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ARTICLE TYPE

# A “light-on” colorimetric assay for anions detection using the inhibitory effect of anions on the catalytic activity of metal nanoparticles for the degradation of methyl orange

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**In this communication, we studied the inhibitory effects of anions on the catalytic activity of metal nanoparticles for the degradation of methyl orange (MO). Some anions have great affinity with specific metal nanoparticles, thus resulting in the change of surface state and inhibition of catalytic activity, which can be observed with naked eye or manifested by UV spectrum of MO for anions detection.**

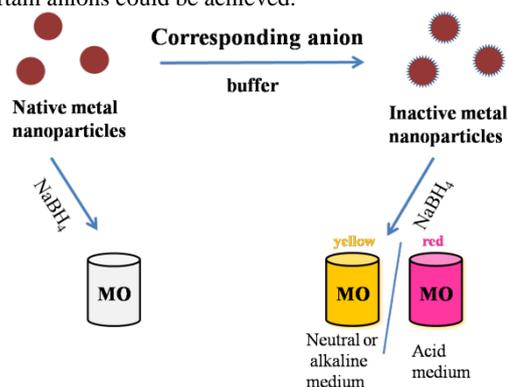
Nanoscale materials are appealing in a wide range of fields covering science and technology currently. Metal nanoparticles, especially, gold and silver nanoparticles (AuNPs and AgNPs) have found great utility on account of their fascinating optical and electronic properties.<sup>1</sup> Moreover, they have attracted great interest as catalyst in both organic and inorganic reactions due to their large surface-to-volume ratio and high surface energy.<sup>2,3</sup> AuNPs, AgNPs and platinum nanoparticles (PtNPs) have widely acted as catalyst in various areas.

Anions play fundamental roles in a great many biological and chemical processes.<sup>4</sup> Increasing attention to the living environment and human health together with the social development make the detection of anions in environmental, medical, and food samples an important issue for analytical chemistry. Towards such purpose, various assays including chromatographic,<sup>5,6</sup> spectrometric,<sup>7,8</sup> and electrochemical methods<sup>9,10</sup> have been developed. Among the reported anion chemosensors, the optical ones, especially colorimetric assays are most eye-catching due to their inherent advantages such as ease of use and observation, economy and convenience. Particularly fascinating are the colorimetric strategies based on AuNPs. Such system features the unique and distinct color changes caused by the transition of AuNPs between dispersed and aggregated states along with a corresponding shift of their surface plasmon absorption spectra.<sup>11</sup> However, laborious premodification of AuNPs is often required.<sup>12,13</sup> Therefore, there is still urgent demand for new methods and probes for the detection of anions, which are convenient, simple, cost-effective and less labor-intensive.

Recently, novel colorimetric sensors have been developed based on analyte-induced inhibition of the catalytic activity of nanoparticles, thereby inhibiting the color evolution of TMB, OPD or ABTS.<sup>14,15</sup> Tseng et al. found that catecholamine could be covalently attached to the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, thus

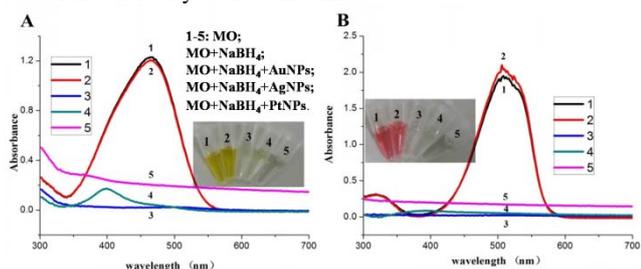
would effectively inhibit the Fe<sub>3</sub>O<sub>4</sub> nanoparticles-catalyzed H<sub>2</sub>O<sub>2</sub> oxidation.<sup>16</sup> Metal nanoparticles have great affinity to anions, especially AuNPs and AgNPs. Based on this, many effective sensors for anions such as I<sup>-</sup>, S<sup>2-</sup> have been developed.<sup>17-19</sup> However, few anion sensors<sup>20</sup> based on their inhibitory effects on the catalytic property of nanoparticles have been reported.

It was reported that metal nanoparticles capped by tannic acid serve as high-efficiency catalysts to trigger the bleaching reaction of methyl orange (MO), a colored azo dye. A color fading could be observed when the dyes were degraded. The reduction of MO by NaBH<sub>4</sub> in the absence of catalyst is thermodynamically favored, while kinetically constrained.<sup>21</sup> Metal nanoparticles could decrease the activation energy, thus remarkably accelerate the reaction rate. In this work, we dissected the effects of anions on the catalytic activity of metal nanoparticles in degradation of MO. Based on the experiment results, selective and quantitative determination of certain anions could be realized. The detection principle is depicted in Scheme 1. In a basic or neutral solution, MO appears yellow and shows a characteristic absorption peak at 464 nm, while in solutions with pH value below 3.1, it exists as a red dipolar ion through protonation, exhibiting an absorption band at 508 nm. The degradation of MO by NaBH<sub>4</sub> could be easily realized with the catalysis of native metal nanoparticles. However, the catalytic process was inhibited in the presence of certain anions, which could be manifested by naked-eye observation or UV-vis spectrum. Based on this feature, detection of certain anions could be achieved.



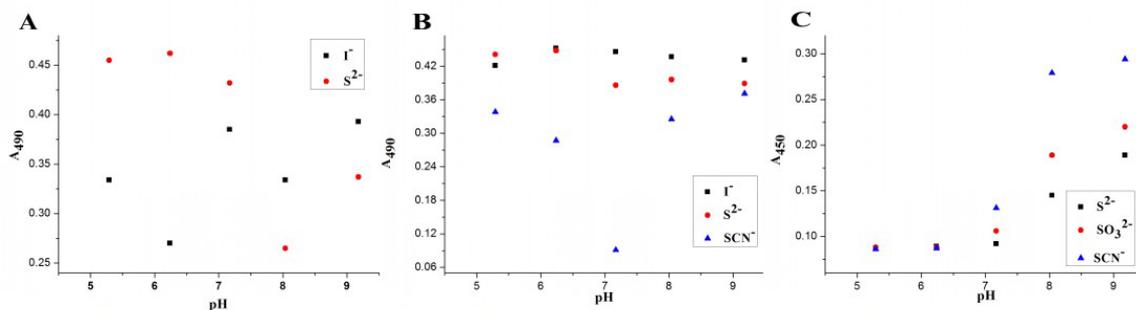
<sup>75</sup> **Scheme 1.** Scheme illustration of the colorimetric sensor for anions based on the inhibition effects on the catalytic activity of metal nanoparticles in the decolorization of MO.

In this study, we chose citrate-capped metal nanoparticles considering their universality. On the other hand, similar to tannic acid, citrate ions as stabilizing agents can be readily replaced. Thus, we speculated that citrate-capped nanoparticles would catalyze the bleaching reaction of MO as well. Fig. 1A reveals the ability of metal nanoparticles to catalyze the reduction of MO by NaBH<sub>4</sub>. The color of MO was yellow in near neutral medium, and the reduction of MO could not occur in the absence of the nanoparticles, even with a large excess amount of NaBH<sub>4</sub> and a long incubation time, as evidenced by the unchanged color of solution and the absorbance at 464 nm. However, once the metal nanoparticles were introduced, the color of MO vanished quickly. The termination of this reaction could be realized by hydrochloric acid (HCl) due to its ability to rapidly consume excess NaBH<sub>4</sub>. After the addition of HCl, the color of MO alone and MO with NaBH<sub>4</sub> changed to red while that with metal nanoparticles as catalyst remained colorless as shown in Fig. 1B. Moreover, the sensitivity might be greatly improved by measuring the absorbance of the acidic form of MO at 508 nm instead of 464 nm, since the absorbance intensity of the acidic form (red) of MO at 508 nm is approximately 1.6 times as that of its corresponding basic (yellow) form at 464 nm with the same concentration. Therefore, in this study, a HCl solution was employed considering that it not only served as the terminator of the decolorization reaction of MO, but also helped to improve the detection sensitivity at the same time.



**Fig. 1.** The absorbance spectra and photographs (inset) of MO in the presence of different reactants (A) before and (B) after the addition of HCl (0.1 M). MO: 50  $\mu$ M, NaBH<sub>4</sub>: 0.15 g/L; the incubation time: 2 min.

Firstly, we studied the amount of metal nanoparticles required for the degradation of MO (Fig. S1, ESI). A 2-min incubation was allowed for the decolorization reaction before the addition of HCl, followed by the absorbance measurement. In order to simplify the operation and improve the measurement efficiency, 96-well microplate was employed and the absorbance was measured on a microplate reader using detection system with fixed wavelengths of 405 nm, 450 nm, 490 nm and 630 nm. So we chose 490 nm



**Fig. 2.** The absorbance of MO in the presence of NaBH<sub>4</sub> and different anions with the catalysis of (A) AuNPs, (B) AgNPs and (C) PtNPs at different pH values. The concentration of anions: 100  $\mu$ M.

and 450 nm as the detection wavelength, which are close to the maximum absorption wavelength 508 nm and 464 nm respectively. Thus, multiple samples could be detected at the same time. It is worth noting that for PtNPs, the original yellow color of solution turned colorless upon the addition of HCl even with small amount of PtNPs. This might be due to that the catalytic effect of PtNPs in strong acidic conditions was too great. In this case, colorimetric detection of ions could not be accomplished by measuring absorbance at 490 nm. So the absorbance at 450 nm before the addition of HCl was employed for the whole experiment involving PtNPs. The optimal amount of nanoparticles was set as the minimum value needed for the completion of the reaction, namely both 4  $\mu$ L for AuNPs, AgNPs 3  $\mu$ L for PtNPs. Next, a number of anions were tested to investigate their inhibitory effects. In a typical procedure, metal nanoparticles and anions were mixed thoroughly to ensure a complete interaction before the addition of MO. Then after 2 min, HCl was added to terminate the reaction. We found that for all these three kinds of metal nanoparticles, PO<sub>4</sub><sup>3-</sup> exhibited no inhibitory effect on their catalytic ability. Therefore, we screened the anion inhibitors in phosphate buffer system. The results revealed that the same anions had different impacts on the three kinds of metal nanoparticles (Fig. S2, ESI). Each kind of nanoparticles responded to some specific anions. I<sup>-</sup>, S<sup>2-</sup> and SCN<sup>-</sup> acted as inhibitors for AuNPs, I<sup>-</sup>, S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> for AgNPs, while S<sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> and SCN<sup>-</sup> exhibited obvious inhibitory effect on PtNPs. The properties of nanoparticles are bound up with the surface condition. We deduced that certain anions interacted with the active sites of specific metal nanoparticles, thus resulting in surface passivation and deactivated catalysis, which could be observed by the color evolution.

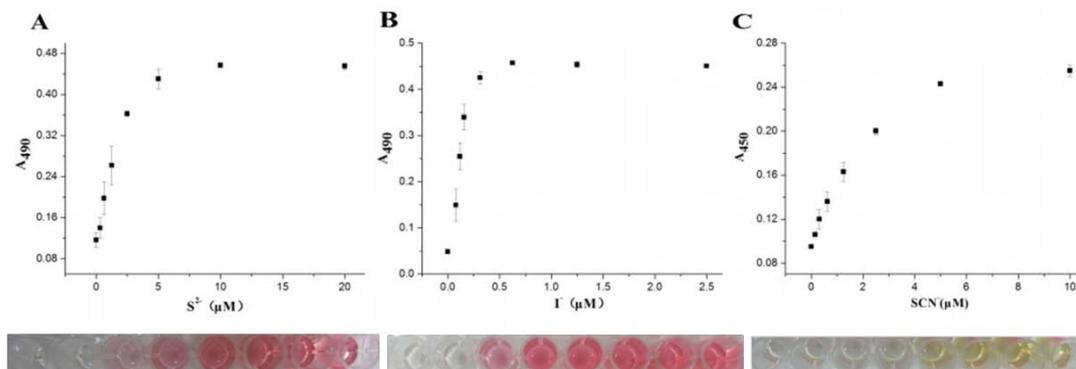
If the selectivity of the inhibitory effect can be improved, a simple way to determine some “poisoning” anions can be provided. It is well known that anions exist in different forms at different pH values depending on its pK<sub>a</sub>, which would have an impact on the electrostatic interaction between the ions and the nanoparticles, thus affecting the ligand exchange and the inhibition efficiency. Therefore, we studied the role of pH value in affecting the selectivity and the results are shown in Fig. 2. For AuNPs, S<sup>2-</sup> gave the largest response while I<sup>-</sup> had a minimum response at pH 6.24. This selectivity provided a simple colorimetric way to detect S<sup>2-</sup>. For AgNPs, SCN<sup>-</sup> had no response while I<sup>-</sup> had a maximum response at pH 7.17. The response of S<sup>2-</sup> could be eliminated by the addition of Pb<sup>2+</sup> (Fig. S3, ESI). For PtNPs, the largest difference of response between SCN<sup>-</sup> and other

two anions appeared at pH 8.04. Thus,  $S^{2-}$ ,  $I^-$  and  $SCN^-$  could be selectively detected by AuNPs, AgNPs and PtNPs respectively at different pH values.

Furthermore, the reaction time of anions with the metal nanoparticles is another crucial factor (Fig. S4). For AuNPs,  $A_{490}$  reached the maximum when the incubation time was 10min. For AgNPs,  $A_{490}$  increased as the incubation time prolonged and reached the maximum at 4 min, and then decreased. Thus, the final reaction time was set at 4min. While for PtNPs, we chose 2 min as the reaction time considering that the reaction time had little impact on  $A_{450}$ .

Under the optimal conditions, various amount of  $S^{2-}$ ,  $I^-$  and

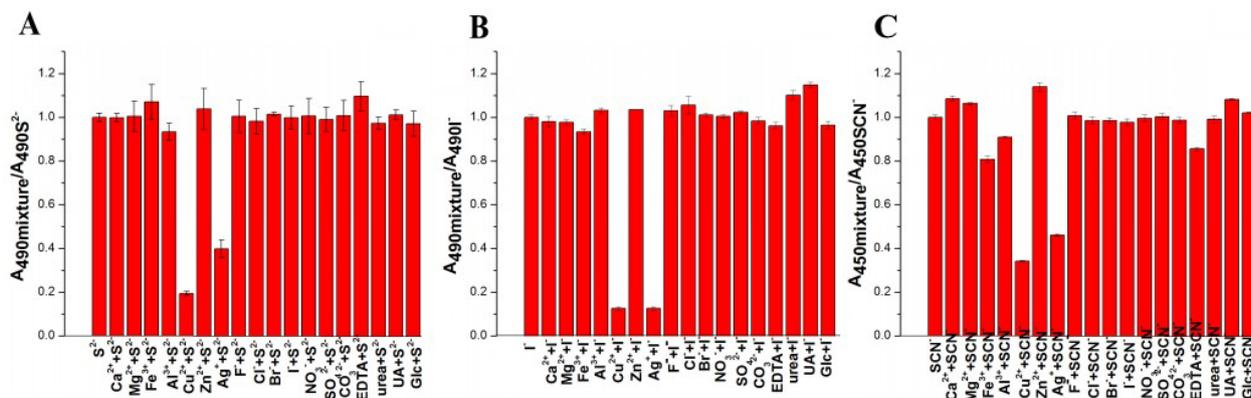
$SCN^-$  were incubated with AuNPs, AgNPs and PtNPs respectively to monitor the inhibitory effects. The results are shown in Fig. 3. As the concentration of anions increased, the color evolution was inhibited gradually, thus the absorbance increased rapidly and then tended to be stable, meaning the catalysis was completely suppressed. The photograph shows the corresponding color changes. Compared with previous reported colorimetric sensors,<sup>17,18,22</sup> this “light-on” probe exhibited higher sensitivity. Using AuNPs as the catalyst, the color evolution can be obviously observed with even down to  $0.325 \mu M S^{2-}$ . For AgNPs, as low as  $100 nM I^-$  can be detected easily, and  $0.156 \mu M SCN^-$  can be detected using PtNPs with naked eyes.



**Fig. 3.** The absorbance of MO (A) in the presence of different concentrations of anions (A:  $S^{2-}$ ; B:  $I^-$ ; C:  $SCN^-$ ) with the catalysis of metal nanoparticles (A, AuNPs; B, AgNPs; C, PtNPs) and the corresponding photographs.

In order to examine the feasibility of practical application, the interferences of common ions and organic compounds were studied. As can be seen from Fig. 4, they all didn't exhibit obvious interferences due to the negligible chemical activity of metal nanoparticles with them except for  $Cu^{2+}$  and  $Ag^+$ . However,

$S^{2-}$ ,  $I^-$ ,  $SCN^-$  are all incompatible with  $Cu^{2+}$  and  $Ag^+$ , so the interferences from  $Cu^{2+}$  and  $Ag^+$  need not be considered.<sup>23</sup> Moreover, we applied this assay to real samples and the results shows the potential value in practical application (Table S1, ESI).



**Fig. 4.** Interferences study of the sensors (A, AuNPs; B, AgNPs; C, PtNPs) in the presence of a mixture of the analyst and another foreign ion ( $20 \mu M S^{2-}$ ,  $2.5 \mu M I^-$ ,  $10 \mu M SCN^-$ ,  $0.1 mM$  other ions and organic compounds). The error bars were estimated from three independent measurements.

Finally, TEM test was carried out to take us to a deeper insight into the mechanism of the inhibitory effects (Fig. S5, ESI). All the three kinds of metal nanoparticles were well dispersed in solution before the addition of anions. However, AuNPs and PtNPs aggregated upon the addition of  $S^{2-}$  and  $SCN^-$  respectively while AgNPs still kept dispersed after the addition of  $2.5 \mu M I^-$ . But further study showed that AgNPs aggregated with the

increase of the concentration of  $I^-$  (data not shown), indicating that the specific anions attached to the corresponding metal nanoparticles to interact with the surface atoms and ions [24], replaced a part of citrate ions and resulted in the change of the surface state and charges, thus affecting their catalytic abilities.

## Conclusions

In conclusion, we have dissected the effects of anions on the catalytic ability of three kinds of metal nanoparticles. Under optimal conditions, a simple and sensitive determination of anions could be easily realized with naked eye, exploiting bleaching of dyes as novel indicator. Moreover, this assay allows multiple samples to be recorded in a few minutes with very low detection limit. The selectivity of this assay was excellent. AuNPs, AgNPs and PtNPs could be employed for the specific determination of  $S^{2-}$ ,  $I^-$  and  $SCN^-$  respectively. Such studies not only open up the application of metal nanoparticles, but also provide a novel colorimetric route to the detection of ions and small molecules.

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## Notes and references

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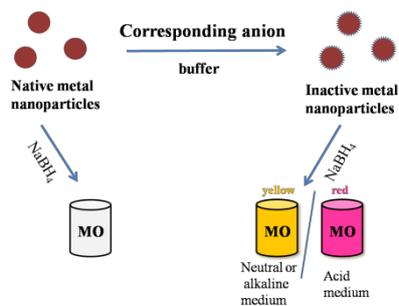
<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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A “light-on” colorimetric method for anions detection using the catalysis ability of metal nanoparticles for MO degradation was developed.