# Supplementary Information

# Combinatorial array of gold nanoparticle with dyes for colorimetric sensing of metal ions

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## *Materials and apparatus*

Three benzylamine dyes (BD), rhodamine B (RB) and methylene blue (MB) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan), malachite green (MG) was purchased from Toronto Research Chemicals (Canada). Chloroauric acid ($HAuCl_4$) and mercury chloride were purchased from Sigma-Aldrich (USA). Sodium citrate, zinc and cadmium chlorides, manganese, ferrous and copper sulphates, nickel and lead nitrates, and other reagents were of analytical grade. All solutions were prepared with double-distilled water. Phosphate buffer solutions (PB, 0.05M) with various pH values were prepared by mixing stock standard solutions of $Na_2HPO_4$ and $NaH_2PO_4$.

An UV–Vis spectrophotometer (UV-2450, Shimadzu) was used to carry out spectral measurement, transmission electron microscopy (TEM, TECRAI20, Philips) was used for characterization of gold nanoparticles.

## *Preparation of GNP–BD sensor array*

Gold nanoparticles with uniform size and monodispersion were prepared by the traditional Frens synthetic (citrate reduction) method [1]. The average diameter of the particle was determined by TEM to be 10 ± 1 nm (see Fig. 1), the concentration of the particle was calculated from its absorption spectroscopy to be ca. 15 nM [2]. Then, 2 nM GNP was mixed with 1 μM BD under a selected pH value, which is controlled by 10 mM PB. Finally, a 3 × 3 array (S1 ~ S9, see Fig. 2) were constructed by combining GNP with the three dyes of RB, MG and MB, respectively, under the three pH of 6.6, 7.2 and 7.8, respectively.

*Combinatorial sensing of metal ions*

Visible spectra were scanned from 400 to 800 nm to measure the change in absorbance before and after the metal ions were added to the sensor. After addition of samples, the absorption spectra were to be unchanged in only several minutes. As control experiments, the metal ions were also added to the individual GNP and dye solution, respectively, which demonstrated almost unchanged spectra (data not shown).

For one metal ion, a series of absorbance shifts at the maximum absorption wavelengths of the GNP and dyes were obtained by the array (Fig.3 shows the spectral changes as addition of $Pb^{2+}$ to the sensor S3, S6 and S9, respectively). The relative shifts in absorbance to that without metal ions ($\Delta A/A_0$) were treated as the relative signal change in the array to generate a characteristic pattern. Each tested sample was repeated three times. All the standard deviations of relative signal changes were less than 0.5%, and the relative signal change greater than 2% was treated as a meaningful response.

All response patterns were analyzed using the PCA method to give an objective result. The PCA score plots grouping the observations and decreasing amounts of variance, and the loading table expressing the relative contributions of the original variables were used to discriminate metal ions and select sensors.

For detection of metal ions in environmental water samples (river water samples collected from Chongqing), none and different levels of various metal ions were added to the samples. Each assay was repeated three times, only the one that all sensors generated meaningful responses repeatedly was read out as the positive, otherwise as the negative.

## References

**1.** G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20.

**2.** P.K. Jain, K.S. Lee, I.H. El-Sayed and M.A. El-Sayed, *J. Phys. Chem. B*, 2006, 110, 7238.

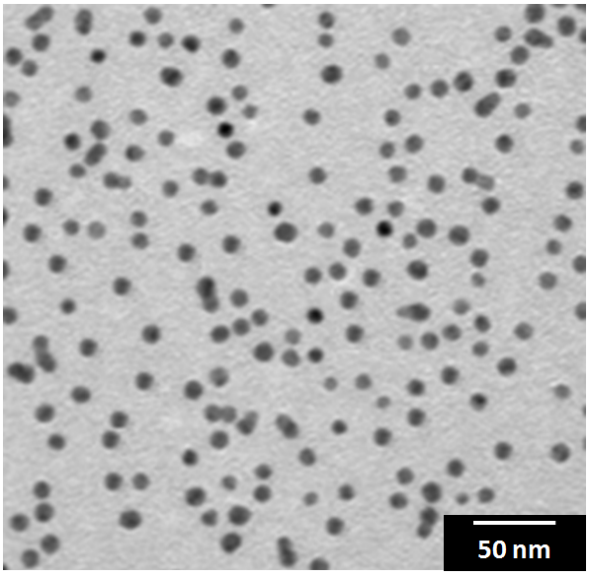
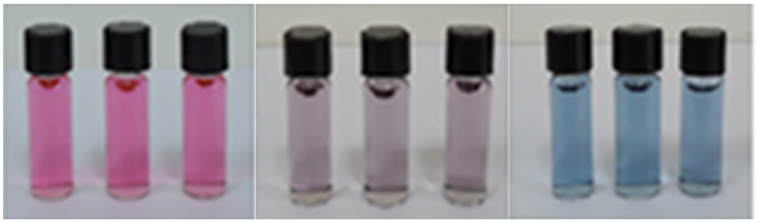



**Fig. 1** TEM image of the prepared 10 nm gold nanoparticles.

**GNP-RB** **GNP-MG** **GNP-MB**



| Sensor No. | GNP (nM) | Dye (μM) RB | MG | MB | pH |
|---|---|---|---|---|---|
| 1 | 2 | 1 | 0 | 0 | 6.6 |
| 2 | 2 | 1 | 0 | 0 | 7.2 |
| 3 | 2 | 1 | 0 | 0 | 7.8 |
| 4 | 2 | 0 | 1 | 0 | 6.6 |
| 5 | 2 | 0 | 1 | 0 | 7.2 |
| 6 | 2 | 0 | 1 | 0 | 7.8 |
| 7 | 2 | 0 | 0 | 1 | 6.6 |
| 8 | 2 | 0 | 0 | 1 | 7.2 |
| 9 | 2 | 0 | 0 | 1 | 7.8 |

**Fig. 2** Image and composition of the 3×3 sensor array (sensors S1~S9).

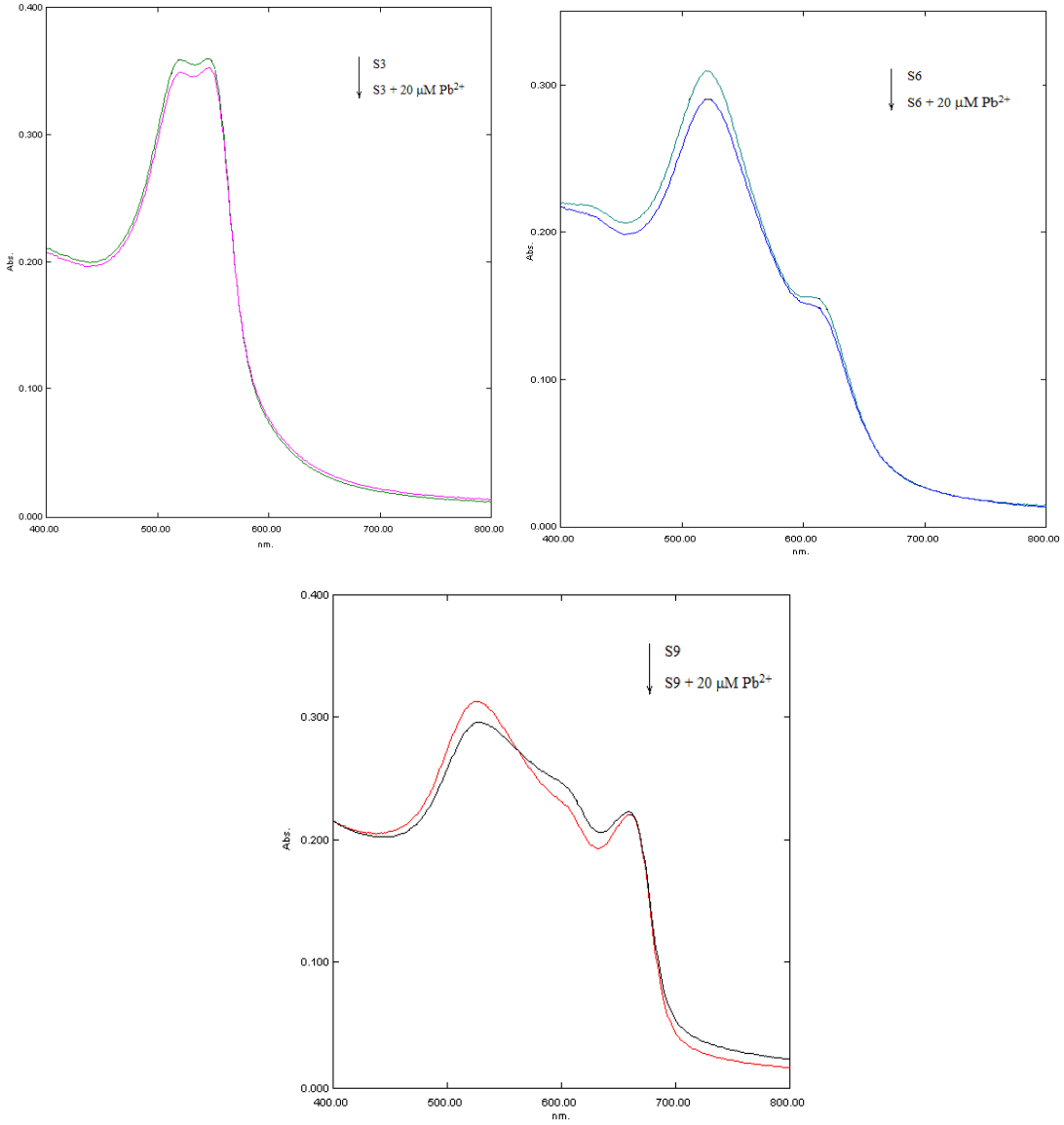



**Fig. 3** Spectral change as addition of $Pb^{2+}$ to the sensor S3, S6 and S9, respectively.