Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Amplification of Localized Surface Plasmon Resonance Signal by Gold Nanorod Assembly and Ultra-Sensitive Detection of Mercury

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The Na_3PO_4 concentration is critical to the formation of the stable GNR assembly and influences the length of the chain. At the same GNR concentration, the length of the GNR chain varies with the Na_3PO_4 concentration as illustrated by the absorption spectra in Fig. S1. When the Na_3PO_4 concentration is below 10^{-5} M, no significant change in the longitudinal peak is observed. However, if the concentration is higher than 0.1 M, a new broad peak with a significant red shift emerges, indicating that the PO_4^{3-} concentration influences the length of the GNR assembly chain. Our results show that the GNR assembly is stable when the Na_3PO_4 concentration is between 10^{-2} and 10^{-4} M.

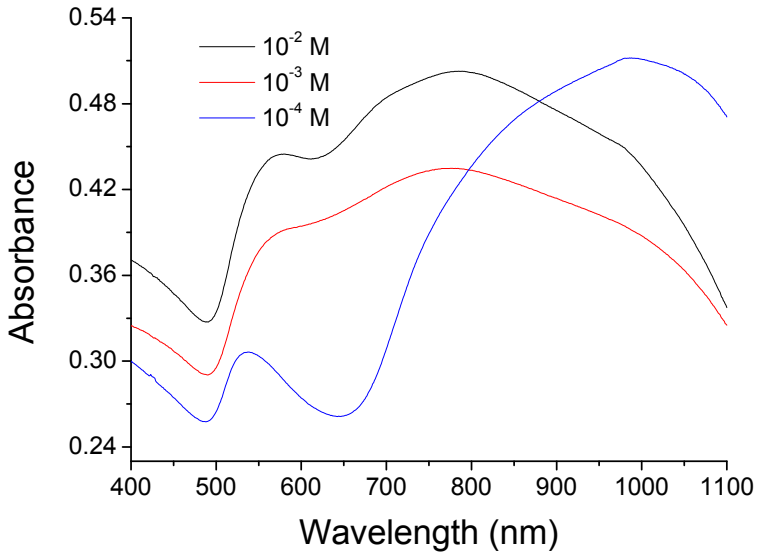

Fig. S1. Effects of concentrations on the Na_3PO_4-induced GNRs assembly.

Reduction of Hg from Hg^{2+} in the aqueous solution changes the coupled plasmon band. The absorption data acquired from the GNR assembly over a period of 2 h

shows no further wavelength changes. With the addition of Hg^{2+}, a significant blue shift is observed in the presence of $NaBH_4$ as shown in Fig. S2. The blue shift in the coupled plasmon band is attributed to amalgamation between Hg and Au. As Hg^{2+} is reduced to Hg by $NaBH_4$, deposition occurs on the surface of the nanorods leading to amalgamation and altered LSPR properties. It is obvious that the surface plasmon resonance signals vary with the concentration of Hg^{2+}. A gradual blue shift in the coupled plasmon peak is observed with increasing Hg^{2+} concentrations. The blue shift in the coupled plasmon band exhibits direct correlation with the Hg^{2+} concentration. High Hg^{2+} concentrations lead to an overlap between the longitudinal and transversal absorption bands. At an Hg^{2+} concentration of 10^{-5} M, only one absorption band is observed, suggesting conversion of the GNR assembly into gold nanosphere assembly (Fig. S3). Because the magnitude of the absorption intensity is directly proportional to the concentration of gold nanorods, one can adjust this parameter to optimize absorption intensity reproducibility. There is a direct correlation between gold nanorods and Hg concentration and that Hg traces are detected only with low nanorod concentrations. Careful investigation of the absorption intensity of the initial gold nanorods led us to set around 0.5, subsequently, the proper amounts of Na_3PO_4 and $NaBH_4$ were added. At last, the detection of Hg^{2+} was performed with the addition of Hg^{2+} sample with multiple runs (n=3). Quantitative analysis might be performed via the successive standard addition method. The reference spectrum was recorded from a 3 mL mixture of solution containing Na_3PO_4, gold nanorods and 5 x 10^{-4} M $NaBH_4$. Then 50 µL of sample solution

containing Hg^{2+} was added, and the corresponding spectrum was recorded. Subsequently, a series of $HgCl_2$ standard solution were added in equal volume increments of 50 μL. Their absorption spectra were recorded after 5 min with the addition of standard solution.

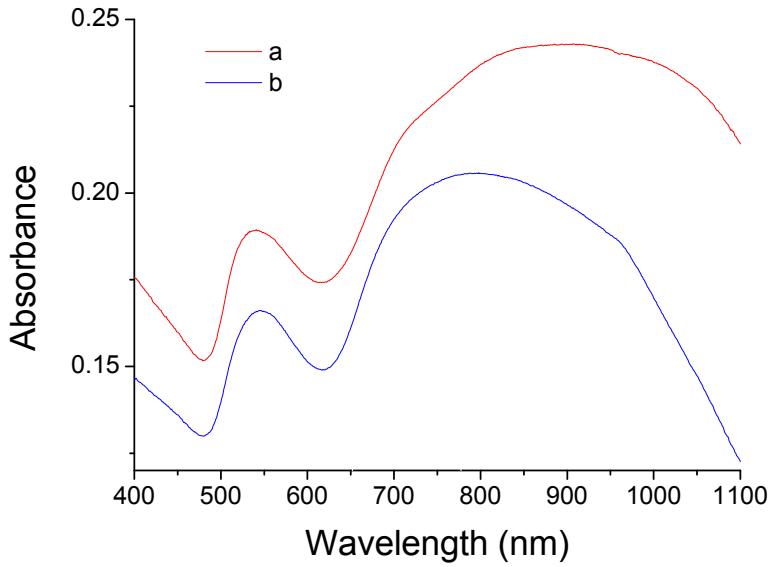

Fig. S2. Absorption spectra of the Na_3PO_4 -induced GNRs assembly: (a) in the absence and (b) in the present of Hg^{2+} and $NaBH_4$.

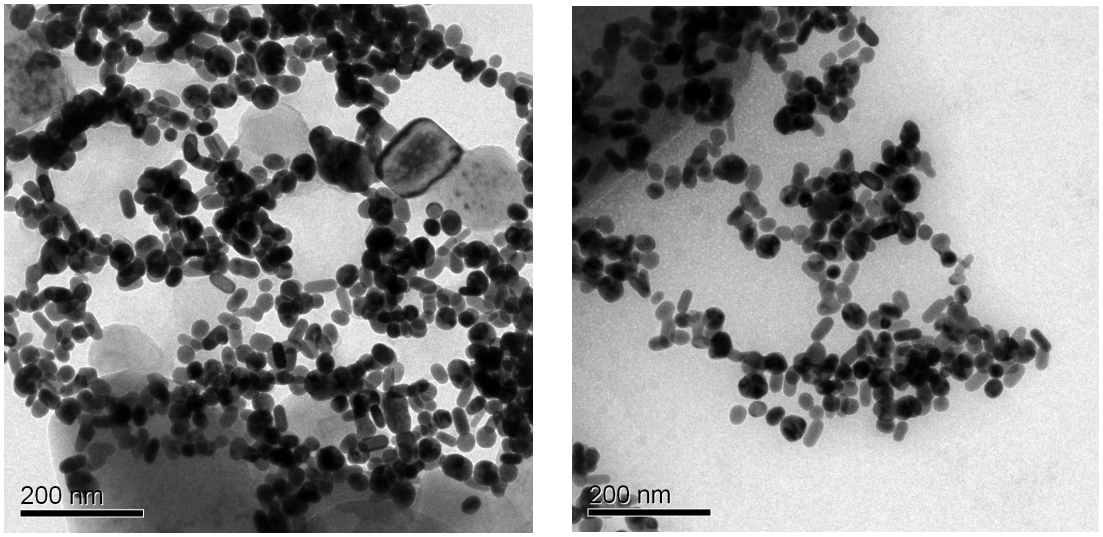

Fig. S3. TEM images obtained from the Na_3PO_4-induced GNR assembly after reacting with Hg^{2+} in the presence of $NaBH_4$.

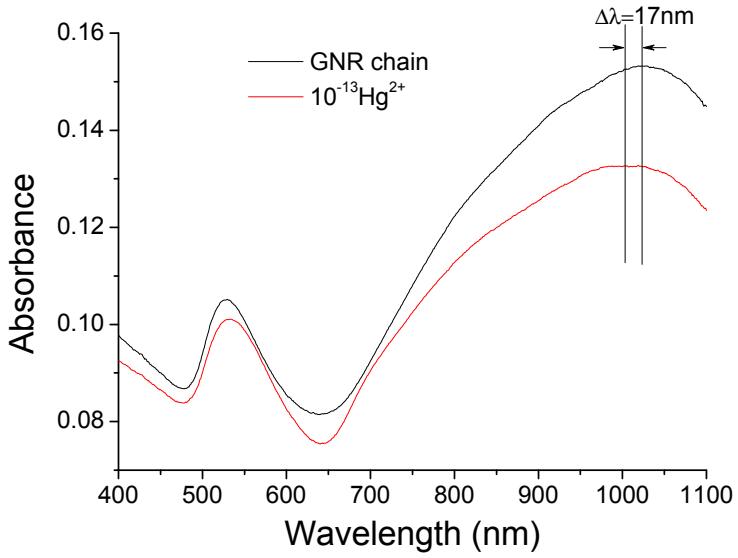

Fig. S4. Absorption spectra of the Na_3PO_4 -induced GNRs assembly in the absence and in the present of 10^{-13} M Hg^{2+} and $NaBH_4$.

The isolated GNRs can detect Hg^{2+} with high sensitivity due to amalgamation between Au and Hg. Fig. S5 illustrates that the absorption spectra of the isolated GNRs change with different Hg^{2+} concentrations. The samples are prepared by adding 100 μL of aqueous $HgCl_2$ with a variable amount of Hg to 1.9 mL of the GNR assembly in the presence of 5 x 10^{-4} M $NaBH_4$. All the spectra are recorded for 5 min after $HgCl_2$ addition and no further spectral shifts can be observed afterwards. The TEM image in Fig. S6 shows that the aspect ratio of GNR changes significantly.

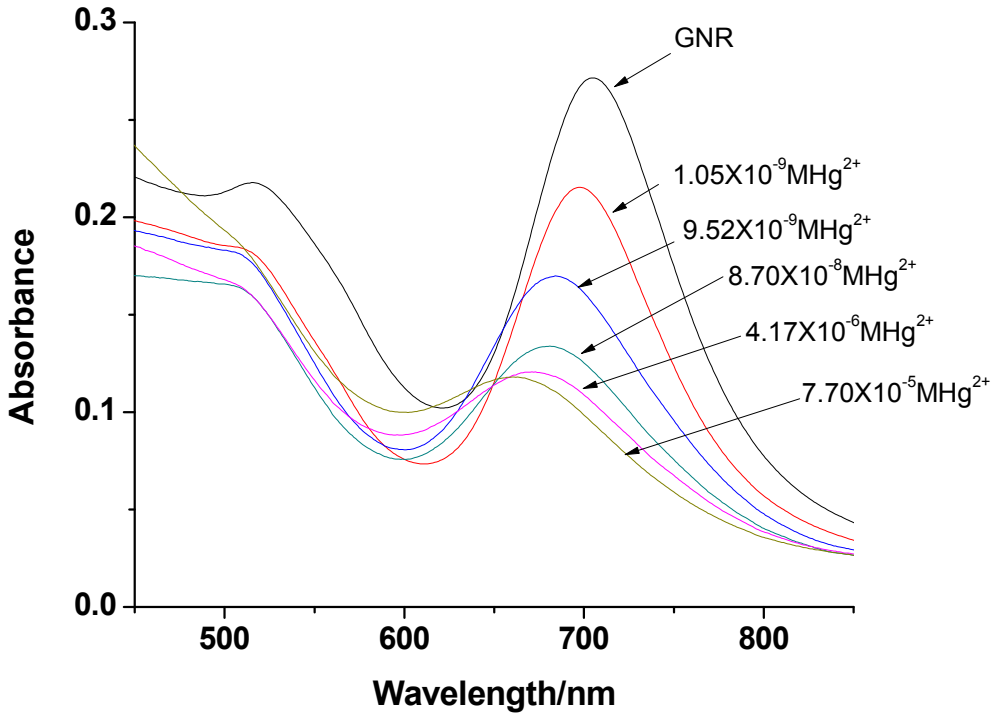

Fig. S5. Absorption spectra showing the spectral shift at various Hg^{2+} concentrations.

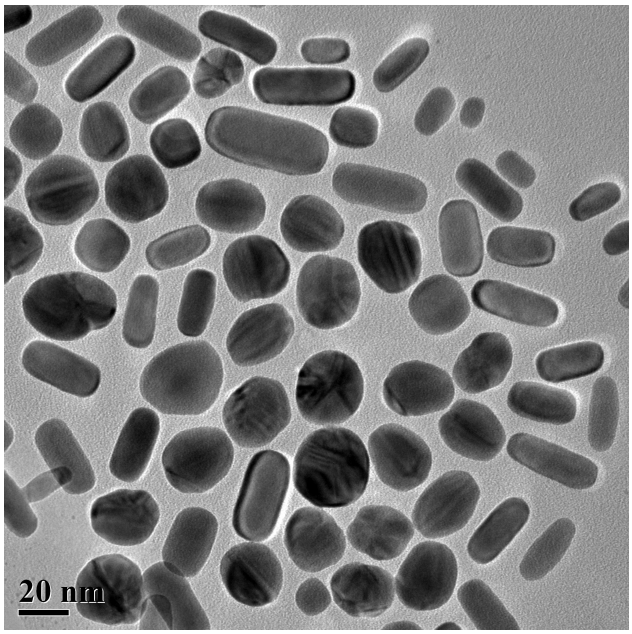

Fig. S6. TEM image obtained from the isolated GNR after the reaction with Hg^{2+} in the presence of $NaBH_4$.