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Supporting Information

Carbon nanotube anions for the preparation of gold nanoparticle-nanocarbon hybrids

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Experimental Section

Reduced SWCNTs were prepared using a modified literature procedure.[1] As-received HiPco SWCNTs batch P2150 were used in experiments without further purification. SWCNTs (12 mg) weighed in a Schlenk flask with a stirrer bar and dried overnight under vacuum at 120 °C. Anhydrous THF (50 mL) degassed by freeze-pump-thaw cycling (4 times) was cannulated under argon to the Schlenk flask containing SWCNTs and sonicated for 15 min in an ultrasonic bath (Ultrawave U50, 30–40 kHz). *n*-BuLi (5.1 mmol) (3.2 mL of 1.6 M solution of *n*-BuLi in hexanes, Aldrich) was added to the SWCNT dispersion drop-wise over 0.5 h. The resulting dispersion was then stirred for 0.5 h, sonicated for 0.5 h in an ultrasonic bath and stirred for 24 h at room temperature. Unreacted *n*-BuLi and THF mixture was filtered using a cannula filtration method under argon. The resulting black solid was redispersed in 30 mL anhydrous/degassed THF (4×) by sonication (1 min) and filtered via cannula under an argon atmosphere to isolate $[(n\text{Bu—SWCNT})^{x-}\cdot\text{Li}_x^+]$. Vacuum dried triphenyphosphinegold(I) chloride, $\text{ClAu(PPh}_3)$, (0.2 mmol, 100 mg) was then transferred into 50 mL of a THF solution containing the reduced nanotubes [(nBu—SWCNT)$^{x-}$·Li$_x^+$] (12 mg), under an argon atmosphere, and the resulting mixture stirred overnight at room temperature. THF solution containing unreacted ClAu(PPh$_3$) was removed by cannula filtration under argon and the remaining solid was redispersed and filtered (cannula) using anhydrous THF (2×30 mL). Methanol (50 mL) was then added to the Schlenk flask and the reaction mixture was stirred for an additional 1 h to dissolve formed metal salts (*e.g.* LiCl) and neutralise unreacted [(nBu—SWCNT)$^{x-}$·Li$_x^+$]. The modified SWCNTs were then filtered through a PTFE membrane (0.2 μm) and subsequently redispersed and filtered using methanol (2×30 mL), THF (2×30 mL), dimethylformamide (2×30 mL), water (2×30 mL) and ethanol (2×30 mL) respectively, and dried overnight at 80 °C. The control SWCNTs (**2** and **3**) were also prepared in anhydrous THF by mechanically mixing SWCNTs with ClAu(PPh$_3$) or HAuCl$_4$ in a Schlenk flask under argon, followed by redispersion and filtration using the same procedure described above. Samples were characterised by electron microscopy (HRTEM, HAADF-STEM, SEM) and spectroscopic techniques (XPS, TGA-MS, ICP-AES and FTIR).

Equipment

High resolution-transmission electron microscopy (HR-TEM). HR-TEM was performed by SC using a FEI Titan TEM/STEM at 80 kV operating voltage. Samples were prepared by dispersing the *n*Bu-SWCNT-Au sample in 2-propanol using bath sonication (30 min, VWR ultrasonic cleaner). The solution was drop-cast on to a TEM grid (holey carbon on 300 copper mesh, TAAB Laboratories Equipment Ltd), and left to dry in air. High resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), combined with energy-dispersive X-ray spectroscopy (EDX) analysis were carried out using an FEI Titan 80/300 fitted with a Cs (image) corrector, monochromator and EDX detector (EDAX, Leicester, UK), operated at an accelerating voltage of 80 kV. STEM experiments were performed with a convergence semi-angle of 14 mrad and inner and outer HAADF collection angles of 49 and 239 mrad, respectively. The probe diameter was <0.5 nm. The intensity of a HAADF-STEM image is proportional to Z^n ($n \sim 2$), therefore, this technique is highly sensitive to atomic number (Z) variations within the sample.

Scanning electron microscopy (SEM). SEM was carried out by AJC on a high resolution field emission gun scanning electron microscope (FEGSEM) Leo Gemini 1525, with a built-in EDX (INCA, using INCA suite software V4.15, 2009, Oxford Instruments Plc., UK). Images were taken with an aperture of 30 µm typically at 5 keV. SEM samples were prepared on Al stubs using silver dag (Agar Scientific, UK with Al foil supplied by VWR, UK).

Thermogravimetric analysis-mass sectroscopy (TGA-MS). TGA experiments were carried out by SAH using a Mettler Toledo TGA/DSC 1 with a GC200 flow controller. The TGA was coupled to a mass spectrometer (Hiden MS fitted with a 200 a.u. quadrupole sensor). Samples were heated from 30 to 100 °C at 35 °C/min, and then held isothermally at 100 °C for 30 min in an inert atmosphere (N_2, 60 mL/min) to remove residual solvents. The temperature was then ramped to 850 °C at 10 °C/min with a switch from N_2 to air at 600 °C. An inert gas flow was used between 100-600 °C to remove the grafted *n*-butyl chains from [*n*-Bu—SWCNTs-AuNPs], before oxidising the SWCNTs >600 °C to leave behind a metal oxide residue consisting of Au/Fe_2O_3.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES). ICP-AES was performed by SAH using a Perkin Elmer ICP 2000 DV OES (dual view optical emission spectrometer) in axial mode. Data was recorded using WinLab32 software. TGA residues (0.1-0.3 mg) were left to dissolve overnight in 1 mL aqua regia (HNO_3:HCl, 1:3) and further diluted with water by a factor of 100 for sampling. Calibration was performed using 1, 5 and 25 ppm solutions of ICP multi-element standard solution IV (Merck, Germany), and a gold standard was prepared from $HAuCl_4$ dissolved in aqua regia and diluted with water to give Au at the same concentrations. A blank 1% aqua regia / water sample was carried out immediately following calibration, as a reference point for samples.

X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded by RM using a Thermo Scientific K-Alpha instrument using focused (400 μm spot) monochromatic Al-Kα radiation at a pass energy of 40 eV. The binding energies were referenced to the sp^2 C 1s peak of graphite at 284 eV.

Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Perkin Elmer ATR Spectrum 100 spectrometer with a resolution of 4 cm^{-1} and 128 scans per spectrum.

Raman Spectroscopy. Raman spectra of powder/drop-cast samples were obtained with a LabRAM Infinity instrument (Horiba Jobin-Yvon Ltd.) with a 532 nm Nd:YAG laser (2.33 eV). All Raman spectra were recorded using a grating of 1800 grooves mm^{-1}. The maximum power of the 532 nm laser at the sample was 24 mW. The laser power was varied to ensure no damage to samples; typically, 25% laser intensity was used for the 532 nm laser. Samples were measured as drop-cast dispersions on glass microscope slides. At least three consistent spectra were measured for each sample at different locations to reduce the effect of sample heterogeneity.

Electrochemical characterisation. A Gamry potentiostat Interface 1000 was used for the cyclic voltammetric (CV) measurements using Gamry Framework Version 6.24. CV experiments were performed inside a glove box. Experiments and analysis were performed by AJC and SAH, respectively. A 10 mL three electrode electrochemical cell was used, with platinum wire working and counter electrodes (Laboratory Reagent, 0.5 x 100 mm) purchased from Fisher Scientific, UK. The reference electrode, Ag/Ag^+, containing 0.01 M silver nitrate and 0.1 M tetrabutylammonium perchlorate in acetonitrile, was purchased from IJ Cambria Scientific, UK. Anhydrous sodium perchlorate ($NaClO_4$) was purchased from Sigma-Aldrich and used as-received. Electrolytic solutions of 0.1 M $NaClO_4$ in THF were further dried by 3 Å molecular sieves and stored in a glove box. The Ag/$AgNO_3$ non-aqueous reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc^+) (+0.15 V *vs.* Ag/$AgNO_3$) and then adjusted to the SHE (Fc/Fc^+ = +0.64 V *vs.* SHE)

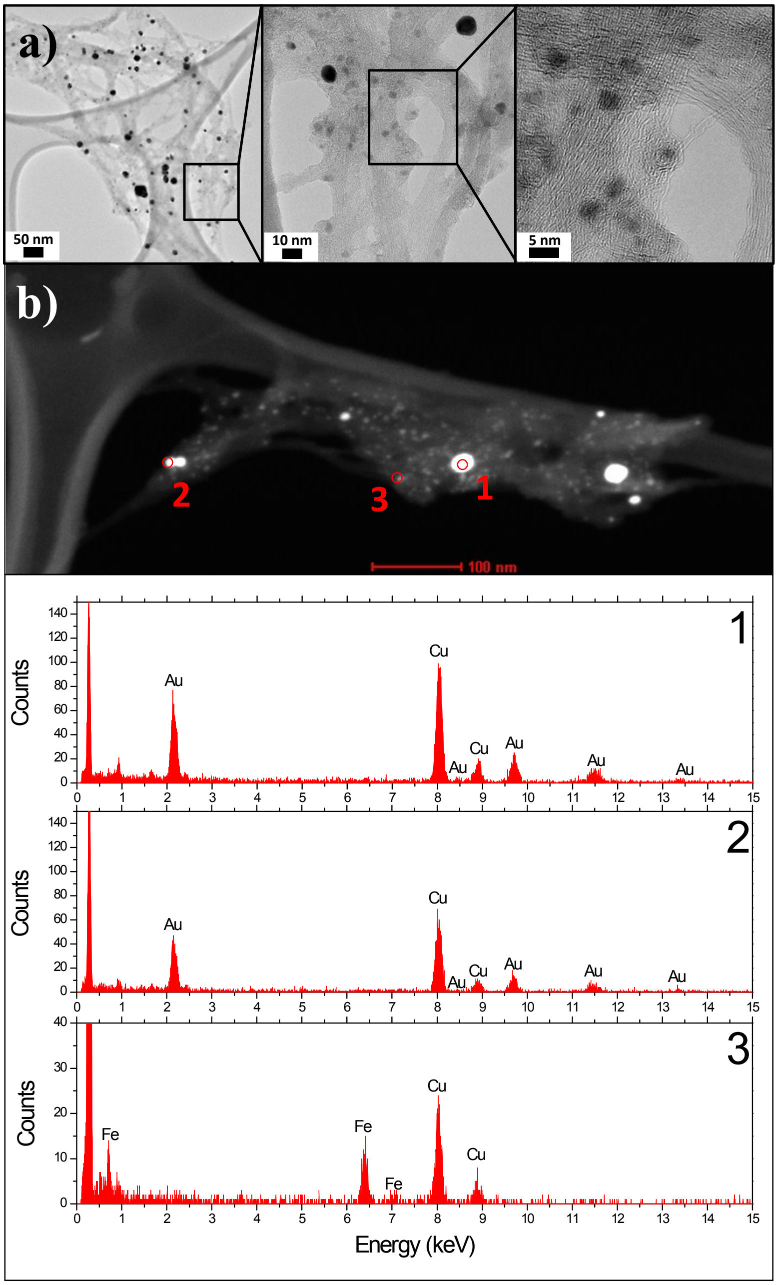

Figure S1. a) HRTEM images of the *n*Bu—SWCNT/Au-NPs, showing the presence of a large fraction of SWCNTs in the analysed sample. b) High-angle annular dark field scanning transmission electron microscopy (HAADF STEM) image (top) following reaction between [(*n*Bu—SWCNT)$^{x-}$·Li$_x^+$]and ClAu(PPh$_3$). Bright features relate to areas of high electron density i.e. metal-NPs. Below shows the corresponding STEM-EDX spectra at three locations of the sample. Regions 1 and 2 show Au—NPs and region 3 reveals a Fe-NP. Note that STEM-EDX provides a much higher spatial resolution EDX analysis than TEM-EDX.

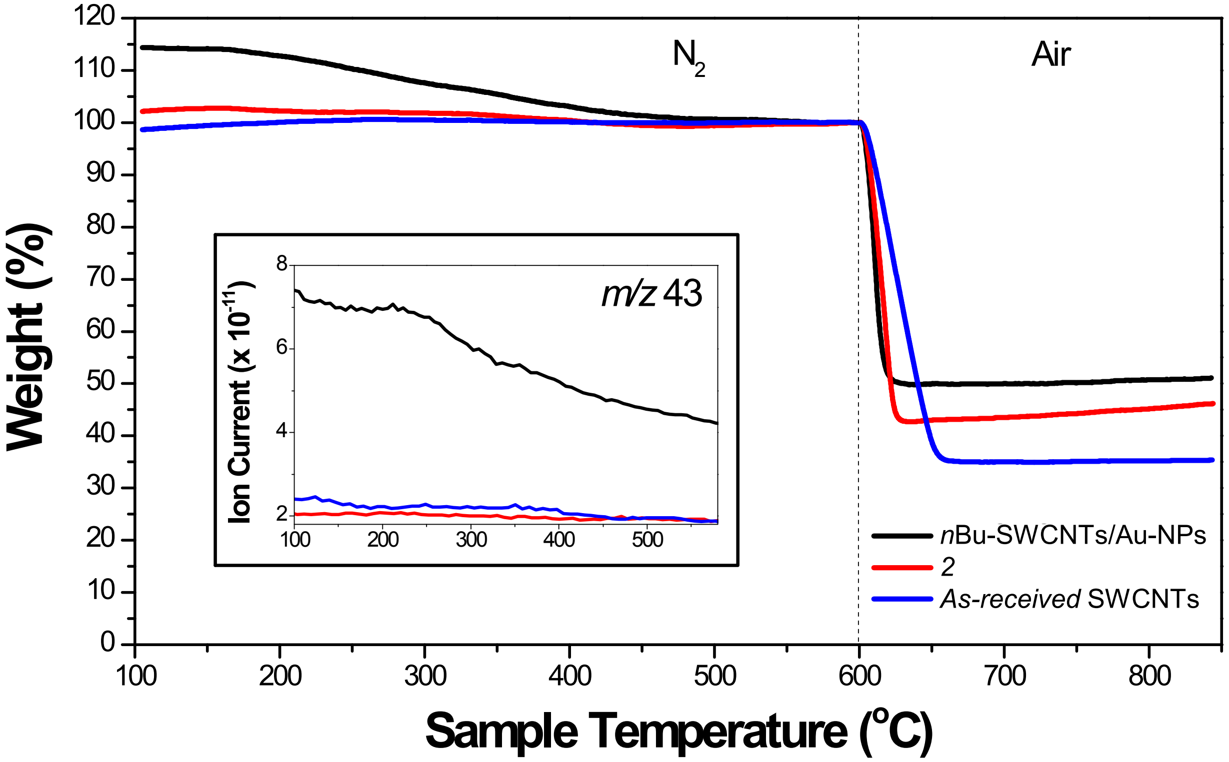

Figure S2. TGA-MS following reaction between $[(n\mathrm{Bu}\text{—}\mathrm{SWCNT})^{x-}\cdot\mathrm{Li}_x^+]$ and $\mathrm{ClAu(PPh_3)}$ (black), **2** prepared by mechanically mixing as-received SWCNTs with $\mathrm{ClAu(PPh_3)}$ followed by washing (red) and as-received HiPco SWCNTs (blue). The temperature is ramped from 100-850 °C (10 °C /min) initially under a nitrogen atmosphere to remove grafted butyl chains, and switched to air at 600 °C (dashed line) to oxidatively decompose the SWCNTs. Spectra are normalised at 600 °C. Inset shows the mass specrum of the corresponding samples, *m/z* 43 (propyl fragment).

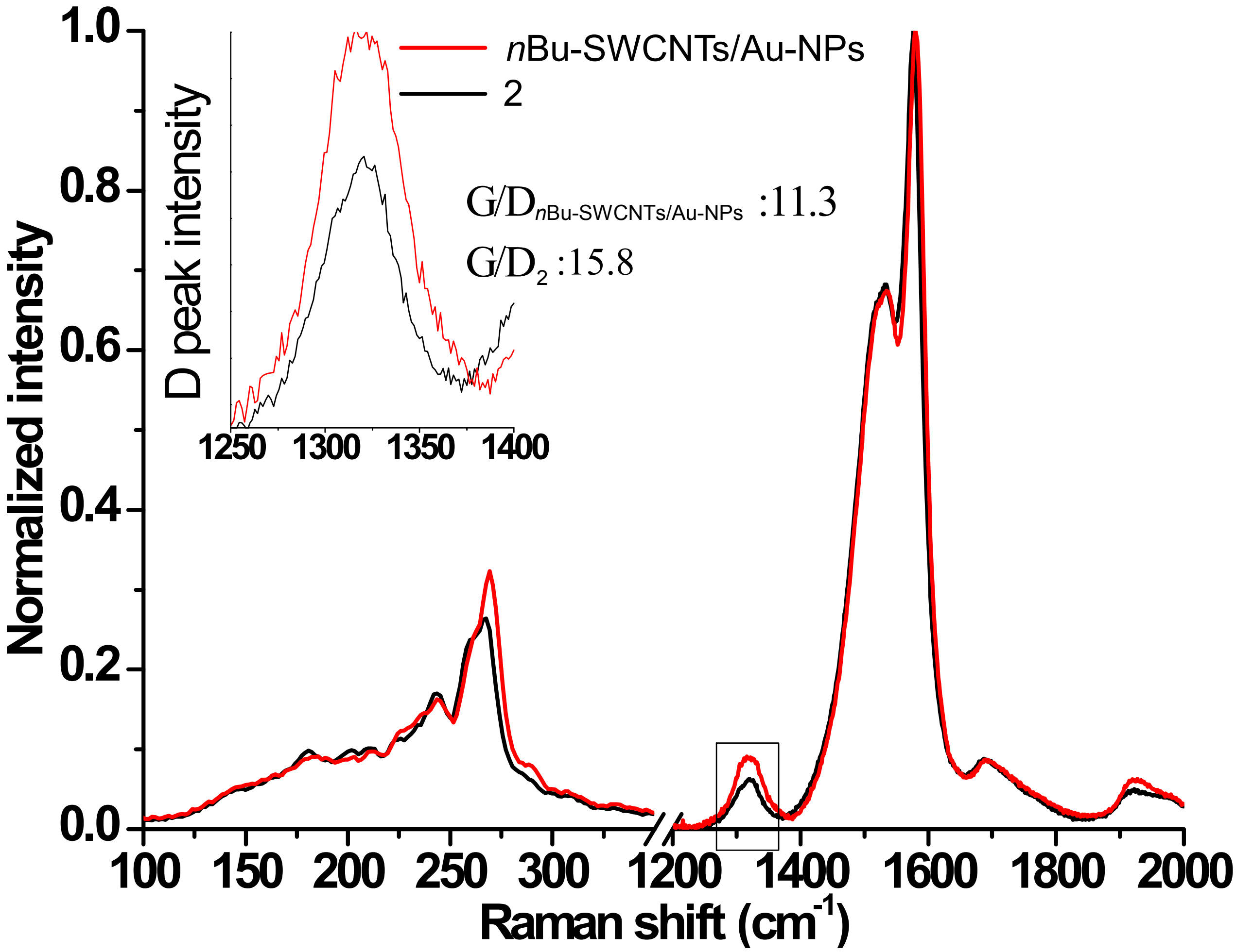

Figure S3. Raman spectra following reaction between [(*n*Bu—SWCNT)$^{x-}$·Li$_x^+$] and ClAu(PPh$_3$) (red) and **2** prepared by mechanically mixing as-received SWCNTs with ClAu(PPh$_3$) followed by washing (black). Increased D-band intensity ~1350 cm^{-1} shows the covalent modification of SWCNTs, but without significant framework damage.

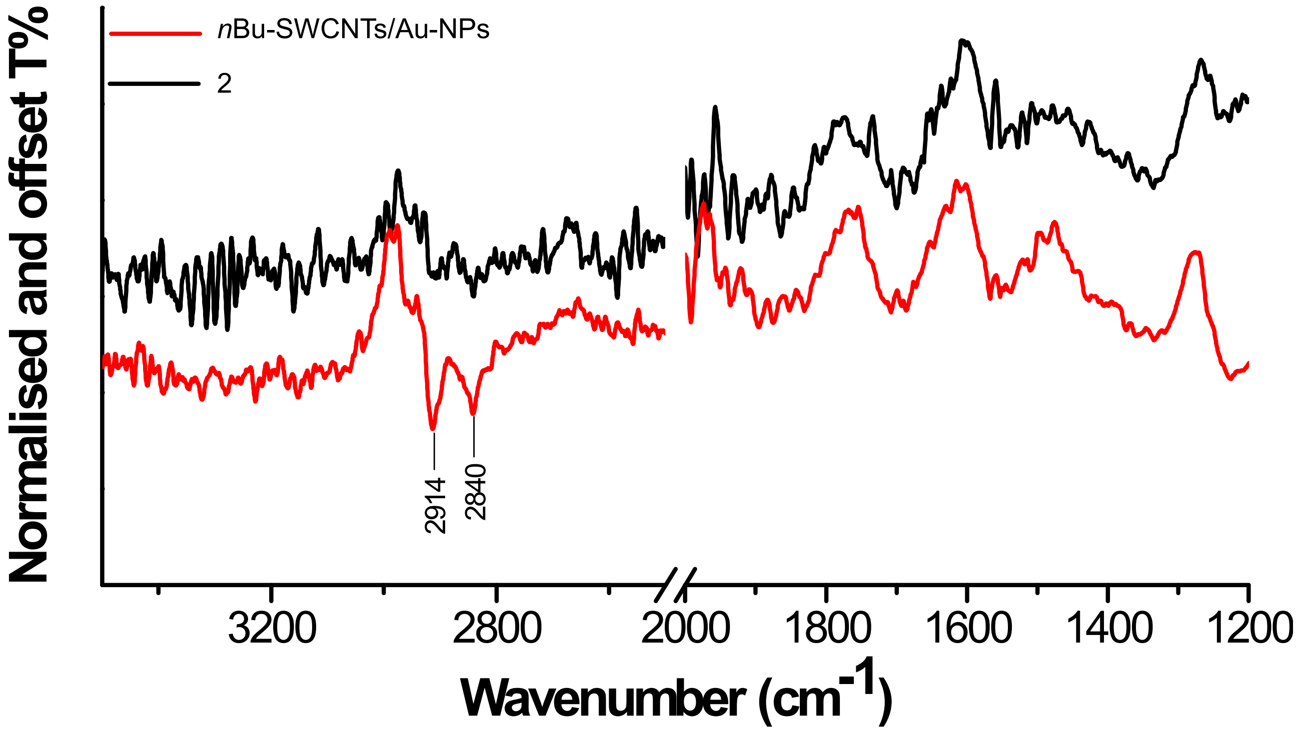

Figure S4. FTIR spectra following reaction between [(nBu—SWCNT)$^{x-}$·Li_x^+] and $ClAu(PPh_3)$ (red) and **2** prepared by mechanically mixing as-received SWCNTs with $ClAu(PPh_3)$ followed by washing (black).

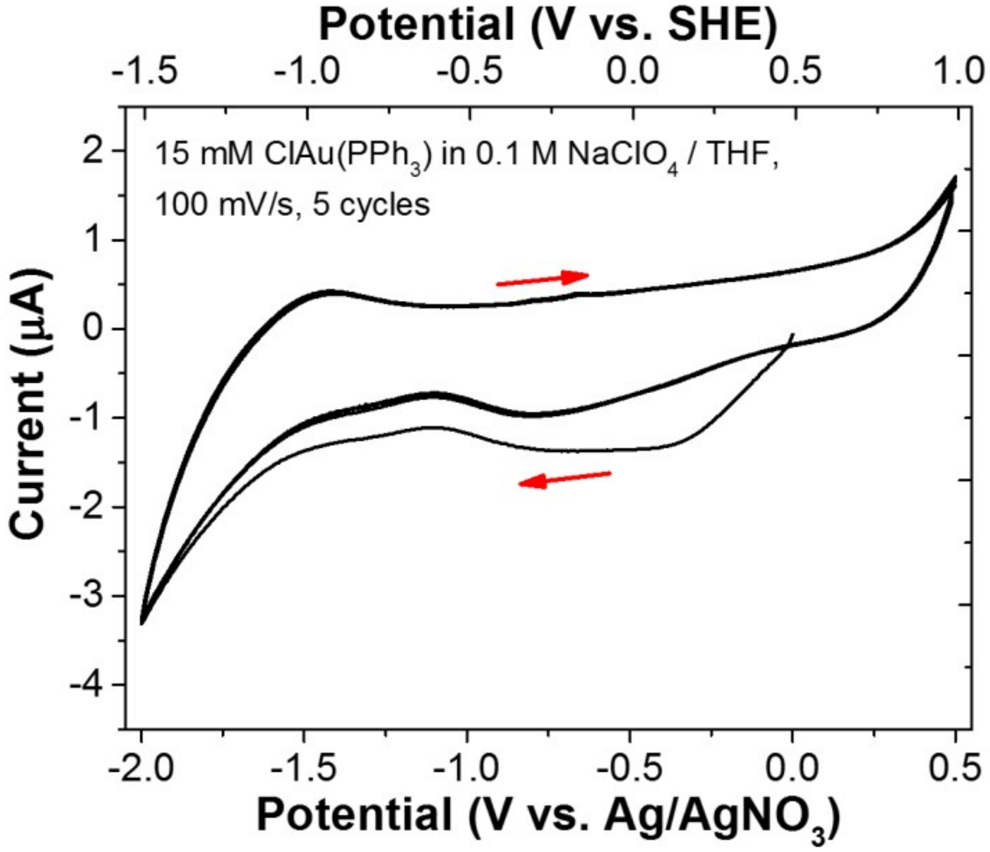

Figure S5. Cyclic voltammetry of 15 mM ClAu(PPh$_3$) at a platinum working electrode in 0.1 M NaClO$_4$ / THF, 100 mV/s scan rate. Arrows indicate the scan direction. The peak reduction of ClAu(PPh$_3$) occurs at -0.80 V *vs.* Ag/AgNO$_3$ (-0.31 V *vs.* SHE).

1. Y. Maeda, K. Saito, N. Akamatsu, Y. Chiba, S. Ohno, Y. Okui, M. Yamada, T. Hasegawa, M. Kako and T. Akasaka, Journal of the American Chemical Society, 2012, 134, 18101-18108.