Analytical Methods

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Graphical Abstract

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

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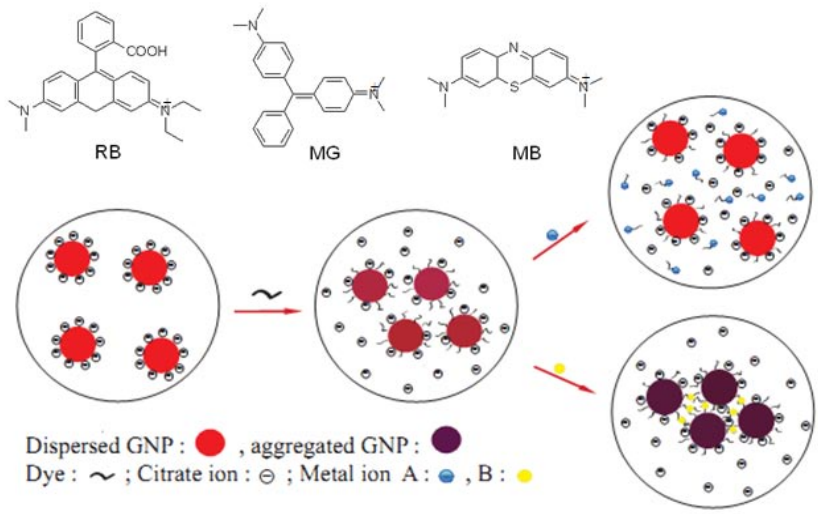

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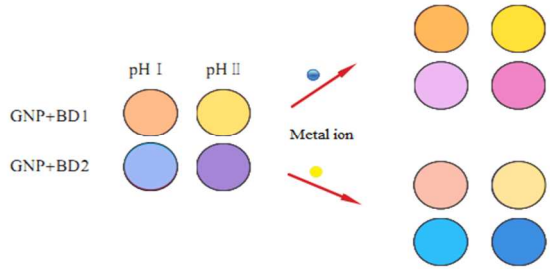
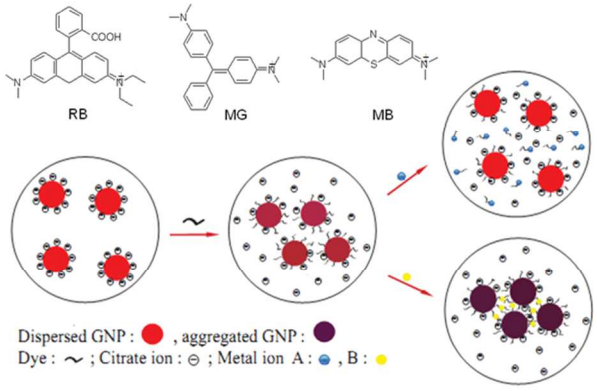
By combining gold nanoparticle with three benzylamine dyes, a minimal size array composed of three sensors was achieved for well discrimination of eight metal ions and their binary mixture.

Inspired by nature, the combinatorial sensing mimics the mammalian tongue and nose for the senses of taste and smell. It utilises a series of sensitive materials that differentially interact with the target and generates a fingerprint-like pattern that is recognized by chemometric tools such as the principal component analysis (PCA). This new strategy of chemo-/bio-sensing offers an alternative to the sensor based on specific recognition and has been attracting great attention.[1] A number of combinatorial arrays have been developed for sensing of various targets, including anions,[2] cations,[3] small molecules,[4] biopolymers,[5] and even cells.[6] Radically, they circumvent the time-consuming design and generation of specific sensors. However, the array-based sensing still faces many challenges including the flexible and diverse generation of receptors, as well as the simple and sensitive transduction of signals.

For sensing of metal ions, the focus of research is shifting to the differential chemosensor, due to the relatively small number of highly specific receptors. For example, a fluorescent sensor array was designed by various conjugated chromophores attached to the receptor hydroxyquinoline.[3a] A unique ratiometric response was resulted from balance of chromophore conjugation and cation coordination. In addition, a sensor system was developed using a fluorescent indicator and a series of thiols.[3b] The thiol switched off the fluorescence, and the metal analyte reversibly bound with the thiol and then modulated the signal. The differential binding of the metal ion with five thiols allowed pattern-based discrimination of five metal ions. Both the protocols hold great potentials, whereas the diversity of these arrays is completely dependent on the molecular structure of its component (indicator or receptor). In a quite different way, metal ions were recognized via changes in electrochemical impedances of chelating electrodes.[3f] Multiple signals (impedances under six frequencies) were acquired with each sensor, so that eight metal ions have been checked out by only two sensors. But, it might be restricted in practical use by need of complicated instrumentation to measure electrochemical impedance spectroscopy.



Scheme 1. Schematic illustration of a combinatorial array of the gold nanoparticle (GNP) and benzylamine dyes (BDs) for colorimetric sensing of metal ions.



Scheme 2. Schematic illustration of interaction among the GNP, the dye and the metal ions.

To meet the above challenges, we present here a novel sensor array constructed by a sort of gold nanoparticle (GNP) and three benzylamine dyes under various pHs (see Scheme 1). In principle, the pattern-based sensing originates from differential interactions of various dyes with the metal analyte. This sensor system has three predominant advantages. First, the GNP endows the sensor with a higher colorimetric sensitivity. It is because surface plasmon resonances of GNPs excited by the visible light would couple with each other in short range. This peculiarity has already been applied in design of numerous optical sensors, based on a subtle change in interparticle space induced by the target.[7] In the proposed sensor, the proximity of particles is dependent on adsorption of the dye on the gold surface, and is changed by interaction of the dye and the metal ion (see Scheme 2). Secondly,

the array diversity could be extended simply and flexibly by only changing the pH of the sensor buffer. Since coordination of the dye's amine group with gold/metal ions is greatly affected by the group's protonation,[8] the sensor buffer can act as a modulator of the differential recognition. Finally, a single sensor gives two optical signals in the visible region from the dye and GNP, doubling the information for one binding event. Therefore, a minimal size array of three sensors was achieved for well discriminating eight metal ions and their binary mixture.

In a prototype, three benzylamine dyes, rhodamine B (RB), methylene blue (MB) and malachite green (MG) were selected to combine with GNP to construct an array for the optical sensing of eight metal ions including Hg^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} and Mn^{2+} (materials and methods see the supplementary information). The optical output of one sensor in the array is characterized by the two absorption signals of the GNP (517 nm) and the dye (552, 616 and 662 nm for RB, MG and MB, respectively) in the visible spectrum, as shown in Fig. 1. It is shown that for the two signals of one sensor only the absorbance was changed while the wavelength remained almost unchanged as the medium pH varied (6.6, 7.2 and 7.8, near the pH of environmental water). Herein, the benzylamine dyes are adsorbed on GNPs through coordination of amine groups with surface gold atoms, replacing the surface-adsorbed citrate ions which stabilize the dispersion of the particles. The exchange of the ionic ligands with benzylamine molecules weakens the electrostatic repulsion between particles, so that the particles are in close proximity and aggregate to some extent (see Scheme 2). Moreover, the strength of the adsorption is affected by the pH of the sensor, which controls the protonation degree of the amine group. As indicated in Fig.1, with varying pH in a narrow range, the change of inter-particle distance was so slight that the shift in the wavelength of GNPs was insignificant. Consequently, GNP and the three dyes were assembled under the three pH to fabricate an array of 3×3 sensors (S1~S9, see the supplementary information).

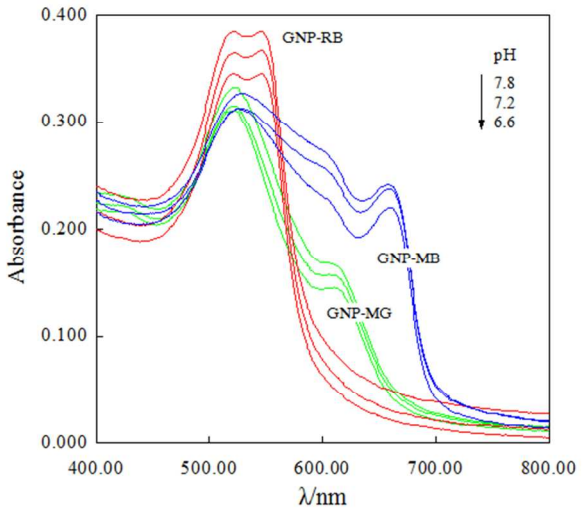


Fig. 1 Spectra of the sensor array composed of gold nanoparticles combined with various dyes under different pH.

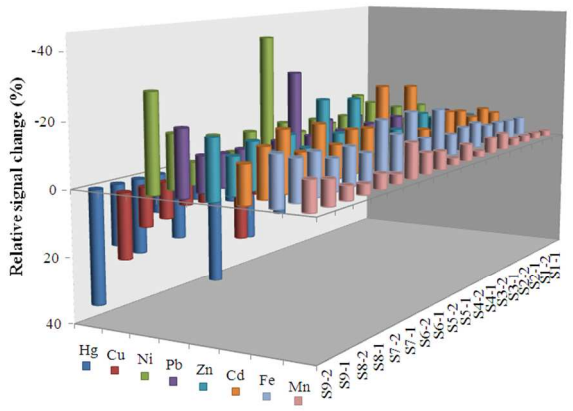


Fig. 2 Response patterns generated by the sensor array to the eight metal ions (20μM). Relative signal change = (A'-A)/A, where A' and A are the absorbance of the sample and the water without metal ions, respectively. The symbols S1-1 and S1-2 denote the signal of GNP and BD of sensor S1, respectively, the others are the similar.

When the array interacted with one metal ion, the optical signals of sensors were changed, resulting in a group of signal changes to produce a response pattern (standard deviations of relative signal changes ≤ 0.5% (n=3), and relative signal change ≥ 2% treated as a meaningful response), as shown in Fig. 2. There were two types of the change for the eight metal ions, that is, increase and decrease in the absorbance. As indicated in Scheme 2, in the former, the metal ion (Hg^{2+}, Cu^{2+}) grabs the particle surface-adsorbed dye due to a stronger complexation with the metal ion than that with the GNP, leading to re-dispersion of the particles. In the latter, the metal ion (Pb^{2+}, Cd^{2+}, etc) coordinates with the dye weaker and couldn't take it away from the particle. Conversely, coordination of the adsorbed dye molecules with this kind of metal ions acts as bridges connecting the particles, leading to a strengthened aggregation.

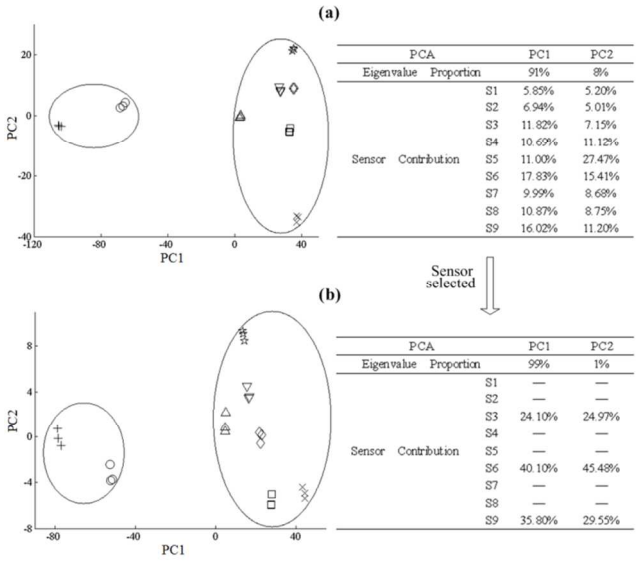


Fig. 3 Reduction of the number of sensor elements in an array using PCA. Score plot (left) and loading table (right) were obtained by (a) the complete set of sensors (S1 - S9), (b) the sensors S3, S6, and S9, for the eight metal ions in 20 μM (+: Hg^{2+}, ○: Cu^{2+}, ×: Ni^{2+}, □: Pb^{2+}, ◊: Zn^{2+}, ☆: Cd^{2+}, ▽: Fe^{2+}, △: Mn^{2+}).

The PCA method was employed to analyze the response patterns of the original 3×3 sensor array to the eight metal ions. It decreases the dimensionality of the array response to simple patterned responses that are comprised of all the individual responses. As can be seen in Fig. 3a, the individual metal ions are obviously discriminated in the score plot, and the contributions of the sensor elements are significantly different in the loading table. Particularly, the score plot could be divided into two regions which are farther apart. One region involves mercury and copper ions, and the other contains the left metal ions, corresponding to the weakened and strengthened styles of aggregation of the particles. In addition, the top three sensors in the loading weights of the array are S6, S9 and S3, which exhibit higher contributions to pattern-based recognition than the other sensors (see the left table in Fig. 3a). It should be noted that the three sensors were composed of the three different dyes under the same pH. It indicates that, in the pH range tested (6.6~7.8), the structure-based differential coordination of dyes plays a more important role than modulation of the interaction with the sensor pH. Finally, the three sensors were selected to reduce the array size to the minimal. The color panel of the selected sensor array in absence and presence of the eight metal ions is given in Fig.4. Although judging by naked-eye, no significant difference can be observed for some ions (e.g. Mn^{2+}), the eight metal ions can be well discriminated by pattern analysis, as illustrated in Fig. 3b. This array was also applied to detect these ions at different levels in environmental water samples (river water samples collected from Chongqing). At the high level (20 μM) all ions were recognized, but at lower levels some couldn't be detected out (Table 1). It indicated that the discriminant ability of the array was different for different ions.

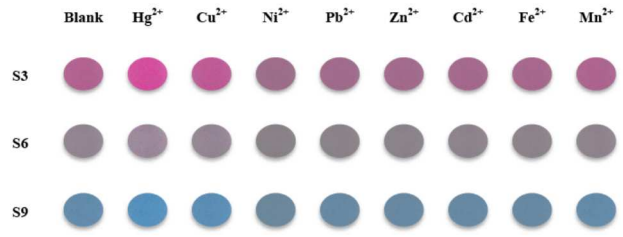


Fig. 4 Color panel of the selected sensor array in absence (blank) and presence of various metal ions (20 μM).

Table 1 Use of the selected sensor array to detection of various metal ions added in river water samples (μM).

Added	Hg^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Fe^{2+}	Mn^{2+}
0	–[a]	–	–	–	–	–	–	–
5.0	+	+	+	–	–	–	–	–
10	+	+	+	+	+	+	+	–
20	+	+	+	+	+	+	+	+

[a] The negative was read out provided one meaningless response (< 2%) was generated.

As metal ions are mostly coexisted in the industrial wastewater, the new array has been adopted to differentiate the binary mixtures of metal ions. For a primary attempt, the minimal size array of the three sensors was used, and lead, zinc, cadmium and manganese ions in the aggregation-strengthened region were selected to compose the binary mixtures. The PCA analysis of the patterns obtained is shown in Fig. 5. It can be seen that the six binary mixtures were well discriminated in the plot. As known, in view of the coordinating ability, the above four metal ions are of little different, further the difference of their binary mixtures should be more insignificant. It should be very difficult to discriminate these mixtures on the basis of the differentiation in coordination. But in fact, these mixtures were well discriminated just by using the sensor array of the minimal size. In our opinion, it may be contributed by the interparticle coupling of surface plasmon resonance. The plasmonic coupling depends upon the adsorption of dye and is affected by interaction with metal ions, which may amplify the differential of metal interaction.

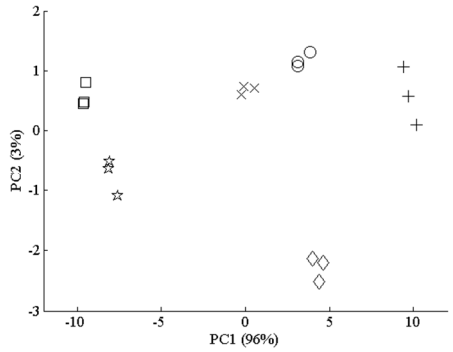


Fig. 5 PCA score plot for binary mixtures of metal ions in 1:1 molar ratio (total concentration of 20 μM). +: Pb^{2+} + Zn^{2+}, ○: Pb^{2+} + Cd^{2+}, ×: Pb^{2+} + Mn^{2+}, □: Zn^{2+} + Cd^{2+}, ◇: Zn^{2+} + Mn^{2+}, ☆: Cd^{2+} + Mn^{2+}.

In conclusion, we have at the first time utilized organic dyes and gold nanoparticles to construct a combinatorial array and realized the visibly optical sensing of individual metal ions and their binary mixtures with satisfactory results. Gold nanoparticles and organic dyes are common and commercially available, and can be optically detected using a portable spectrometer. The combinatorial sensing based on a non-specific receptor array and pattern analysis enables the sensor design be more flexible and simple. In particular, it provides a great power for differentiation relied on that the adsorbed dyes induce interparticle plasmonic coupling. Furthermore, changing the structure of organic dyes together with flexible modulation with pH would lead to recognize more analogues that interact with dyes. The proposed chemical sensor array displays a great potential for practical applications such as initial in-situ screening of heavy metal-contaminated sites in protection of environmental water.

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Notes and references

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† Electronic Supplementary Information (ESI) available: materials and methods for preparation of the sensor array. See DOI: 10.1039/c000000x/

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