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Supplementary information for new journal of chemistry

Self-Assembly of Ultrathin Gold Nanowires and Single Walled Carbon Nanotubes as a Highly Sensitive Substrate for Surface Enhanced Raman Spectroscopy

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1.1 Reagents and apparatus

Gold (III) chloride trihydrate ($HAuCl_4$ $3H_2O$, >99.9 % trace metals basis), Triisopropylsilane (99%), Single walled carbon nanotube (>90%, 0.7-0.9nm diameter), Sodium borohydride (99.99% trace metals basis), 4-mercaptobenzoic acid (97%) were purchased from Sigma-Aldrich. All chemicals were used as received. Milli-Q water (resistant > 18.2 MΩ cm^{-1}) was used to prepare all the solutions in this study.

The morphology of the GNWs and hybrid GNWs/SWCNTs were characterized by Atom Force Microscopy using a Bruker Multimode 8. Silicon tips on nitride lever were used. Absorption spectra of GNWs and hybrid GNWs/SWCNTs were recorded by UV-Vis spectroscopy at room temperature using CARY 300 Bio UV-Vis spectrometer. An ultrasonic water bath (Grand Ultrasonic Bath XUBA3) was used when preparing hybrid GNWs/SWCNTs.

1.2 Synthesis of hybrid GNWs/SWCNTs

GNWs were synthesized by the protocol reported previous[1]. 44 mg $HAuCl_4 \cdot 3H_2O$ were dissolved in 40 ml hexane with the presence of 1.5 ml oleylamine. Then 2.1 ml triisopropylsilane (TIPs) were added to the solution as reducing agent. The solution was kept still for 4-5 hours at room temperature and the colour of solution changed from yellow to dark red. To remove the oleylamine from the solution, 2.5 ml solution was added into 8 ml ethanol and centrifuged at 4500 rpm for 15 min and dissolved in 2.5 ml hexane for use. The washing process was proceeded twice to remove the-oleylamine. Hybrid GNWs/SWCNTs were prepared as follows. 0.1 mg SWCNTs were dispersed into 20ml hexane (0.005 mg/ml) and put into ultrasonic water bath for 30 min. 1 ml SWCNTs solution was added in 20 µl GNWs solution (0.5 mg/ml) with gently shaking for 20 min to fully self-assemble. 10 µl of 24 mM sodium borohydrate was dropped on the hybrid GNWs/SWCNTs on silicon wafer and then rinsed with ethanol to remove oleylamine and sodium borohydride from hybrid GNWs/SWCNTs surface.

1.3 Surface enhanced Raman spectroscopy of hybrid GNWs/SWCNTs

Raman spectroscopy measurements were conducted using a Renishaw Invia Raman Microspectrometer (Renishaw pic, Gloucestershire, UK) and a thermo-electrical cooled CCD detector. The original laser power measured at the sample of ca 12 mW was reduced to 1-6 mW to prevent heating and photochemical damage to the samples. Acquisition parameters used for spectra data collection included 10 s exposure time and 4 cm^{-1} spectra resolution. For Raman spectra of hybrid GNWs/SWCNTs, 10µl hybrid GNWs/SWCNTs solution was dropped onto silicon wafer and dried, then used for Raman spectroscopy. 514 nm laser and 100 × optical telescope were used for the

detection. To study the reproducibility of hybrid GNWs/SWCNTs, ten drop of the hybrid GNWs/SWCNTs solution were used to drop on silicon wafer and detect the Raman spectroscopy. From the Raman spectroscopy of hybrid materials, the Raman spectroscopy of ten individual drop of hybrid material solution is similar with each other which indicate the reproducibility of the hybrid materials shown in Fig. S2b. For surface enhanced Raman spectroscopy, 10 μl of 10^{-5} M, 10^{-4} M and 10^{-3} M of 4-mercaptobenzoic acid (MBA) solution resolved in methanol were dropped on the hybrid GNWs/SWCNTs substrate, respectively. As a control experiment, the Raman spectroscopy of the same sample were measured without using hybrid GNWs/SWCNTs. Different wavelength laser (457 nm, 488 nm, 514 nm , 633 nm and 785nm) are used to detect the same point of hybrid GNWs/SWCNTs substrate with 5×10^{-4} M MBA for laser selectivity detection. For the removal of oleylamine layer of GNWs with $NaBH_4$, different concentration of $NaBH_4$ and different reaction time were chosen for the washing process. For Raman spectroscopy of Australia 50 dollar paper note, the paper note was first washed with ethanol to remove the contamination and used for Raman spectroscopy. A special point with uniform yellow dye on the note was chosen for Raman detection using 100× optical telescope and 785 laser. Then drop 10 μl hybrid GNWs/SWCNTs on the same position of paper note and wait to dry for the same Raman spectroscopy detection.

In order to study the enhancement ability of GNWs/SWCNTs on complicated substrate, we chose 50 dollar bank note as a representative sample with Raman background. We selected 4-MBA and Rhodamine 6G as two probe molecules for trace level detection with SERS substrate of GNWs/ SWCNTs. As shown in fig S4a and b, we observed the characteristic peak from 4-MBA and Rhodamine 6G is clearly clear which shown with detection of limit up to 10^{-6} M. And the Raman peaks of the MBA peaks at 1074 cm^{-1} and 1588 cm^{-1} from 10^{-3} M 4-MBA and 10^{-6} M 4-MBA is consistent and the same concentrations for Rhodamine 6G detection.

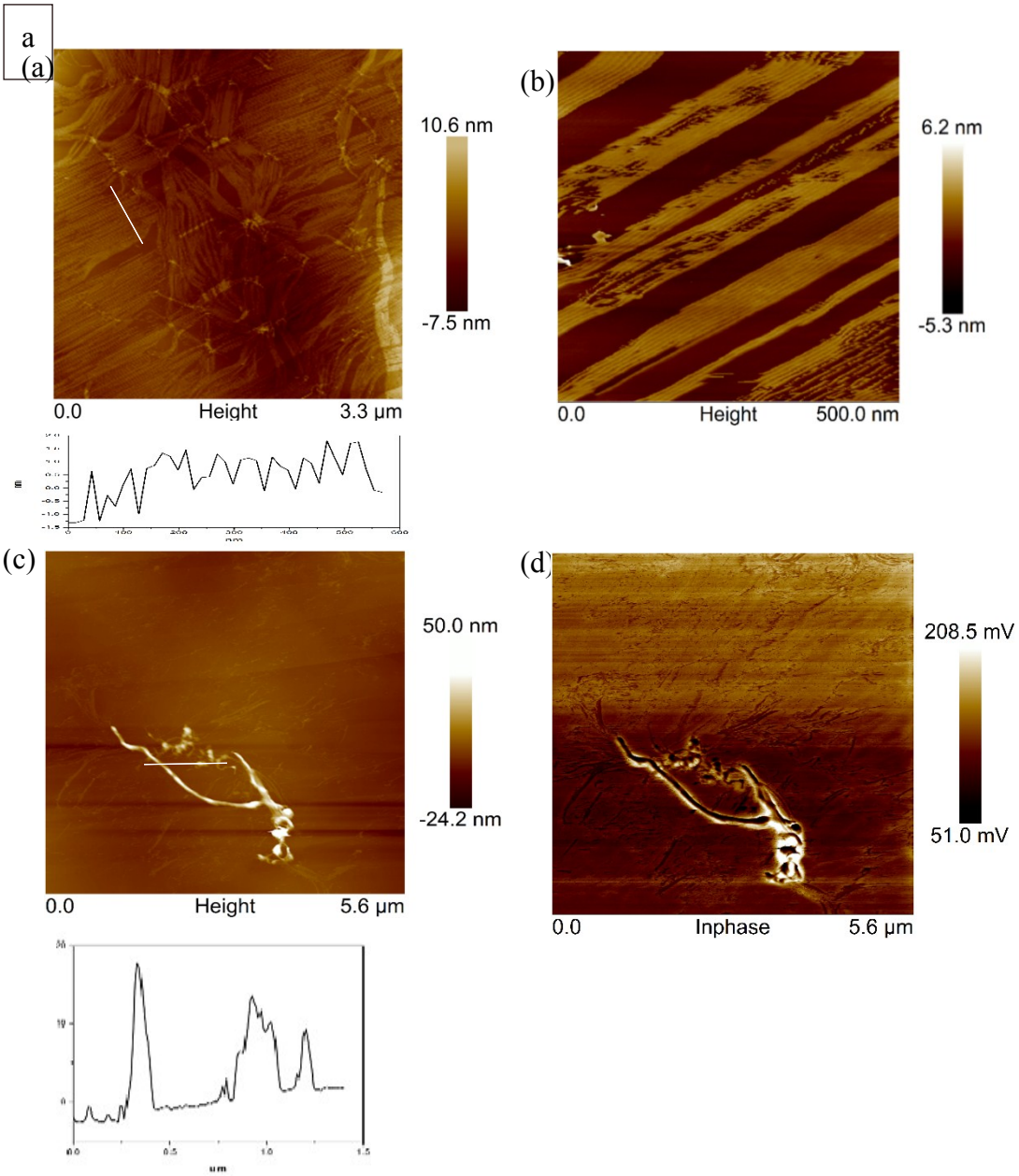

Fig.S1. AFM of (a) GNWs with 2-D stuctures (b) GNWs bundles with parallel GNWs (d<2nm) (c)Hight image of hybrid GNWs/SWCNTs (d) Inphase image of hybrid GNWs/SWCNTs.

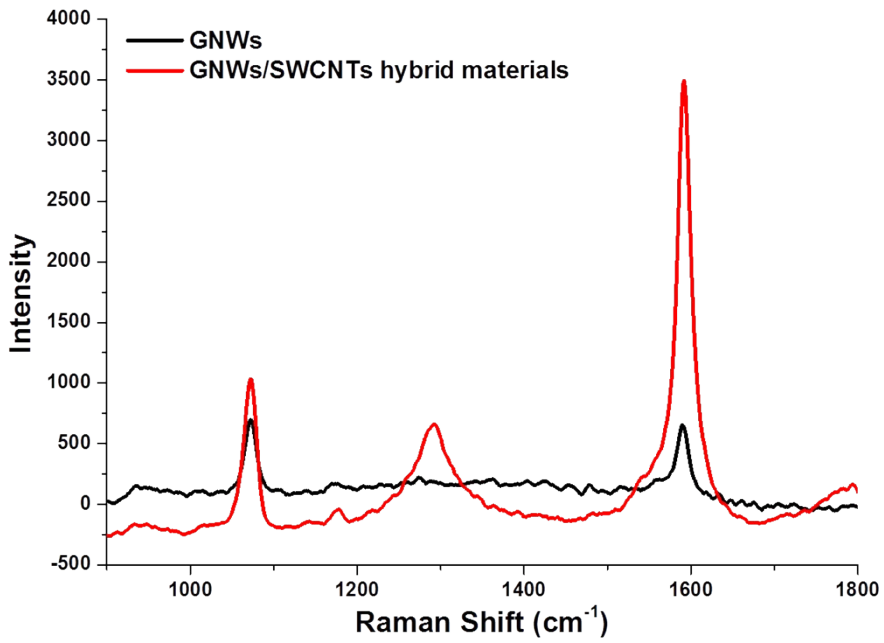

Fig. S2a. Raman spectroscopy of 4-MBA (10^{-4} M) on GNWs and GNWs/SWCNTs hybrid materials

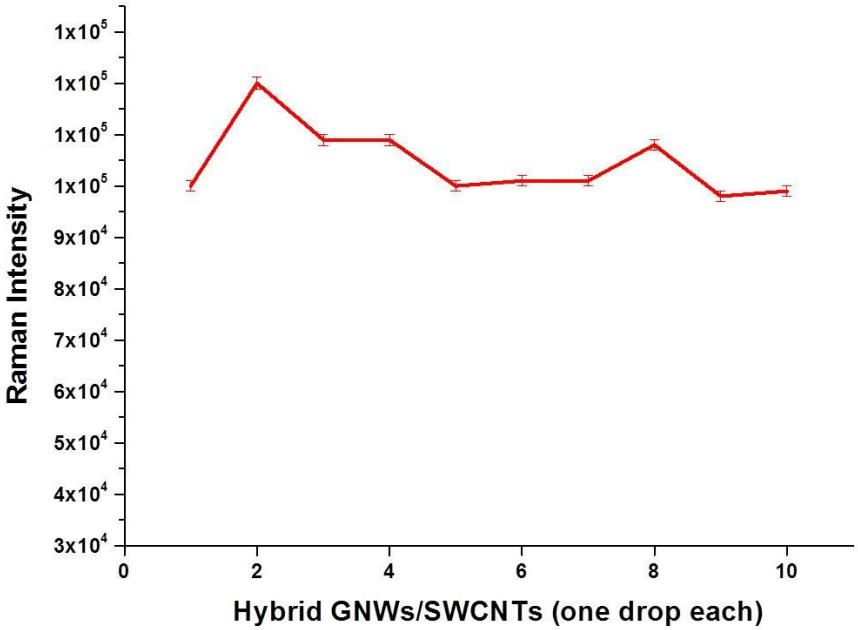

Fig. S2b. Reproducibility of GNWs/SWCNTs hybrid materials

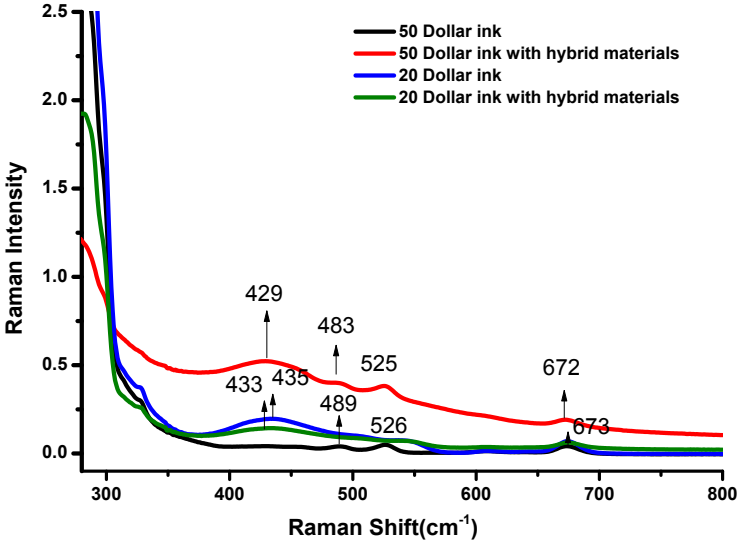

Fig. S3a. UV-Vis spectroscopy of ink dissolved in chloroform (20 AUD and 50 AUD) and the UV-Vis spectroscopy of ink with GNWs/SWCNTs hybrid materials.

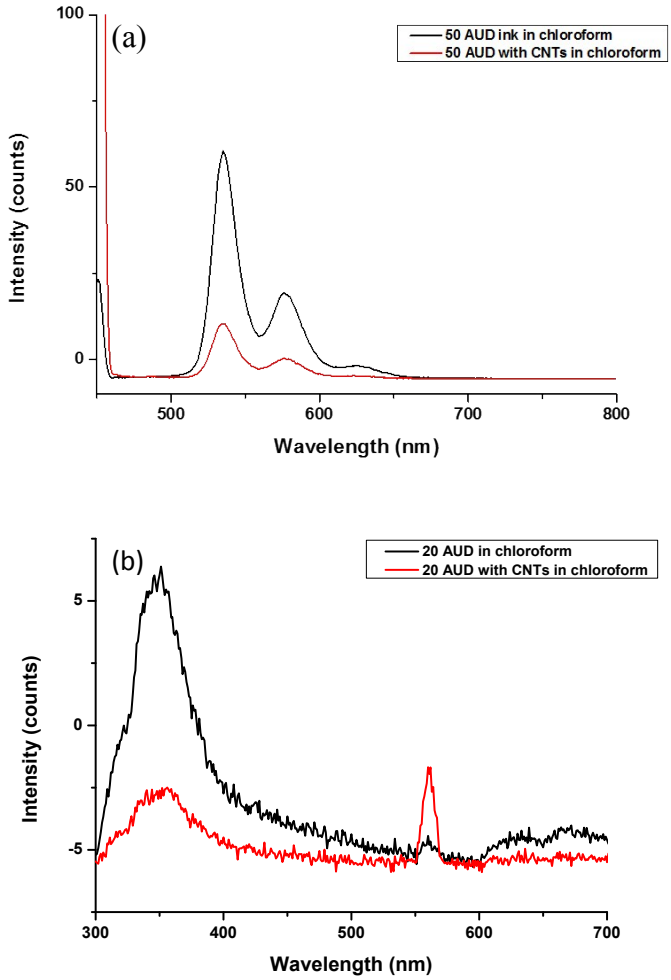

Fig S3b. Fluorescence of ink dissolve in chloroform (20 AUD and 50 AUD) and fluorescence quenching with SWCNTs.

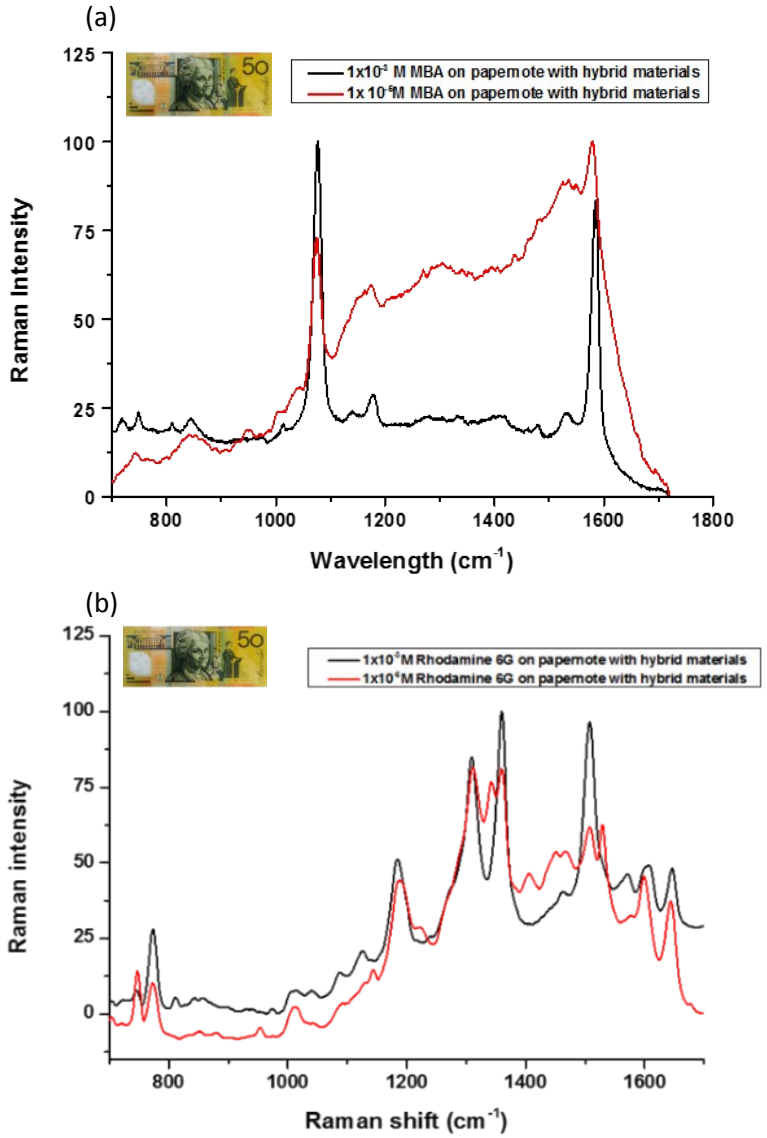

Fig. S4 (a). Trace level detection of 4-MBA on 50 dollar banknote with the enhancement of GNWs/SWCNTs hybrid materials. (b).Trace level detection of Rhodamine 6G on 50 dollar banknote with the enhancement of GNWs/SWCNTs hybrid materials.

1. H. Feng, Y. Yang, Y. You, G. Li, J. Guo, T. Yu, Z. Shen, T. Wu and B. Xing, Chemical Communications, 2009, 15, 1984-1986.