Supplementary information

Homogeneous Coating of Au and SnO_2 Nanocrystals on Carbon Nanotubes via Layer-by-Layer Assembly: A New Ternary Hybrid for Room-Temperature CO Gas Sensor

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Experimental Section

Preparation of CNTs/Au/SnO_2 hybrid nanotubes: The carbon nanotubes (CNTs) with diameters of about 30~50 nm purchased from *Times-nano Nanotech Co. Ltd* were used without further purification. Poly(diallyldimethylammonium chloride) (PDDA), M_w<500000 Da, and poly(sodium 4-styrenesulfonate) (PSS), M_w<70000 Da, were purchased from *Alfa Aesar Co. Ltd*. The CNTs were firstly modified by polyelectrolyte (PDDA/PSS/PDDA) in sequence, as was previously reported [15]. Briefly describing, 30 mg CNTs were sonicated for 1 h in 50 ml NaCl (1 M) solution, and 80 mg PDDA was added, followed with 0.5 h stir. Subsequently, the excessive PDDA was removed by six cycles of centrifugation/wash. Likewise, the PSS and PDDA layers were successively coated on the surface of the PDDA modified CNTs, thus ultimately obtaining the polyelectrolyte modified CNTs. The polyelectrolyte modified CNTs were put into 100 ml water added with 0.5ml $HAuCl_4$ solution (0.25M) and 0.2 g trisodium citrate dihydrate, which was sonicated for 20 min. Then,

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40 ml $NaBH_4$ (0.02 g/ml) aqueous solution was slowly dropped into the above-mentioned solution under sonication. After 1 h reaction, 20 ml $SnCl_4$ solution (0.05 M) was dropped into the solution. Finally, the reaction proceeded 3 h under sonication. The resulting products were centrifuged, washed with distilled water and ethanol to remove the ions possibly remaining in the final products, and dried at 100 ^oC in air.

Preparation of CNTs/SnO_2 nanotubes: The experimental procedures were similar to that for the preparation of CNTs/Au/SnO_2 nanotubes without the deposition of Au nanocrystals on carbon nanotubes.

Preparation of Au and SnO_2 hybrid nanocrystals: The experimental procedures were similar to that for the preparation of CNTs/Au/SnO_2 nanotubes in absence of the CNTs.

Gas sensor characterization of CNTs/Au/SnO_2 nanotubes and Au and SnO_2 hybrid nanocrystals: The CNTs/Au/SnO_2 nanotubes films were fabricated on the top of the Pt electrodes by spin coating, followed by annealing at 100 ^oC for 3 h before electrical and sensing measurement. Gas sensor behavior of the CNTs/Au/SnO_2 nanotubes based sensor was measured at room temperature using the Keithley 236 Source Measure Unit. The chamber was firstly purged by N_2 until a steady baseline of the sensor resistance was reached. Then the tested vapor, CO, was injected at different concentrations (500-2500 ppm) in N_2. In general, the DC voltage was fixed at 10V, and the changes of current with the time were recorded. The sensitivity S was defined as I_g/I_a, where I_g and I_a are the current through the sensor in the tested gas and that in

air, respectively. The response and recovery time of the sensor is defined as the time needed to reach 90% of the original resistance.

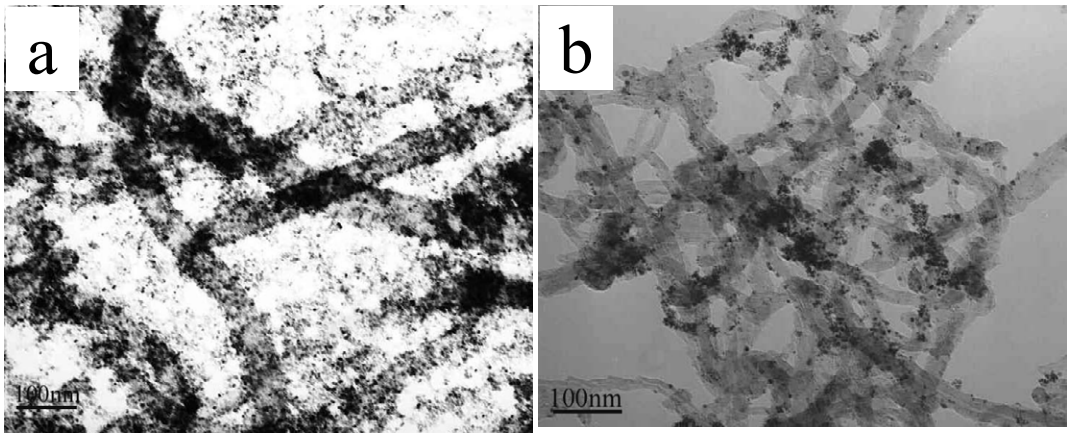

Figure S1 TEM images of the CNTs/Au hybrids generated by addition of 2 ml $HAuCl_4$ (0.025 M) solution as the reactant without polyelectrolyte modification (a) and with two-layer polyelectrolyte modification (b).

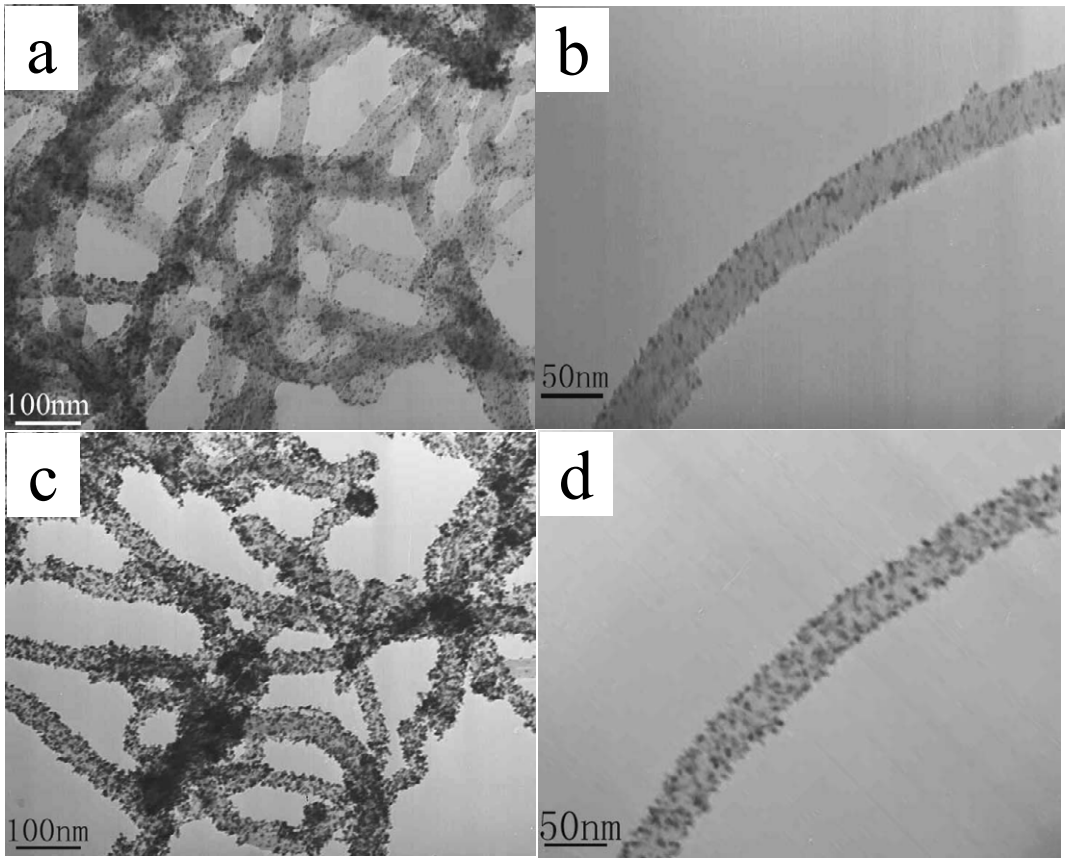

Figure S2 TEM images of the CNTs/Au hybrids generated by addition of 0.5 (a), (b) and 2 ml $HAuCl_4$ (c) (d) (0.025 M) solution as the reactant, respectively.

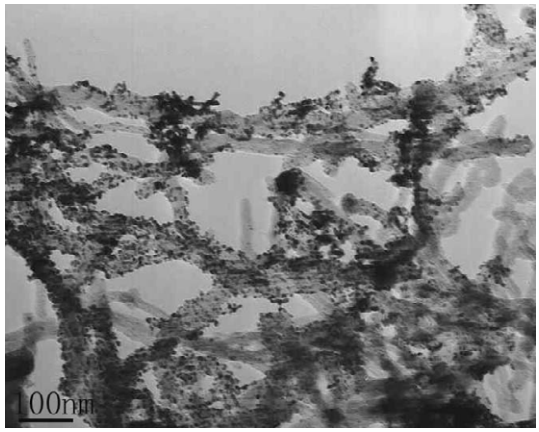

Figure S3 TEM images of the CNTs/Au hybrids generated by addition of 2 ml $HAuCl_4$ (0.025 M) solution as the reactant in absence of trisodium citrate dehydrate.

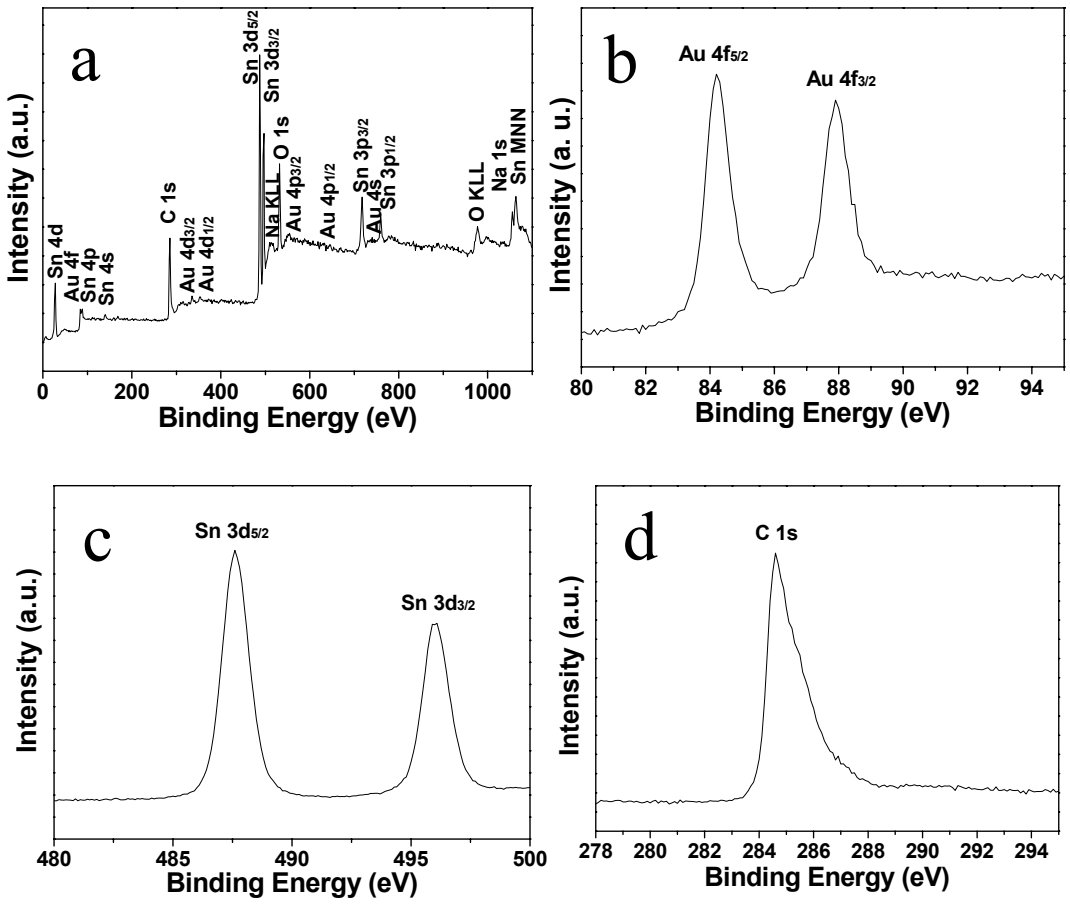

Figure S4 XPS spectra of CNTs/Au/SnO_2 nanotubes.

To determine the elements and their valence presented in the coating layer on the CNTs, X-ray photoelectron spectroscopy (XPS) analysis was carried out. Figure S4a shows the survey spectrum of CNTs/Au/SnO_2 nanotubes. The detected elements are tin (Sn 3p, 3d, 4s, 4p, 4d), aurum (Au 4s, 4p, 4d, 4f), oxygen (O 1s), sodium (Na 1s) and carbon (C 1s). Sodium and aurum comes from the polyelectrolyte and metal Au nanocrystals, respectively. Tin and oxygen are expected from the chemical composition of SnO_2. Figure S4b shows the multiplex spectrum of Au peaks. Double peaks with binding energies of 84.3 eV and 87.9 eV correspond to Au $4f_{5/2}$ and Au $4f_{3/2}$ of metal Aurum, respectively. [17] The XPS of the regions of Sn 3d from

CNTs/Au/SnO_2 nanotubes is shown in Figure S4c. The peaks of tin at 487.6 eV and 496.0 eV can be assigned to Sn $3d_{5/2}$ and $3d_{3/2}$, respectively, which are close to standard data for SnO_2. [18] Figure S4d shows the XPS C 1s spectrum of the as-synthesized CNTs/Au/SnO_2 nanotubes. The peak at 284.6 eV is due to the graphite-like carbon atoms of the tube wall. [19]

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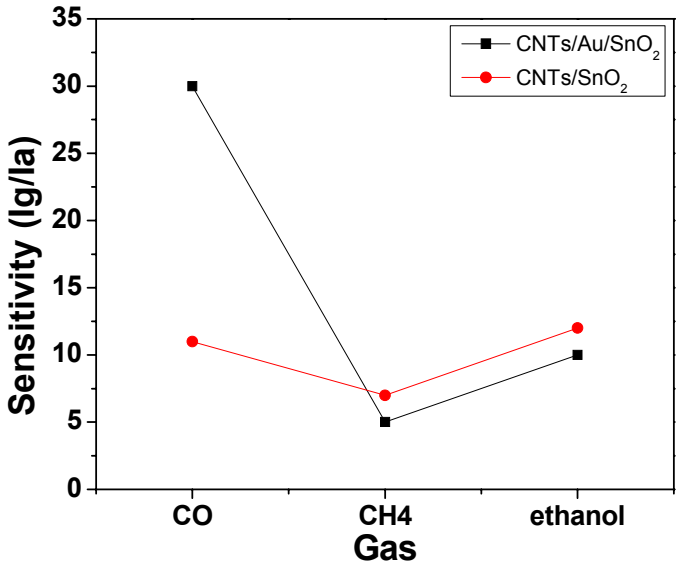

Figure S5 Sensitivity response versus CO, CH_4 and ethanol with the same concentration of 500 ppm based on CNTs/Au/SnO_2 and CNTs/SnO_2 nanocrystals hybrids.

In order to identify the selectivity, the CNTs/Au/SnO_2 nanotubes and CNTs/SnO_2 nanotubes were applied in CO, CH_4 and ethanol gas sensor with the same concentration of 500 ppm (figure S3). As can be seen, CNTs/Au/SnO_2 nanotubes show much higher sensitivity to CO than CH_4 and ethanol (more than double). On the contrary, the difference of the sensitivity to CO, CH_4 and ethanol based on CNTs/SnO_2 nanotubes gas sensors is small and the sensitivity is relatively low. Therefore, the gas sensor based on CNTs/Au/SnO_2 nanotubes shows better selectivity to CO than that based on CNTs/SnO_2 nanotubes gas sensors.