Supplementary information

Gold Nanoparticle-loaded Filter paper: A Recyclable "Dip-Catalyst" for Real-Time Reaction Monitoring by Surface Enhanced Raman Scattering

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Experimental Section

Chemicals. Oleylamine (technical quality, Acros), tetrachloroauric acid trihydrate ($HAuCl_4.3H_2O$), toluene, sodium borohydride ($NaBH_4$), 1-Napthalenethiol (1-NAT), 4-nitrophenol (4-NP) and 4-nitrothiophenol (4-NTP). All the chemical were purchased from Sigma-Aldrich and used them without any further purification. Milli-Q water with a resistivity higher than 18.2 MΩ cm was used throughout the experiments.

Synthesis of the Au NPs. Oleylamine capped Au NPs were prepared in toluene by a previously reported method.[1] In a typical synthesis 50 mg of $HAuCl_4$ that was dissolved in a mixture of 1.0 ml oleylamine and 1.0 ml toluene was quickly injected to a boiling solution containing 2.9 ml. After few minutes of heating, the solution becomes colorless and then finally to red. The reaction was continued for 2 hours under boiling with continuous stirring. After 2 hrs of reaction time, the solution was cooled down to room temperature and then 50 ml of ethanol was added to precipitate the particles. The precipitate was collected by centrifuged (rpm: 5000; t: 10min) and dispersed into the 10ml of toluene solution.

Preparation of Au NP-loaded filter paper. Ordinary filter paper was cut into strips, with 1.3 cm wide and 5.0 cm long. Au NPs were loaded into paper by simply dipped the paper into as prepared Au NPs in toluene for few seconds, followed by drying using hair-dryer and the whole process was repeated for 5 times to obtain bifunctional dip-catalysts. The prepared Au NP-loaded paper substrates were washed with water and ethanol and then dried in oven at 60 °C. In order to remove oleylamine molecules from the Au NPs attached to paper, the substrates were washed by dipping Au NP-loaded paper substrates into 0.2 M solution of $NaBH_4$ for 5 min,[2] followed by rinsed with water and this process was repeated for 5 times and finally dried in oven at 60 °C.

Kinetic studies of the reduction of 4-NP to 4-AP. In a typical reaction, solution of 10 mL, 10^{-4} M solution of 4-nitrophenol was mixed with 10 mL, 0.1 M solution of $NaBH_4$ in a flask under gentle stirring at room temperature. The addition of $NaBH_4$ leads to the conversion of 4-NP to 4-nitrophenolate ions, which have absorption peak at 400 nm. To initiate the reaction, three Au NP-loaded paper strips were immersed into reaction flask and then the reaction progress was monitored by using a UV-visible-NIR spectrophotometer (Agilent 8453) and 1.0 cm path length quartz cuvette. To monitor the reaction, An aliquot of 2.5 mL was withdrawn from the reaction medium at each designated time and dispersed back into reaction medium immediately after the absorbance measurement. As the reaction progresses, the absorption peak at 400 nm, which corresponds to 4-nitrophenolate ions decreased gradually and a peak at 300 nm corresponds to 4-AP increased. The rate of reaction was determined by fitting the reaction kinetics (absorbance at 400 nm vs. time), using the first-order rate equation

$$A_t = A_f + \Delta A e^{-kt}$$

where A_t is the absorbance of the solution at time t, A_f is the final absorbance, and k_{obs} is the obtained first-order rate constant for the reaction.

Catalyst recycling. The catalyst was recycled simply by pulling out from the reaction medium and then rinsed with water, followed by dried in over at 60 °C. The catalytic efficiency of paper strips did not alter even after 20 reaction cycles using the same strips.

Characterization. UV-vis extinction spectra of Au NPs in toluene were recorded using an Agilent 8453 UV-Vis spectrophotometer. TEM images were obtained using a JEOL JEM 1010 microscope operating at an acceleration voltage of 100 kV. SEM images were obtained using FEG JEOL JSM 6700F. For SEM measurements, Au NP-loaded papers were first coated with a carbon by vacuum evaporation to make their surface conductive to minimize charging effects. It was observed that the paper fibers swells under electron beam at higher magnifications.

SERS measurements. SERS measurements were performed using a micro-Renishaw InVia Reflex system equipped with Peltier charge-coupled device (CCD) detector with three excitation wavelengths 633, 785 and 830 nm. In order to measure the SERS activity of Au NP-loaded paper, it was incubated with different concentrations of 1-NAT (or 1-NTP) solutions (2 mL) for 3 hrs, followed by rinsed with ethanol to remove unbound 1-NAT molecules (or 1-NTP). The substrate was mounted on the glass and recorded SERS signals using Raman microscope with 20X objective. Excitation wavelength dependent SERS measurements were performed on a substrate that was immersed in 1 mM 1-NAT (or 1-NTP) solution.

To test the ability of paper strips to monitor the catalytic reaction by SERS, Au NP-loaded paper strips were functionalized with a monolayer of 1-NTP by immersing them in 10^{-4} M NTP solution. The NTP functionalized substrate (1 cm X 0.3 cm) was transferred into a plastic Petri dish and then 50 μL of $NaBH_4$ solution (0.1M) was added to initiate the reaction on the surface of paper. The reaction progress was monitored by the continuous collection of SERS signals (each scan from 200 cm^{-1} to 1800 cm^{-1} took ~1.5 min) from the paper surface during the reaction. In order avoid contact between objective and $NaBH_4$ solution during SERS measurements, 10X objective was used to keep the working distance maximum. In addition, 10X objective collects SERS signals from large area, so the signal intensity is more uniform from point to point on the paper surface.

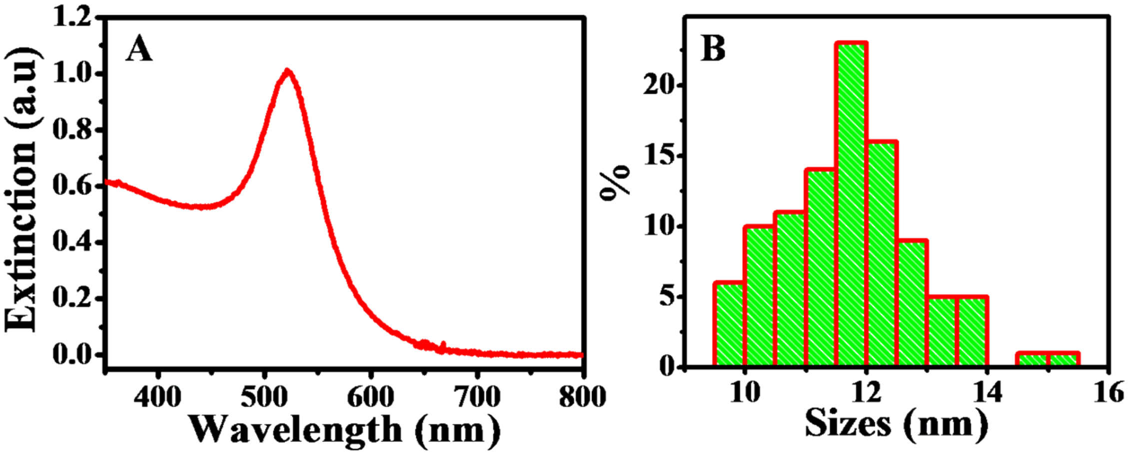


Figure S1. (A) Extinction spectra of Au NPs in toluene, showing surface plasmon resonance at 522 nm (B) Size distribution histogram of Au NPs obtained from TEM images.

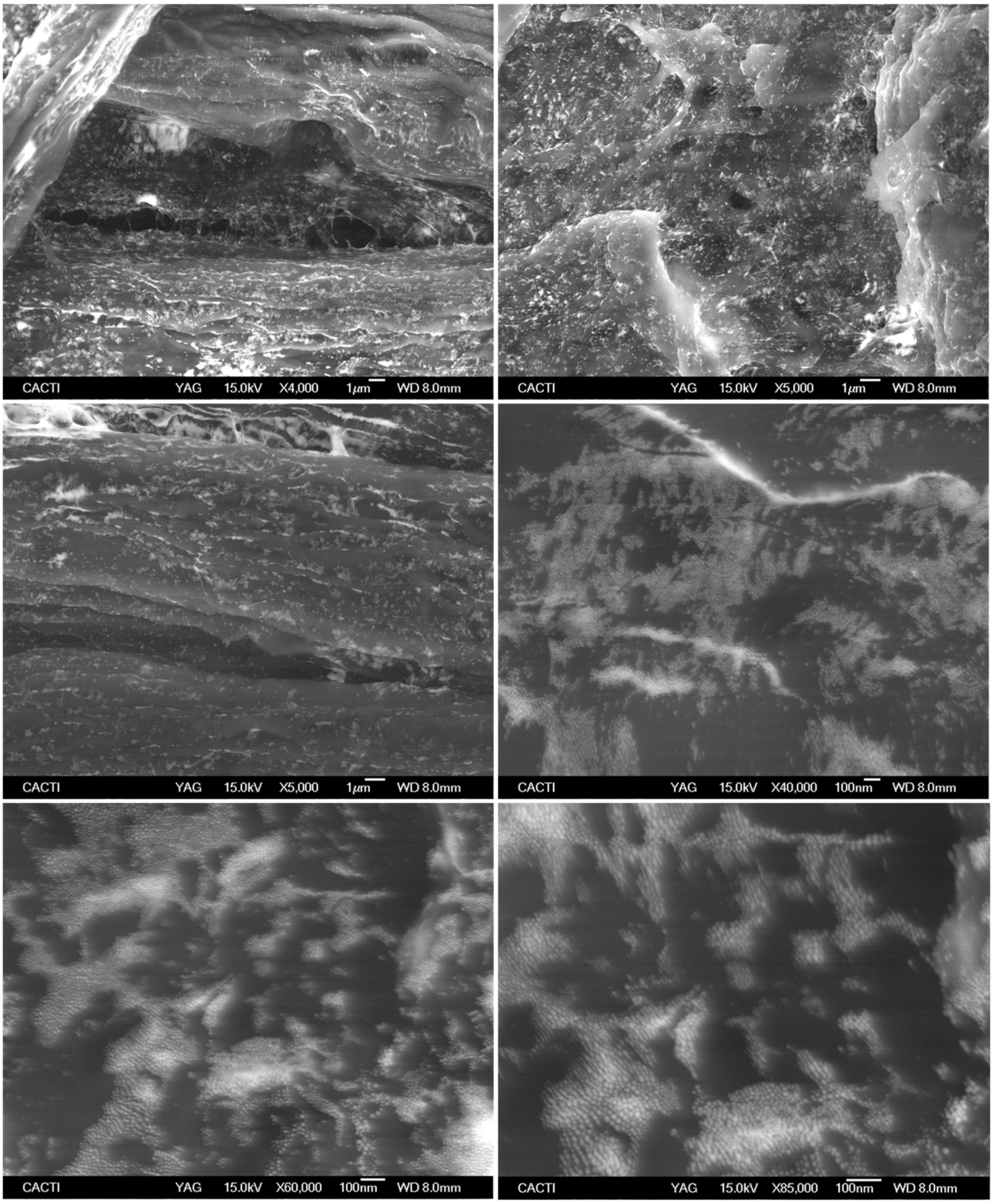


Figure S2. Representative SEM images of Au NPs on paper (after prepared by dip coating process) at different magnifications

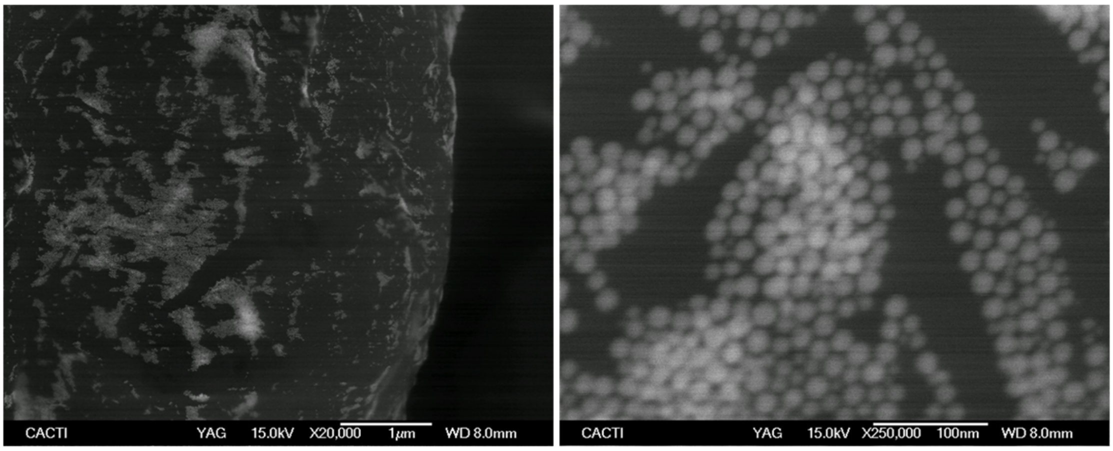


Figure S3. Representative SEM images of Au NPs on paper (after washing process) at different magnifications.

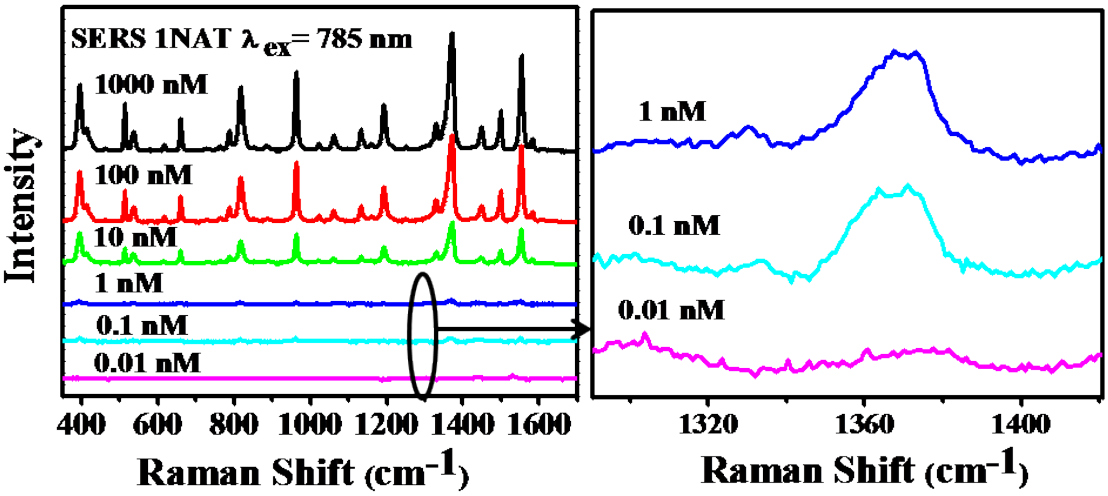


Figure S4. SERS spectra of different concentrations of 1-naphthalenethiol (1NAT) on paper with 785 nm excitation, showing a detection sensitivity of ~0.1 nM.

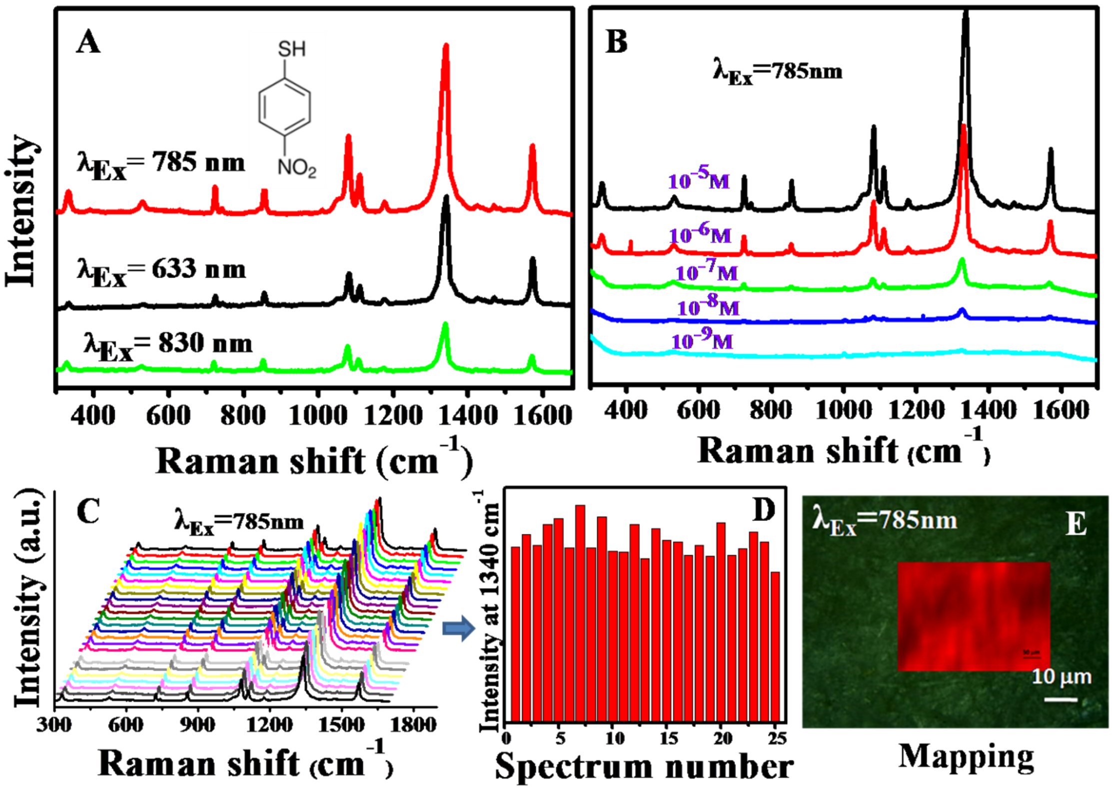
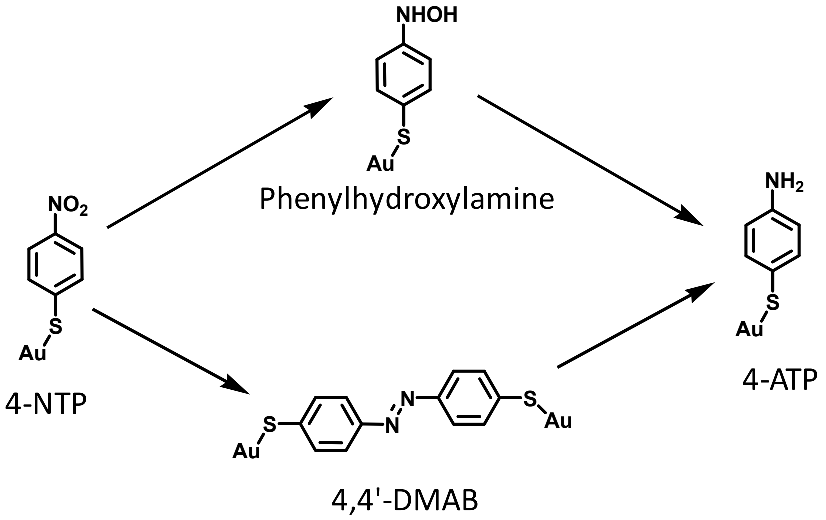


Figure S5. (A) SERS spectra of 4-NTP with three excitation lasers 633, 785 and 830 nm. (B) SERS spectra of different concentrations of 4-NTP on paper with 785 nm excitation, showing a detection sensitivity of ~1 nM. (C&D) SERS spectra of 4-NTP acquired from 25 different spots on Au NP-loaded paper substrate with 785 nm excitation. (E) Optical microscopy image of paper at which the Raman mapping of 4-NTP with 785 nm excitation was performed together with Raman intensity map at 1343 cm^{-1}.



Scheme S1. Intermediates proposed for the nitro to amine (aniline) conversion; a direct route via a hydroxylamine intermediate or via condensation route trough the formation of 4,4'-dimercaptoazobenzene.[3]

References

(1) Hiramatsu, H.; Osterloh, F. E. *Chem. Mater.* **2004**, *16*, 2509.

(2) Ansar, S. M.; Ameer, F. S.; Hu, W.; Zou, S.; Pittman, C. U.; Zhang, D. *Nano Lett.* **2013**, *13*, 1226.

(3) Blaser, H. U. *Science* **2006**, *313*, 312.