Electronic Supporting Information

Sulfite recognition and sensing using Au nanoparticle as colorimetric probe: A judicious combination between anionic binding sites and plasmonic nanoparticles

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1. Experimental section

1.1. Reagents and apparatus

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), 3-mercaptopropionic acid, Melamine, and 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma-Aldrich chemical company, Inc. (USA). Trisodium citrate dihydrate, sodium sulfite, and other inorganic chemicals were obtained from Beijing Chemical Reagent Company (China). They were all used without additional purification. Milli-Q water (18.2 MΩcm) was used throughout the experiment. The room temperature at which the experiment was conducted was 12-14 ^{o}C. To avoid the oxidation of sulfite at their low concentrations, the working solutions of sulfite were freshly prepared by diluting the stock solution (0.1 M) with water.

UV/vis absorption spectra were recorded with a Cary 50 UV/vis spectrophotometer (Varian). Photographs were taken with a Canon PSA490 digital camera (Canon). ESI-MS analysis was performed on a LTQ XL mass spectrometer (Finnigan). The solution sample was dissolved in chloroform and it was infused into the source via a syringe pump at a flow rate of 5 μL/min. The spray voltage was set to 3.5 kV. The capillary voltage was set to 31 V and the tube lens offset to 100 V. The source temperature was set at 275 ^{o}C, and the flow rates for sheath and auxiliary nitrogen gas were fixed at 30 arbitrary units.

1.2. Synthesis of citrate-capped Au NPs

The citrate-capped Au NP of an average 13 nm diameter was synthesized by the Natan's method,[s1] and the synthesis of 28 nm and 43 nm Au NPs was copied from the literature.[s2] Their concentrations were determined by the maximum absorbance at 520, 527, and 534 nm, using the molar absorptivity equal to 2.7 × 10^8, 3.0 × 10^9, and 6.7 × 10^9 $M^{-1}cm^{-1}$, respectively.[s3]

1.3. Reaction between melamine and MPA and Functionalization of Au NP

In a typical experiment, 10 mL of MPA aqueous solution (5 mM) was added with 5 mL of melamine aqueous solution (10 mM) and 9.6 mg of EDC. The reaction temperature was set at 2-4 °C, and the solution was kept stirring for 5 h. Afterwards, the obtained solution was stored at 4 °C. The melamine concentration in the final solution was 3.33 mM.

For the functionalization of Au NP with the thiolated melamine derivative, the solution after reaction was first diluted 100-fold and a specific volume of diluted solution was spiked to Au suspension ensuring a specified melamine/Au molar ratio. After being stirred for 90 min, the Au suspension was stored at ambient conditions for 24 h before analysis. The functionalization of Au NP with melamine or MPA itself was in a similar manner with the previous one.

1.4. The procedure for sulfite detection

Typically, 50 μL of Au suspension (melamine/Au molar ratio = 80) was initially spiked with 1 mM of CO_3^{2-} and different concentrations of sulfite, followed by the addition of 50 μL of buffer (10 mM Tris-HCl, pH = 7.0). After mixing for several seconds, it was incubated for 5 min before the absorbance measurement.

1.5. Sulfite analysis of real samples by the colorimetric sensor

The real samples, i.e. fresh beer, fruit juice and distilled liquor, were subject to no other pretreatment than being diluted by different fold with buffer and centrifuged in special centrifugation tubes filled with a 3 kDa cut-off polymer membrane. After this, it was spiked to the sensor solution (melamine/Au molar ratio = 80;

10 mM Tris-HCl buffer, pH = 7.0; 50 μL Au + 50 μL buffer; [CO_3^{2-}] = 1 mM). To identify the credibility of the assay, standard addition was employed by adding known amounts of sulfite to each sample before the sample dilution. Percent recovery was then measured.

2. Additional figures

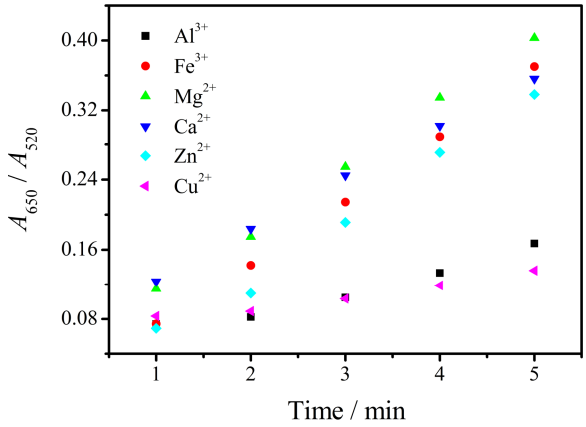

Fig. S1 The kinetic responses of A_{650}/A_{520} ratio within 5 min recording the changes in spectra for the probe in the presence of metallic cations. The buffer was 10 mM Tris-HCl, pH = 7.0, and the melamine/Au molar ratio was 80.

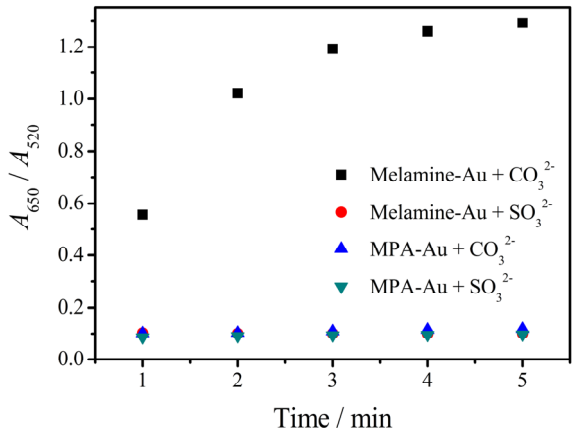

Fig. S2 The kinetic responses of A_{650}/A_{520} ratio within 5 min recording the changes in spectra for individual melamine-Au NP and MPA-Au NP in the presence of carbonate (1 mM) and sulfite (1 mM).

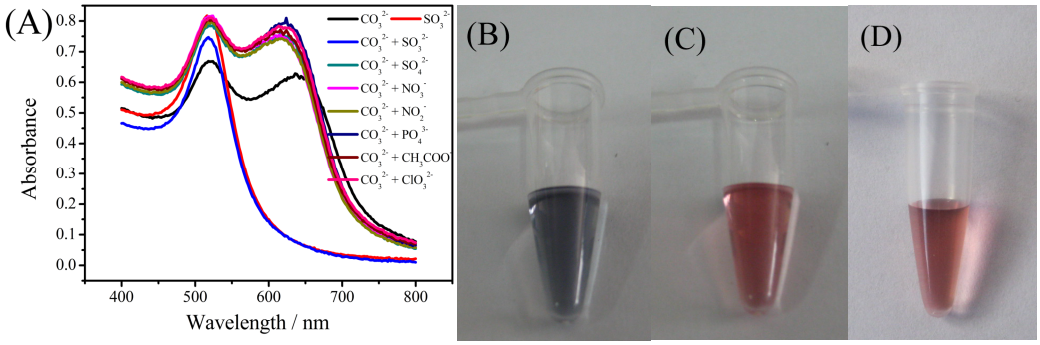

Fig. S3 (A) The spectra of the probe (melamine/Au = 80) in buffer (pH = 7.0, 10 mM) after the addition of carbonate, sulfite, and mixtures of carbonate and another anion for 5 min. The concentrations of all anions were 1 mM. (B-D) Photographs corresponding to the spectra for the probe in the presence of CO_3^{2-}, SO_3^{2-}, and CO_3^{2-} + SO_3^{2-}, respectively.

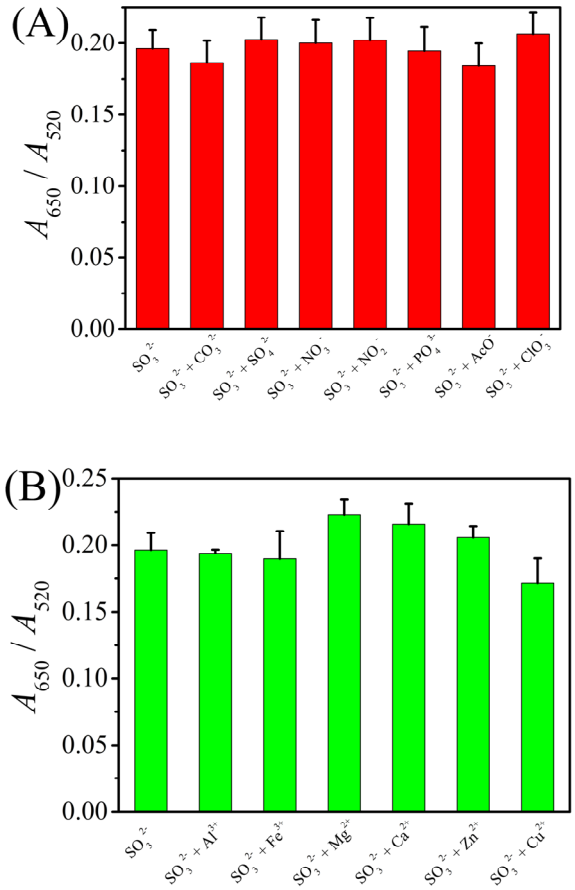

Fig. S4 Effect of (A) anions (100 μM) and (B) metallic cations (100 μM) on the sensing of sulfite (0.5 μM) by the specific probe, for which the buffer was 10 mM Tris-HCl, pH = 7.0, the melamine/Au molar ratio was 80, and the concentration of the added carbonate was 1 mM.

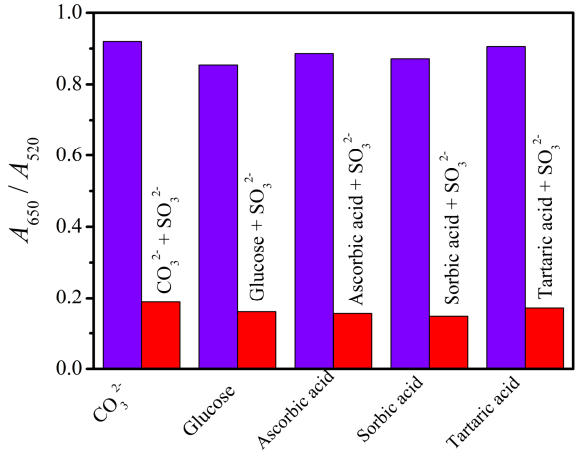

Fig. S5 Influence on the responses by sulfite (0.5 μM) of glucose, ascorbic acid, sorbic acid, tartaric acid (all 0.1 mM). By comparison, influence of carbonate (1 mM) was also shown.

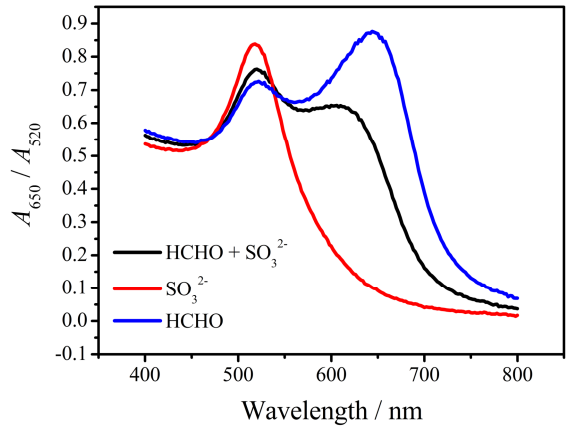

Fig. S6 The spectra of the probe (melamine/Au = 80, [carbonate] = 1 mM) in the presence of sulfite (1 mM), formaldehyde, and mixture of sulfite and formaldehyde, respectively. The buffer was 10 mM Tris-HCl, pH = 7.0, and the incubation time was 5 min.

3. References

s1 K. G. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735.

s2 S. K. Ghosh, A. Pal, S. Kundu, S. Nath and T. Pal, *Chem. Phys. Lett.*, 2004, **395**, 366.

s3 J. Lee, S. I. Stoeva and C. A. Mirkin, *J. Am. Chem. Soc.*, 2006, **128**, 8899.