NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

NJC

LETTER

Highly sensitive and selective colorimetric sensor for the detection of Mn^{2+} based on Supramolecular silver nanoparticle clusters

Ren Hu, Liang Zhang and Haibing Li[*]

A highly sensitive and selective colorimetric sensor for the detection of Mn^{2+} based on the aggregation of functionalized silver nanoparticles (Ag NPs) had been developed. The Ag NPs were decorated with β-cyclodextrin (β-CD) and assembled into clusters with adamantine (ADM). The detection limit for Mn^{2+} was found as low as 5×10^{-7} M.

Manganese is an essential nutrient which is important for a normal process in our body. However, overdoing exposure to Manganese may result in manganism.[1] The intoxicated person may suffer depression, mood swings, compulsive behaviours and psychosis.[2] Therefore, a lot of optical methods for detecting Mn^{2+} have been developed, such as atomic absorption spectrophotometry (AAS),[3] inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).[4] Nevertheless, most of them require sophisticated equipment and complex procedures, which makes them inconvenient and time-consuming.[5] On these scores, the development of sensitive, selective, and simple sensing strategy for the detection of Mn^{2+} is still urgently necessary.

Colorimetric methods, which have extraordinary sensitivity to the applications in the detection with metal ions, having attracted great attention and become the effective means, moreover, they can be understood with the naked eyes, in some cases at the point of use.[6] To date, there are various colorimetric sensors based on the functional metal nanoparticles (NPs).[7] Silver nanoparticles(Ag NPs) are extremely attractive because of their remarkable optical, electrical and chemical properties, as well as the detection with minimal material consumption.[8] However, a critical drawback of these methods is poor sensitivity, therefore, it would be desirable to design a colorimetric sensor to enhance the sensitivity of this detection.

Recent studies have shown that the self-assembly technique has been regarded as an effective strategy to enhance the sensitivity of colorimetric sensors.[9] For example, Velders and his co-workers have reported that the sensitivity of nanoparticle sensors can be boosted by assembling the nanoparticles into clusters through multivalent host-guest interactions.[10] Nogami has demonstrated a simple strategy for self-assembling silver nanochains on glass substrates that can enhance several orders of magnitude in the metal chainlike aggregated and are responsible for the enhanced SERS signals.[11] In conclusion, we construct a colorimetric sensor based on the self-assembly of Ag NPs, furthermore, due to the interface modification, the functional metal nanoparticles formed aggregates with the substrate, leading to enhance the sensitivity of nanoparticle sensors.

In recent years, nanometer-sized supramolecular assemblies created by the simple inclusion complexation of host CDs and guest molecules have attracted more and more attention because of their potential to serve as functional materials.[12] Studies have reported that β-CD strongly binds to ADM by forming a 1:1 inclusion complex with a stability constant[13] on the order of 10^4 M^{-1}.[14] Harada have prepared the novel β-CD host dimer and the ADM guest dimer bound by poly-(ethylene glycol)[15]. Newkome and his co-workers have synthesized the acid-terminated adamantane-modified dendron, and finally the dendron was planted in β-CD.[16] Herein, we chose β-CD as a candidate for modifying the Ag NPs based on two ideas. On one hand, Ag NPs are considerably stable when they are decorated with β-CD (β-CD Ag NPs) because of the hydrophobic interactions between silver nanoparticles and CD molecules are sufficient strength to prevent agglomeration.[17] On the other hand, it can introduce the host-guest interaction between β-CD and guest molecule such as adamantane (ADM). Furthermore, in order to design of a highly selective and sensitive colorimetric sensor for detection of Mn^{2+}, we synthesize the acyclic crown azo-crown ether with ADM as terminal group, because they are known for the unusual property of providing the coordination site for transition metal ions. Moreover, the addition of ADM leads to

the self-assembly of the nanoparticles into clusters (β-CD-ADM Ag NPs) through host-guest interactions. As a consequence, we have constructed a novel colorimetric sensor (β-CD-ADM Ag NPs) using β-CD as stable circumstance under the conditions for analysis and its Mn^{2+}-induced the self-assembly of the nanoparticles into larger clusters.

The β-CD-ADM Ag NPs were synthesized according to a very simple and rapid chemical method as follows (Scheme 1): Firstly, silver nitrate was reduced by sodium borohydride at room temperature to yield colloidal silver nanoparticles (Ag NPs). Secondly, β-CD was added rapidly into the solution and stirred for 2 h. Finally, ADM was added into the above β-CD Ag NPs solution and the synthesized (β-CD-ADM Ag NPs) was purified by repeating centrifugation and redispersion in water. The resulting Ag NPs showed very good stability in water without any apparent aggregation for two weeks (Fig. S1).

Scheme 1 Synthesis of β-CD-ADM-modified Ag NPs
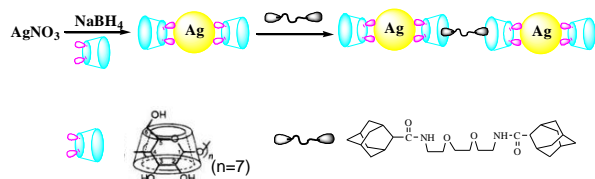
The synthesized silver nanoparticles were characterized by the IR spectra and transmission electron microscopy (TEM). From the comparison of the IR spectra of β-CD and β-CD-ADM Ag NPs (Fig. S2), in addition to the -OH stretching mode absorption band shifting lower for silver particles in the presence of β-CD, the framework vibration of β-CD remained unchanged, which demonstrated that β-CD was successfully modified on the surface.[18] After in the presence of ADM, the characteristic peaks of methylene at 2912 cm^{-1} and 2840 cm^{-1} appeared in β-CD-ADM Ag NPs, which indicated that the ADM had been successfully attached onto β-CD. To further validate the inclusion interaction, the TEM image shows β-CD Ag NPs are highly dispersed and uniform in aqueous solution (Fig. 1A). Nevertheless, as seen from Figure 1B, in the presence of ADM, by the aid of host-guest interactions between the β-CD and ADM, the distance between nanoparticles was reduced to form silver nanoparticle clusters. These results further confirmed that due to the host-guest inclusion complexation between β-CDs and ADM motifs, the silver nanoparticle clusters have been successfully developed.
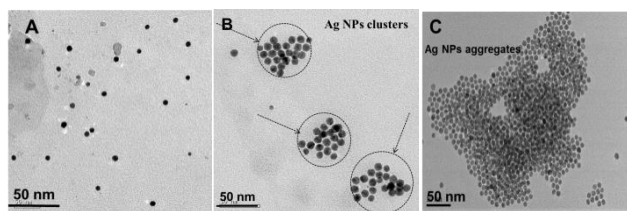

Fig.1 TEM images of β-CD-ADM Ag NPs: (A) Ag NPs are decorated with β-CD, the nanoparticles are highly dispersed and uniform;(B) Addition of ADM leads to the self-assembly of the nanoparticles into clusters, indicating that the ADM has been successfully attached onto β-CD.(C) In the presence of Mn^{2+}, the Ag NPs clusters were much larger with broader size aggregates, The scale bars are both 50 nm.

To investigate the selectivity of our developed approach toward Mn^{2+}, various metal ions were added into the β-CD-ADM Ag NPs solution. Figure 2 show that the colour changes

and the UV/Vis spectra of the β-CD-ADM Ag NPs solution after the addition of 1 mM metal ions aqueous solution. Over 5 minutes later, Figure 2A displays only in the presence of Mn^{2+} occurring a distinct colour changes from yellow to red, which corresponds to a dramatic increase of the absorbance intensity at 530 nm. To quantify the spectral changes at 400 nm and 530 nm, the absorbance ratio at two wavelengths ($R=A_{530}/A_{400}$) of β-CD-ADM Ag NPs in the presence of 1 mM metal ions is determined. In the presence of Mn^{2+}, it is an obvious enhancement of the R value that we observed. However, the other metal ions had no obvious effect on colour and UV-vis absorption, which demonstrated that β-CD-ADM-Ag NPs are efficiently selective for Mn^{2+}.
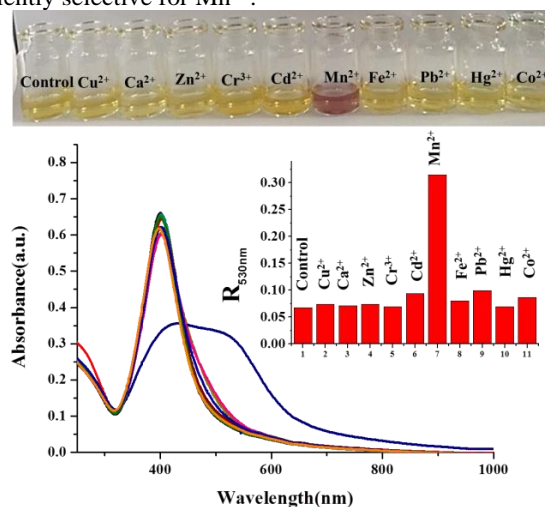

Fig. 2 (A) photographic images and (B) The UV-vis spectra solution of β-CD-ADM Ag NPs in the presence of 1 mM different metal ions. Inset: the absorbance ratio R of β-CD-ADM Ag NPs in the presence of 1 mM different metal ions aqueous solution. Monitoring was started 5 min, after addition of different metal ions, only in the presence of Mn^{2+} occurring a distinct color changed from yellow to red. It proved that the β-CD-ADM Ag NPs are efficiently selective for Mn^{2+}.

In order to explore the colour change and the differences of UV-vis absorption, we observed the TEM image of β-CD-ADM Ag NPs before and after addition of Mn^{2+}. The TEM image (Fig. 1C) shows that after the addition of Mn^{2+}, the Ag NPs clusters were much larger with broader size aggregates, this aggregation resulted in the yellow-to-red colour change reflecting to the Mn^{2+}-induced the functional Ag NPs in the aggregated states. We proposed that the mechanism of the phenomenon is shown in Scheme 2.
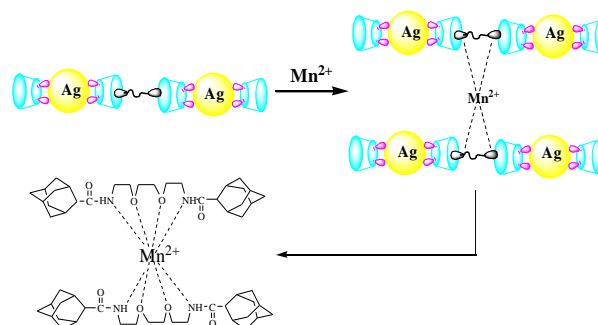
Scheme 2 Synthesis of β-CD-ADM-modified Ag NPs

The possible complexation could be carried out with the acyclic azo-crown ethers, they are known as the strong metal ion chelators because of their oxygen-rich structure, which has

been shown to form stable complexes with metal ions,[19] and furthermore, the imino groups can improve the binding of metal ions. According to the hard-soft acid-base principle, the hard acids prefer to bind to hard bases and vice versa.[20] Mn^{2+} ion, as a hard acid forms stronger complexes with oxygen donors. According to the reported literatures, although Cr^{3+} and Ca^{2+} are also classified as the hard acid,[21] the acyclic azo-crown ethers can exhibit an excellent selectivity for the recognition of Mn^{2+}. What's more, Mn^{2+} shows greater sensitivities to the acyclic azo-crown ethers (hard base) than the other ions (Cu^{2+}, Cd^{2+} and Hg^{2+} are classified as the soft acid, Zn^{2+}, Co^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+} are classified as the borderline acids)[22] In order to verify the rationality mechanism, as a control, the same metal ions (1 mM) were added into β-CD Ag NPs, most of the tested transition metal ions can make β-CD Ag NPs solution colour change in 5 min (Fig. S3), which suggests that β-CD Ag NPs do not have selective response to Mn^{2+} before the addition of ADM. It is reasonable to believe that the recognition and signal amplification ability are attributed to Mn^{2+}-induced β-CD-ADM Ag NPs clusters forming larger agglomerates.

Quantitative analysis was performed by titrating the Mn^{2+} ions and monitoring the absorption peak and the colour of the system changes. The absorption intensity of the Ag NPs suspension at 401 nm decreased with increasing Mn^{2+}, while the band maximum at 550 nm increased. Meanwhile, a clear colour progression from yellow to orange to red with increasing Mn^{2+}, concentration was observed (Fig. 3A). Therefore, the absorbance ratio at 550 and 401 nm was used to quantify the colour of the system. A low ratio was associated with dispersed particles and a yellow colour, and a high ratio was associated with aggregated particles and a red colour. The curve can reach a platform when the concentration of Mn^{2+} is above 5×10^{-7} M. According to this, the limit of colorimetric detection for Mn^{2+} was 5×10^{-7} M.
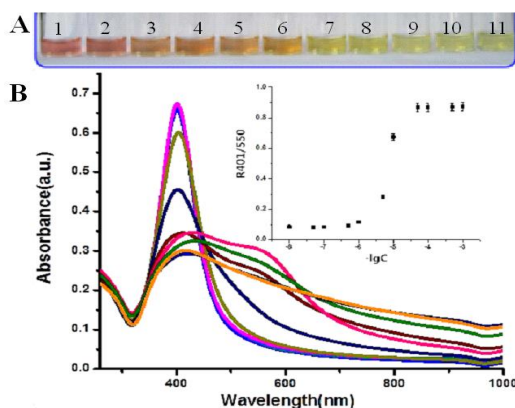

Fig. 3 (A)The colour change of β-CD-ADM-Ag NPs s solution after adding different concentrations of Mn^{2+} from 1×10^{-3} M to 1×10^{-8}M, and (B) the UV-vis absorption spectra of β-CD-ADM-Ag NPs solution after adding different concentrations of Mn^{2+}. The concentration of Mn^{2+} is (1) 10^{-3} M; (2) 5×10^{-4} M; (3) 10^{-4} M; (4) 5×10^{-5} M; (5) 10^{-5}M; (6) 5×10^{-6}M; (7) 10^{-6} M; (8) 5×10^{-7} M; (9) 10^{-7} M; (10) 5×10^{-8} M; (11) 10^{-8} M. Insets: absorption ratios. The detection limit for Mn^{2+} ions was 5×10^{-7}M.

In our previous works, we have synthesized NPEY (1, 2-bis-(2-pyren-1-ylmethylamino-ethoxy) ethane) modified graphene nanosheets (NPEY-GNs) for Mn^{2+} determination with the detection limit of 4.6×10^{-5} M.[23] It also has reported a novel pH-controlled recognition method for the discriminative detection of Mn^{2+} and Cu^{2+} ions via CdTe QD fluorescence sensing, the detection limits of Mn^{2+} are 10^{-6} M to 5×10^{-3} M.[24] In contrast,

the novel colorimetric sensor (β-CD-ADM Ag NPs) we have designed is lower two or more orders of magnitude than the other methods, which confirmed the exquisite sensitivity of our designed colorimetric sensor. Furthermore, the developed method was also successfully applied for detecting Mn^{2+} in Yangtze River water with the detection limit of 5×10^{-6} M (Fig. S4).

Conclusions

We have developed a facile, sensitive and selective colorimetric sensor for Mn^{2+} determination. The Ag NPs were decorated with β-CD and assembled into clusters with ADM. In the presence of Mn^{2+}, the Ag NPs clusters were much larger with broader size aggregates, which resulted in colour change and the differences of UV-vis absorption. The most attractive feature of this novel probe when compared with other reported optical methods is the highly sensitive and selective, the detection limit for Mn^{2+} was found as 5×10^{-7} M.

Experimental

Materials and reagents

All chemicals and solvents unless otherwise specified were analytical grade, and triply distilled water were used throughout. $AgNO_3$ and $NaBH_4$ were purchase from Shanghai Chemical Factory, China. Metal ions ($CuCl_2$, $CaCl_2$, $ZnCl_2$, $CrCl_3$, $CdCl_2$, $MnCl_2$, $FeCl_2$, $PbCl_2$, $CoCl_2$, and $HgCl_2$) were obtained from Beijing Chemical Corp (Beijing, China). All salts standards were dissolved in triply distilled water and stored at room temperature.

Characterization

UV-vis absorption spectra were acquired on an S-3100 UV-vis spectrometer. IR spectra were measured with a NEXUS FT-IR spectrometer (Thermo Nicolet Co.), Transmission electron, micrograph (TEM) was recorded by a JEOL-JEM 2010 electron microscope operating at 200 kV.

Preparation of β-CD-ADM Ag NPs

1 mL of 10^{-2} mol/L of silver nitrate ($AgNO_3$) aqueous solution was added into 96 ml of triply distilled water, and then 10 mg of sodium borohydride ($NaBH_4$) were added into the silver nitrate solution with stirring for 20 min, the color of nanoparticle solution turn golden yellow, and then 1 mL of 1 mM concentrated aqueous solution of β-CD was added rapidly into solution and stirred for another 2 h at room temperature to get β-CD Ag NPs.

1 mL of 10^{-3} mol/L aqueous solution of ADM was added into the β-CD Ag NPs, then the reaction mixture was centrifuged at 3000 rpm for 10 min for three times, the dispersed in distilled water to get β-CD-ADM Ag NPs.

Colorimetric assay for Mn^{2+}:

The colorimetric tests of β-CD-ADM Ag NPs responding to metal ions were operated as follows: 0.5 mL of 1mM aqueous solution of various metal ions was added to 1.5 mL of β-CD-

ADM Ag NPs and after combining 5 min, the solutions were test.

Notes and references

1 B.A. Pappas, *Neurotoxicol. Teratol.*, 1997, **19**, 17-25.
2 M. G. Cersosimo and W. C. Koller, *Neuro.Toxicology*, 2006, **27**, 340.
3 (a)J. M. Hamty, T. C. Haver, B. Golden and W. R. Wolf, *Anal. Chem.*, 1979, **51**, 2007; (b) V. Majidi, J. T. Rae and J. Ratliff, *Anal. Chem.*, 1991, **63**, 1600-1602.
4 H. M. Swaidan and G. D. Christian, *Anal. Chem.*, 1984, **56**, 120-122.
5 (a)W. T. Chan and H. C. Yip, *Anal. Chem.*, 1997, **69**, 4872-4877; (b) N. J. Miller-Ihli, *J. Agric. Food Chem.*, 1996, **44**, 2675-2679.
6 S. Kim, N. H. Lee, S. H. Seo, M. S. Eom, S. A. and M. S. Han, *Chem. Asian J*, 2010, **5**, 2463-246.
7 (a)D. J. Xiong, M. L. Chen and H. B. Li, *Chem.Comm.*,2008,880; (b) B. A. Gorman, P. S. Francis, D. E. Dunstan and N. W. Barnett, *Chem. Commun.*, 2007, 395.
8 J. M. Wessels, H. G. Nothofer, W. E. Ford, F. von Wrochem, F. Scholz, T. Vossmeyer, A. Schroedter, H. Weller and A. Yasuda, *J. Am. Chem. Soc.*, 2004, **126**, 3349.
9 B. Kowalczyk, D. A. Walker, S. Soh and B. A. Grzybowski, *Angew. Chem. Int. Ed.*, 2010, **49**, 5737 – 5741.
10 R. D. Rica, R. M. Fratila, A. Szarpak, J. Huskens and A. H. Velders, *Angew. Chem., Int. Ed.*, 2011, **50**, 5704.
11 Y. Yang, J. Shi, T. Tanaka and M. Nogami, *Langmuir*, 2007, **23**, 12042–12047.
12 (a)Y. W. Yang, Y. Chen and Y. Liu, Inorg. Chem., 2006, 45, 3014–3022 ;(b) Y. Liu, Y. L. Zhao, H. Y. Zhang and H. B. Song, *Angew. Chem., Int. Ed.*, 2003, **42**, 3260–3263.
13 A. L. Godı´nez, L. Schwartz, C. M. Criss, and A. E. Kaifer, *J.Phys. Chem. B.*, 1997, **101**, 3376-3380.
14 G. R. Newkome, H. J. Kim, K. H. Choi, and C. N. Moorefield, *Macromolecules*, 2004, **37**, 6268–6274.
15 Y. Hasegawa, M. Miyauchi, Y. Takashima, H. Yamaguchi, and A. Harada, *Macromolecule*s, 2005, **38**, 3724–3730.
16 G. R. Newkome, K. K. Kotta, and C. N. Moorefield, *Chem. Eur. J.*, 2006, **12**, 3726 - 3734.
17 Y. Liu, K. B. Male, P. Bouvrette, and J. H. T. Luong, *Chem. Mater.*, 2003, **15**, 4172-4180.
18 J. P. Sylvestre, A. V. Kabashin , E. Sacher, M. Meunier, and J. H. T. Luong, *J. Am. Chem. Soc.*, 2004, **126**, 7176-7177.
19 Y. X. Gao, J. W. Xin, Z. Y. Shen, W. Pan, X. Li and A. G. Wu, *Sensors and Actuators: B*, 2013, **181**, 288-293.
20 I. Oehme and O. S. Wolfbeis, *Microchim. Acta.*, 1997, **126**, 177-192.
21 Y. Zhou, H. Zhao, C. Li, P. He, W. B. Peng, L. F. Yuan, L. X. Zeng and Y. J. He. *Talanta,* 2012, **97**, 331–335..
22 (a)Pearson and G. Ralph, *J. Am. Chem. Soc.*, 1963, **85**, 3533-3539; (b)I. Kaya, M. Yıldırım and M. Kamacı, *Synthetic Metals*, 2011,**161,** 2036-2040.
23 X. W. Mao, H. Y. Su, D. M. Tian, H. B. Li and R. H. Yang, *Appl. Mater. Interfaces*, 2013, **5**, 592-597.
24 S. H. Xu, C. L. Wang, H. S. Zhang, Q. F. Sun, Z. Y. Wang and Y. P. Cui, *J. Mater. Chem.*, 2012, **22**, 9216-9221.

New Journal of Chemistry Accepted Manuscript