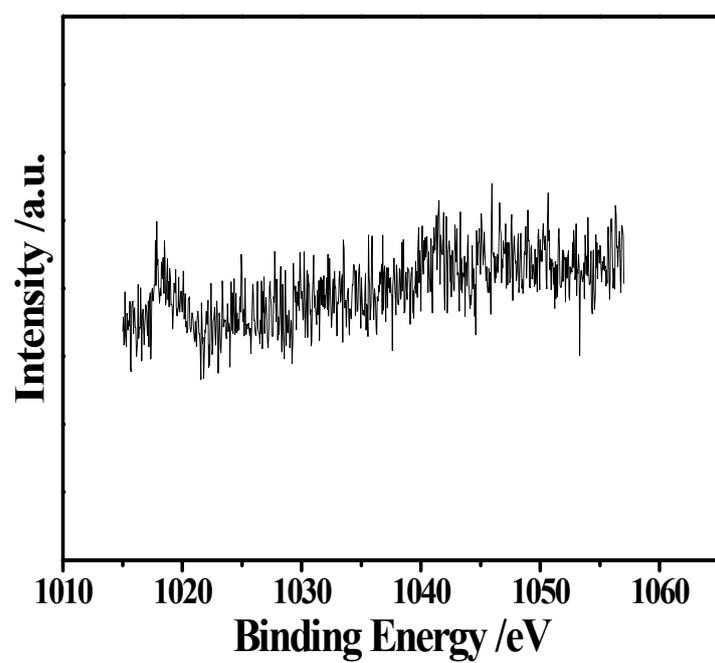
**Fig. S7** UV-vis absorption spectrum of the catalytic films (blue line). As a comparison, the UV-vis spectrum of the carbonized PDA films is also given (black line). However, due to the strong background of the carboneous materials, the well-known size-dependent SPR absorbance of the AuNPs was not very clearly seen.



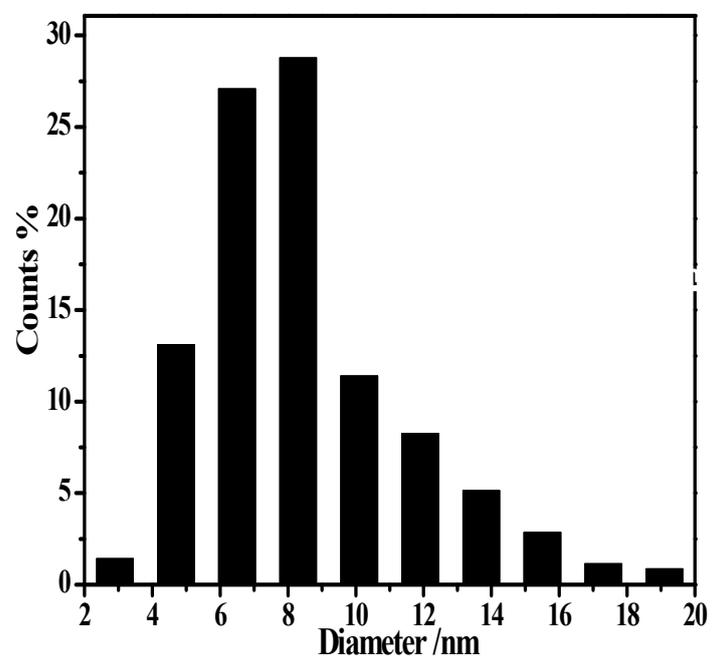
**Fig. S8** SEM image of the films produced by carbonization of the ZnO/PDA/AuNPs composite films, followed by removal of ZnO template. It can be seen that the tubes were collapsed, indicating the interesting effect of the location of the AuNPs on the carbonized PDA, because the ZnO/AuNPs/PDA composite films could produce the arrayed AuNP-embedded pBIDI-CNTs films after the same carbonization and ZnO removal procedure. The exact reason is not clear at present and the relative investigation is under way in our lab.



**Fig. S9** EDS spectrum of the AuNPs-embedded pBIDI-CNTs films.

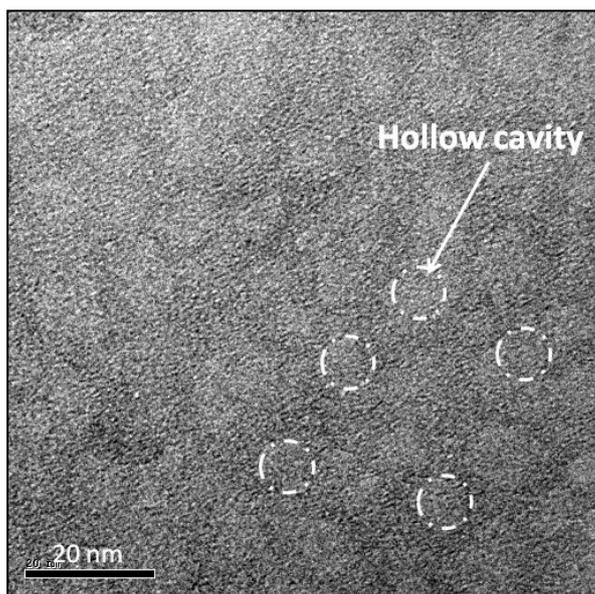


**Fig. S10** XPS spectrum of the catalytic films for detecting ZnO.

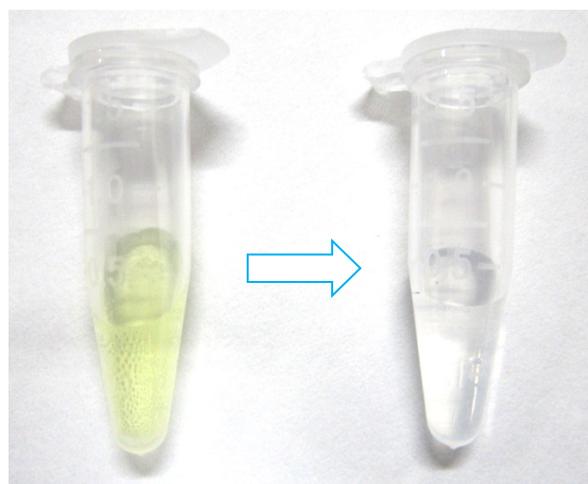


**Fig. S11** Histogram of size distribution of the Au NPs inside the pBIDI-CNTs.

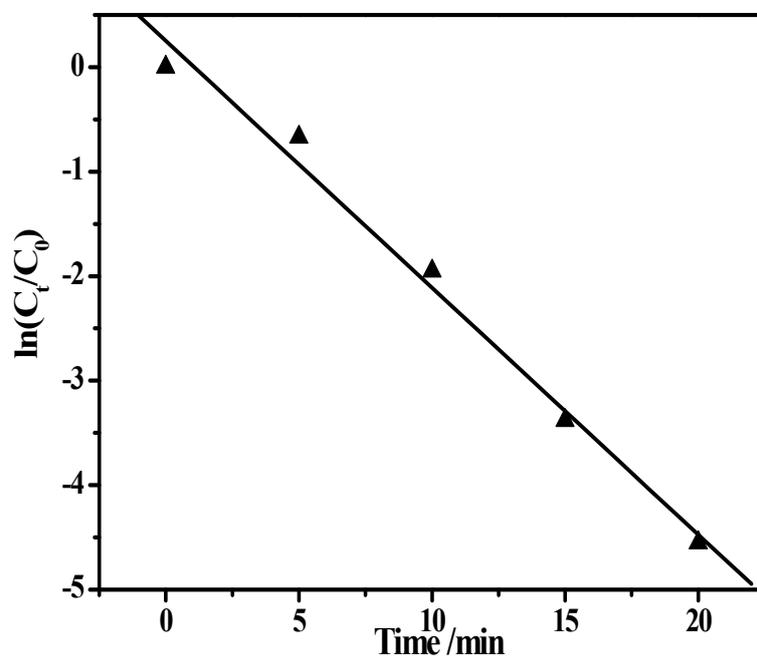
**Cysteamine-induced etching of the AuNPs:** The catalyst film was dipped into 10 mM cysteamine solution freshly prepared with 25 mM Tris-buffer solution (pH 8.5), and then the cysteamine-induced etching of the embedded AuNPs was allowed to proceed at 60 °C for 1 h. Finally, the film was rinsed with deionized water and dried at 60 °C. TEM was used to detect the hollow cavities left after removing AuNPs through thiol-induced etching. Some hollow cavities were labelled with the white circles.



**Fig. S12** TEM image of the hollow cavity formed by thiol-induced etching of the AuNPs in the catalyst films.



**Fig. S13** Photographs of the color change in the solution of 4-NP after the Au-catalyzed reduction.



**Fig. S14** The linear relationship between  $\ln (C_t/C_0)$  and reaction time.