Supplementary information

Alkylamine Capped Metal Nanoparticle "Inks" for Printable SERS Substrates, Electronics and Broadband Photodetectors

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Synthesis of silver nanoparticle ink is shown in photographs



 $\begin{array}{l} {\rm Ag~NO_3+Oleylamine+~Toluene} \\ {\rm mixture~was~sonicated~until~Ag~NO_3} \\ {\rm dissolved} \end{array}$



NaBH₄ was added into the mixture



Aqueous layer was separated



Silver nanoparticle ink after reduction



The organic layer was filtered to remove any undissolved impurities



The toluene was fully evaporated from the filtered solution



Ethanol was added to precipitate the nanoparticles and remove the unreacted oleylamine





Nanoparticle precipitate was separated by centrifugation



Ag nanoparticles+ unreacted oleylamine



Nanoparticle precipitate after remove the ethanol and unreacted oleylamine



The solution was filtered to remove any further un-dissolved impurities.



The purified precipitate was dissolved in toluene.



Toluene was fully removed to measured the weight of the particles



The nanoparticles were dispersed in toluene with the required concentration



SERS measurements using gold nanoparticle films

Figure S1. Extinction spectra (a) and AFM images (b-e) of the oleylamine capped gold nanoparticle film annealed at 100, 150, 200, and 250° C and f) SERS spectra of Rh6G (1µM) on these Au nanoparticle films.

The extinction spectra of the oleylamine capped gold nanoparticle films annealed at different temperatures are shown in Figure S1a. The extinction spectrum became broader as the annealing temperature increased. When the film was annealed to 200 °C and above, the nanoparticles were found in close contact with each other and the films became even more smooth (Figure S1d&1e) due to the coalescence of gold nanoparticles at higher temperatures. The extinction spectrum became broader due to the strong coupling between the nanoparticles. When the gold nanoparticle film was annealed at 250°C, the extinction spectrum showed the bulk like properties, which is different from the temperature dependent extinction spectrum of the silver film. The SERS spectra of Rhodamine6G measured on the four gold nanoparticle substrates are shown in Figure S1f. The maximum SERS enhancement was observed on the film prepared by annealing at 150°C.

SERS measurement of 1nM Rh6G using silver substrate annealed at 200 °C.



Figure S2. SERS signals of 1 nM Rhodamine 6G on oleylamine capped silver nanoparticle substrate annealed at 200 $^{\circ}$ C.

Comparison of maximum SERS enhancement for Ag and Au nanoparticle substrates.



Figure S3. SERS spectra of Rh6G (1 μ M) on the oleylamine capped Ag and Au nanoparticle substrates prepared by annealing the Ag substrate at 200°C and Au substrate at 150°C. Ag nanoparticle substrate gave SERS signals 17 times larger than the Au nanoparticle substrate.

Surface morphology of gold nanoparticle film after annealing

Figure S4. a) Optical microscopic image, b) AFM image and c) dark field image of the conductive gold nanoparticle film prepared from oleylamine capped gold nanoparticle ink. The AFM image shows that the nanoparticles were interconnected to form conductive film after annealing at 250° C.





Figure S5 a) UV-visible spectra of oleylamine capped gold nanoparticle film annealed at different temperatures. **b)** Electron relaxation dynamics of the oleylamine capped Au nanoparticle films annealed at 50, 180 and 250° C.

The ultrafast relaxation dynamics of the gold nanoparticle film annealed at 50, 180 and 250°C in air were measured by using reflection pump-probe experiments, which were performed by using a femtosecond Ti:sapphire laser system (Spectra Physics). The laser pulses were generated from a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 2 mJ at 800 nm and a repetition rate of 1 kHz. The 800 nm laser beam was split into two portions. The larger portion of the beam was passed through a BBO crystal to generate the 400 nm pump beam by frequency-doubling. A

small portion of the 800 nm pulses was used to generate white light continuum in a 1 mm sapphire plate. The white light continuum was split into two beams, a probe and a reference beam. The reference beam and reflected probe beam from the sample was directed to the photodiodes that are connected to lock-in amplifiers and a computer. The intensity of the pump beam was attenuated with the neutral density filter. The pump beam is focused onto the sample with a beam size of 300 μ m and overlaps the smaller-diameter (100 μ m) probe beam. The delay between the pump and probe pulses was varied by a computer-controlled translation stage. The pump beam was modulated by an optical chopper at a frequency of 500 Hz. The decay dynamics of the gold nanoparticle film was measured by exciting the film with 400 nm laser pulses with pulse energy of 0.2 nJ.

Figure S5 shows the electron relaxation dynamics of oleylamine capped gold nanoparticle films annealed at 50, 180 and 250°C with probe wavelength at their SPR band maximum at 540, 600 and 600 nm respectively. The electron relaxation time becomes faster as the annealing temperature increases. The film annealed at 50 °C exhibited a relaxation time of 1.4 ps. The relaxation time becomes 0.8ps for annealing temperature of 250 °C, which is very close to the relaxation time of bulk gold.¹ As the annealing temperature increases, the metal-amine bond breaks and particles tend to aggregate. The aggregation increases with the increasing temperature due to the removal of alkylamine at higher temperatures. The electron relaxation in aggregated structures can be explained on the basis of the intercolloid electronic coupling within the nanoparticle aggregates. When the film was annealed above the coalescence temperature, the nanoparticles in the film interconnect each other, which provides an extra electron relaxation pathway and results in a faster electron relaxation time. These results suggest that the there is strong coupling within the nanoparticles after annealing the film above the

coalescence temperatures, which is responsible for the dramatic increase of conductivity of the film above the coalescence temperature.

Synthesis of Graphene Oxide (GO)

GO was synthesized from graphite via a modified Hummers and Offeman's method.² 1.5 g graphite flakes (Asbury Carbons Ltd.) and 1.0 g NaNO₃ were placed in 500 mL round bottom flask. 45 mL of concentrated H₂SO₄ was subsequently added into the flask. The mixture was stirred overnight at room temperature. 6.0 g KMnO₄ was then slowly added into the mixture at ice bath to avoid rapid heat evaluation. After 4 hrs the flask was shifted to an oil bath and reaction mixture was stirred at 35 °C for 2 hrs. The temperature was slowly increased to 60 °C and stirred for 4 hrs. Finally, the reaction mixture was added into 40 mL of water and stirred at 90 °C for 5 hrs. The reaction was ended by adding 10 mL of 30% H₂O₂, which resulted in change of colour from yellow to brown. The warm solution was then filtered and washed with 5% HCl and water. The obtained solid was then dissolved in water sonicated to exfoliate oxidized graphene. The oxidized graphene was centrifuged at 1000 rpm for 2 min. After removing all visible graphite particles, it was again centrifuged at 15,000 rpm for 2 hrs. This washing procedure was repeated till the pH became 4-5. For complete oxidation, the above dried GO was further treated with 70% HNO₃ (10 mL of HNO₃/100 mg of GO). The mixture was sonicated for 8 hrs at 60 °C and the sediment was dispersed in water. The obtained GO was purified by washing multiple times with ethanol and water. The product was spin coated onto the silica substrate for AFM image measurements. The AFM images showed that most of the GO sheets are single layer and there are some GO with a few layers. The topographic heights of these GO sheets are 1-2 nm. (See Figure S6 for AFM image).

AFM image of Graphene Oxide (GO):



Figure S6. AFM image of the graphene oxide nanosheets as prepared.

Multi-layer graphene film field-effect transistor (MLG-FET)



Figure S7.Graphene based filed-effect transistor. Inset shows the optical microscope image of the prepared FET and schematic representation of the reduced GO thin film FET.



Figure S8. Resistance measurement of the reduced graphene film prepared on Si/SiO₂ substrate for FET measurements.

Here we employed gold nanoparticles as printable electrodes for source and drain contacts on a multi-layer graphene film field-effect transistor (MLG-FET) with layer thickness of ~ 15 nm (Fgure S7). GO film derived from small-sized GO flakes with a typical lateral dimension of $\leq 10 \ \mu m$ was drop-casted uniformly onto a SiO₂/Si substrate and annealed at 1000 °C in vacuum to restore the π – electron network. The source and grain were prepared by depositing gold nanoparticles onto the GO film using micropipette followed by annealing the film at 250°C for 5 min. The two-point probe configuration was used to determine the back-gated transistor response. The gate leakage current was limited to 100 pA. The graphene film gave a film conductivity of 2116 S/m (see Figure S8 for the I-V curve) after normalizing geometrical factors. Carrier mobility can be extracted from the linear regime of the transfer characteristics, using $\mu = [(\Delta I_{ds}/V_{ds})(L/W)]/C_{ox} \Delta V_g$ where L and W are channel length (~100 μ m) and width (~2 mm) respectively, C_{ox} is silicon oxide gate capacitance (which is 1.21×10^{-8} F/cm² for a gate oxide thickness of 285 nm), I_{ds} , V_{ds} , and V_g are drain-source current, drain-source voltage (fixed at 1 V) and gate voltage, respectively. Figure S7 shows the transfer characteristics of a typical FET device. P-Type response was reproducibly observed for all devices with a maximum hole mobility of 26.4 cm²/(V·s). The absence of an ambipolar response of the MLG film might be due to

residual hydroxyl groups acting as electron traps.³ We have previously shown that the ntype behaviour could be restored by optimizing several key steps in film processing and device fabrication.⁴ These experiments demonstrated these gold nanoparticle "Inks" could act as attractive materials for printable electrodes and be extended to applications in organic electronics.



Figure S9. Electric I-V characteristics of the Au and Ag nano particle films that were used for photocurrent response.

References:

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