

## **Supporting Information**

### **Unusual Red-to-Brown Colorimetric Sensing Method for Ultrasensitive Silver(I) Ion Detection Based on a Non-aggregation of Hyperbranched Polyethylenimine Derivative Stabilized Gold Nanoparticles**

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### Preparation of 35-nm AuNPs

Citrate-protected AuNPs were synthesized by means of the classical citrate reduction of hydrogen tetrachloroaurate (HAuCl<sub>4</sub>).<sup>1, 2</sup> 6 mL of sodium citrate (1%) was rapidly added to 110 mL of aqueous solution of HAuCl<sub>4</sub> (0.01%) that was boiled under vigorous stirring. Within 5 min the colour of the solution changed to purple red, and heating continued for 10 min. Then, the solution of AuNPs was cooled to ambient temperature.

### Preparation of 3-nm AuNPs

A solution of HAuCl<sub>4</sub> ( $2 \times 10^{-3}$  M, 1.0 mL) was added to 9.0 mL of a solution of the HPEI-TMAm (3 mg/mL). Subsequently, a fresh solution of NaBH<sub>4</sub> ( $6 \times 10^{-3}$  M, 4.0 mL) was added to this mixture under vigorous stirring. Immediately the solution turned brown.

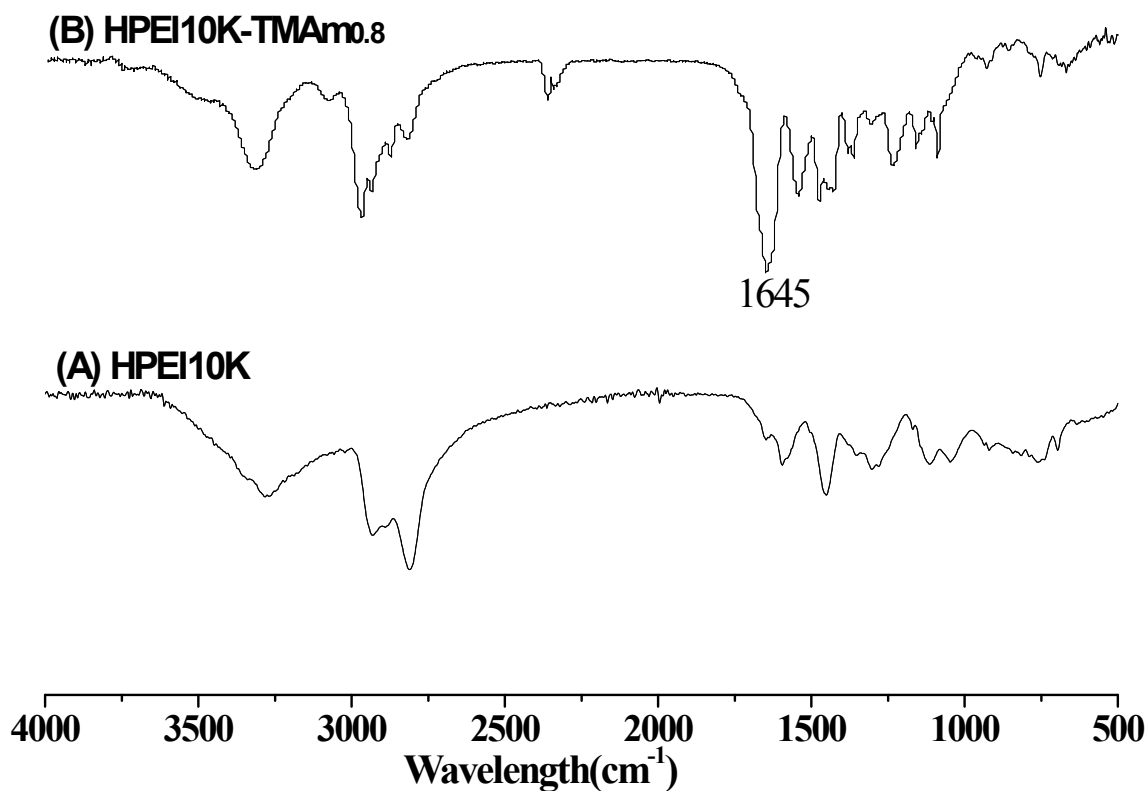


Figure S-1 FTIR of HPEI (A) and HPEI-TMAm (B)

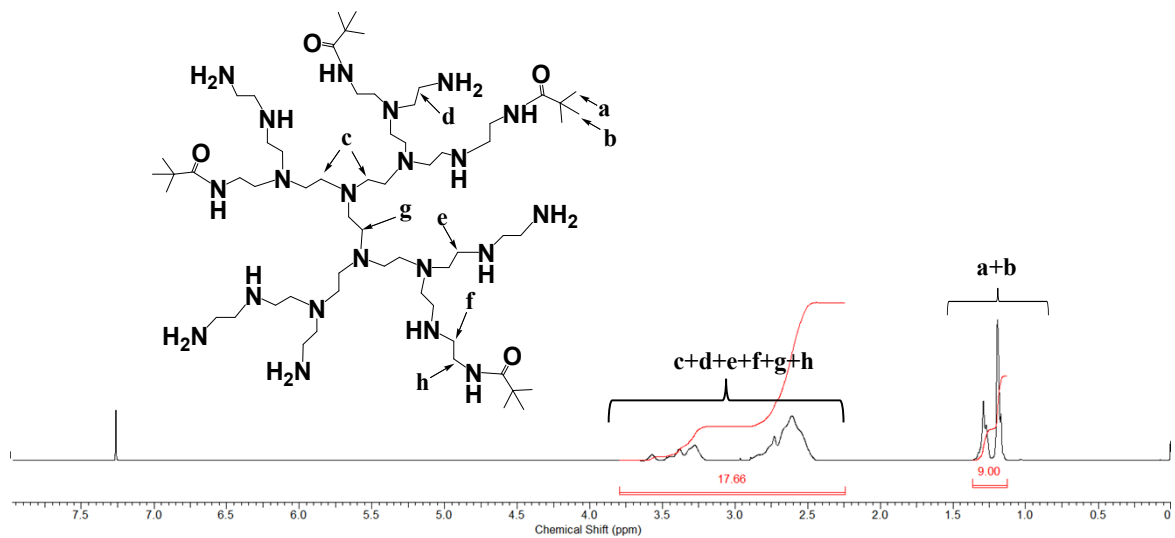


Figure S-2  $^1\text{H}$  NMR spectra of HPEI-TMAM

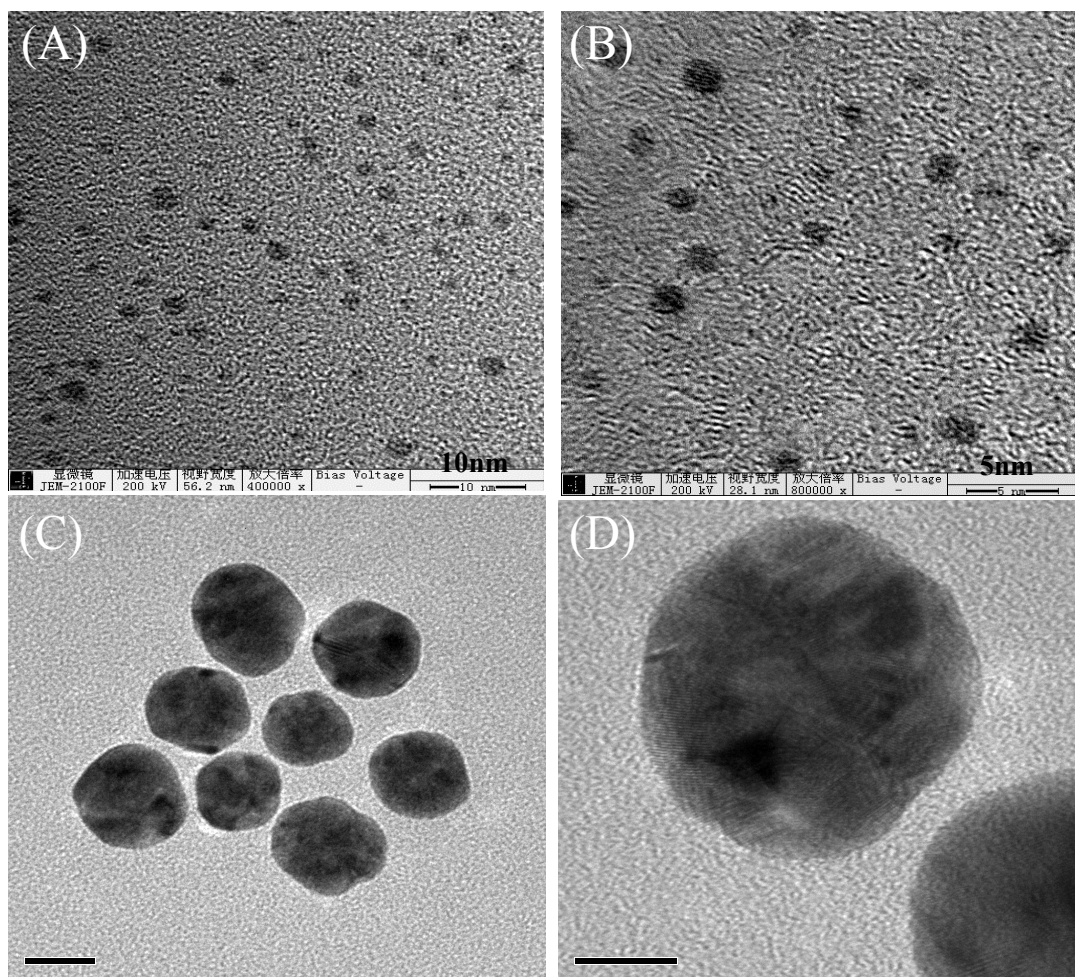


Figure S-3 Typical TEM images of the AuNPs: (A)&(B) sodium borohydride as the reductant; (C)&(D) sodium citrate as the reductant.

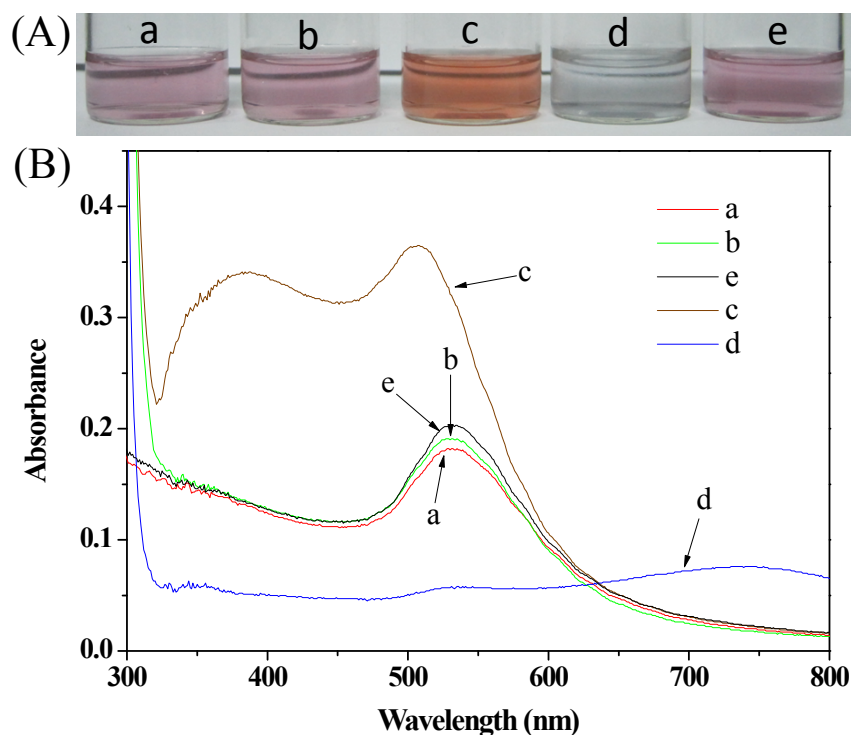


Figure S-4 Colorimetric response of the sensor: (A) colour changes and (B) absorption spectra of (a) 0.6 nM HPEI-TMAM-AuNPs; (b) 0.6 nM HPEI-TMAM-AuNPs with 6.3 mM AA (in the absence of  $\text{Ag}^+$ ); (c) 0.6 nM HPEI-TMAM-AuNPs with 6.3 mM AA in the presence of 4.38  $\mu\text{M}$   $\text{Ag}^+$  with a red to reddish brown colour change; (d) 0.6 nM citrate-capped AuNPs with 6.3 mM AA (in the absence of HPEI-TMAM); (e) 0.6 nM HPEI-TMAM-AuNPs with 4.38  $\mu\text{M}$   $\text{Ag}^+$  (in the absence of AA).

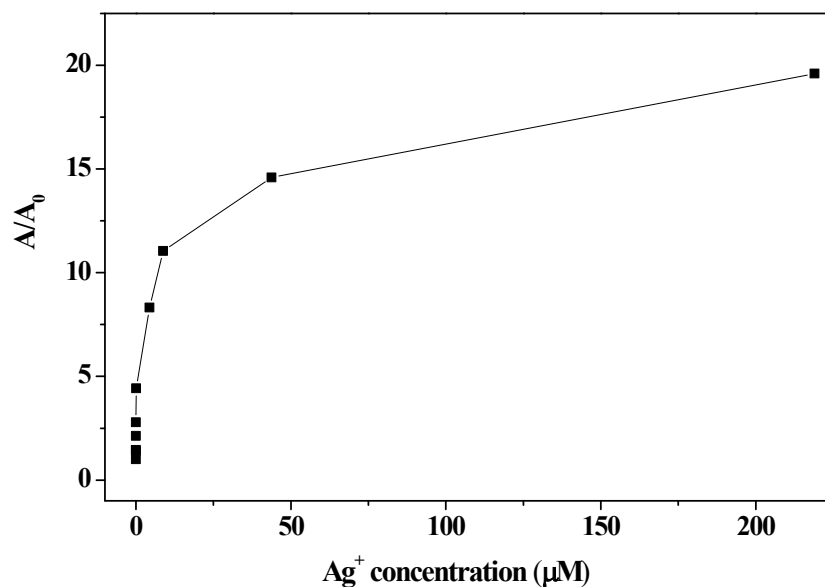


Figure S-5 The  $A/A_0$  value of the absorbance at 400 nm versus the concentration of  $\text{Ag}^+$ . ( $A$  and  $A_0$  are the absorbance at 400 nm obtained from the system with and without  $\text{Ag}^+$ , respectively)

Table S-1 Gold nanoparticle-based sensors for Ag<sup>+</sup> detection

Probe	Detection techniques	LOD(nM)	Time (min)	Ref
Tween 20-AuNPs	Colorimetry and absorption	100	5	3
Tween 20-AuNPs	Colorimetry and absorption	10	3	4
Gold nanorod (GNR)	Absorption	10	30	5
Au <sub>25</sub> nanocluster	Fluorometry	200	Up to 3 min	6
Au <sub>16</sub> NCs@BSA	Fluorometry	100	20	7
MUA/THPC-AuNCs	Fluorometry	9	No mention	8
Core-shell AuNPs	Absorption	10	30 min	9
Oligonucleotide-functionalized core/shell magnetic silica sphere @ AuNPs	Surface-enhanced raman scattering	10	More than 5 h	10
Pyridines-functionalized AuNPs	Colorimetry and absorption	1000	More than 30 min	11
Cytosine-rich DNA decorated AuNPs	Surface-enhanced raman-scattering	15	No mention	12
Cationic polymer-directed AuNPs	Colorimetry and absorption	48.6	More than 120 min	13
DNA probe and AuNPs	Colorimetry and absorption	500	22 min	14
AuNPs	Resonance rayleigh scattering	202	60 min	15
Oligonucleotide/AuNPs	Localized surface plasmon resonance and colorimetry	62	10 min	16
DNA based AuNPs	Colorimetry and absorption	12 nM by naked eyes and 0.59 nM by UV-vis spectra	More than 30 min	17
Hyperbranched ployethylenimine derivatives stabilized AuNPs	Colorimetry and absorption	8.76 nM by naked eyes and 1.09 nM by UV-vis spectra	1 to 2 minutes	This work

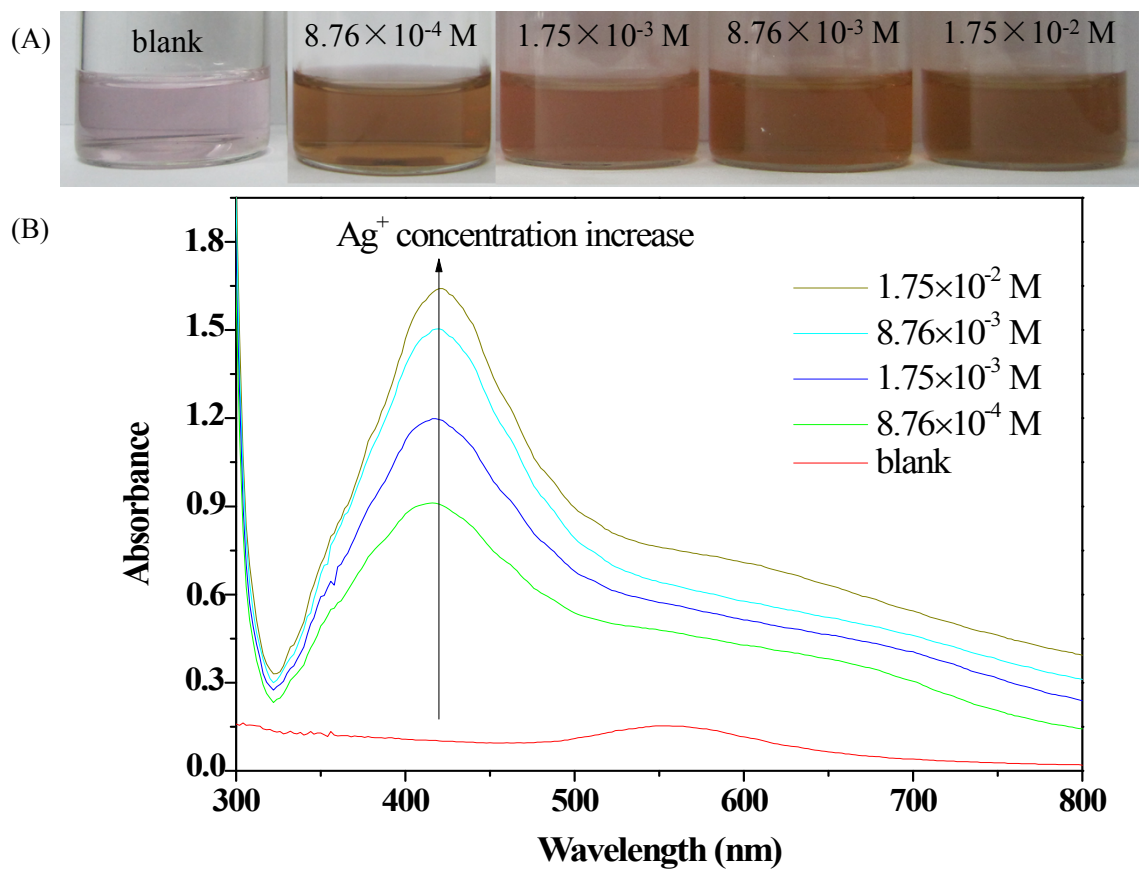


Figure S-6 (A) Photographs and (B) Absorption spectra of 0.3 nM HPEI-TMAM-Au NPs and 10 mM AA solutions with different  $\text{Ag}^+$  concentrations.

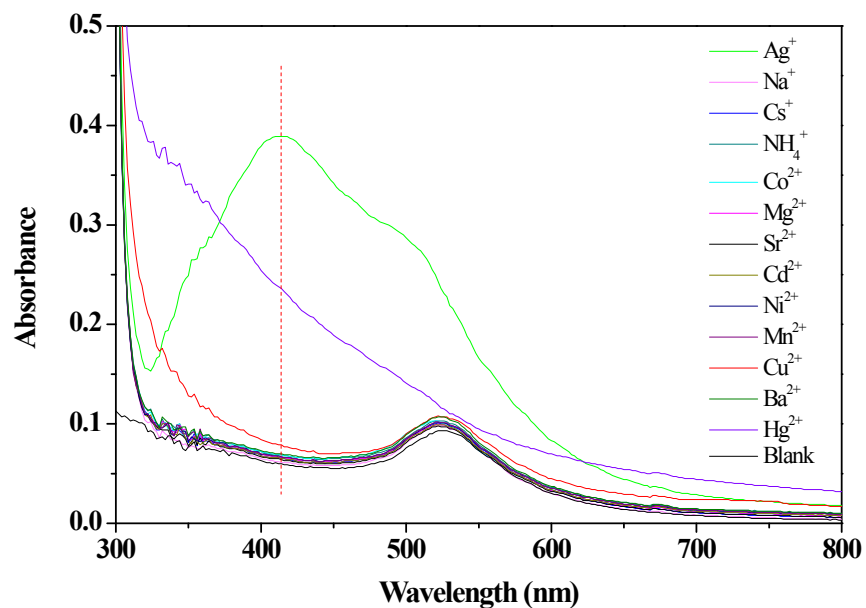


Figure S-7 Selectivity of the sensor: Absorption spectra of the colorimetric assay containing HPEI-TMAM-AuNPs (0.3 nM) and AA (10 mM) solutions with  $\text{Ag}^+$  (4.38  $\mu\text{M}$ ) and several other metal ions (43.8  $\mu\text{M}$ ).

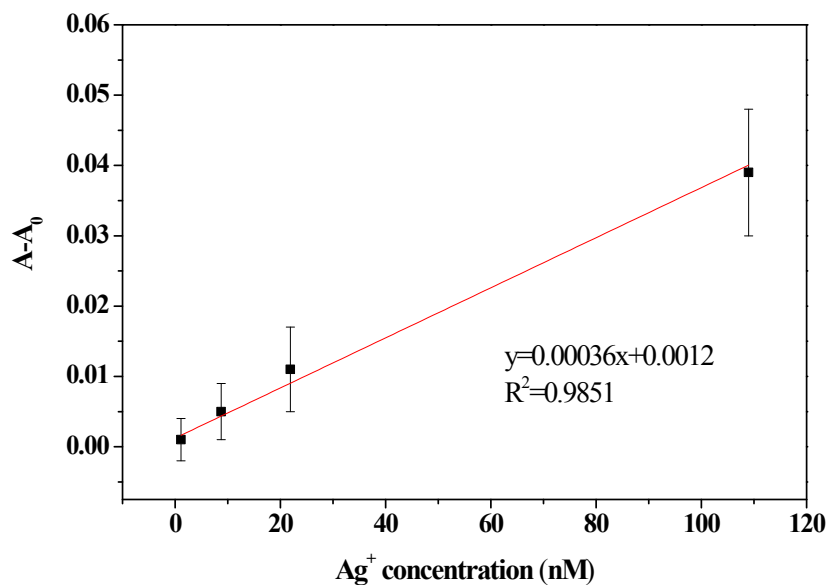


Figure S-8 Colorimetric sensing of  $\text{Ag}^+$  in tap water: The  $A-A_0$  value of the absorbance at 400 nm versus the concentration of  $\text{Ag}^+$ . ( $A$  and  $A_0$  are the absorbance at 400 nm obtained from the system with and without  $\text{Ag}^+$ , respectively) The error bars represented standard deviations based on three independent measurements. (0.3 nM HPEI-TMAM-AuNPs and 10 mM AA solutions in tap water with different  $\text{Ag}^+$  concentrations)

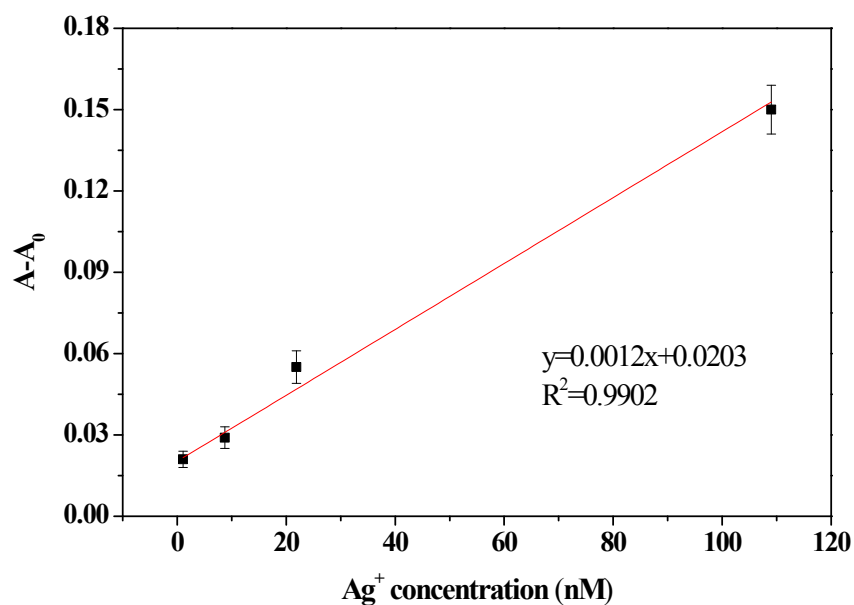


Figure S-9 Colorimetric sensing of  $\text{Ag}^+$  in drinking water: The  $A-A_0$  value of the absorbance at 400 nm versus the concentration of  $\text{Ag}^+$ . ( $A$  and  $A_0$  are the absorbance at 400 nm obtained from the system with and without  $\text{Ag}^+$ , respectively) The error bars represented standard deviations based on three independent measurements. (0.3 nM HPEI-TMAM-AuNPs and 10 mM AA solutions in drinking water with different  $\text{Ag}^+$  concentrations)

## References

- 1 G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20.
- 2 K. C. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735.
- 3 C. Y. Lin, C. J. Yu, Y. H. Lin and W. L. Tseng, *Anal. Chem.*, 2010, **82**, 6830.
- 4 T. T. Lou, Z. P. Chen, Y. Q. Wang and L. X. Chen, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1568.
- 5 H. Huang, S. Chen, F. Liu, Q. Zhao, B. Liao, S. Yi and Y. Zeng, *Anal. Chem.*, 2013, **85**, 2312.
- 6 Z. Wu, M. Wang, J. Yang, X. Zheng, W. Cai, G. Meng, H. Qian, H. Wang and R. Jin, *Small*, 2012, **8**, 2028.
- 7 Y. Yue, T. Y. Liu, H. W. Li, Z. Y. Liu and Y. Q. Wu, *Nanoscale*, 2012, **4**, 2251.
- 8 J. Sun, Y. Yue, P. Wang, H. He and Y. Jin, *J. Mater. Chem. C*, 2013, **1**, 908.
- 9 H. Huang, C. Qu, X. Liu, S. Huang, Z. Xu, B. Liao, Y. Zeng and P. K. Chu, *ACS Appl. Mater. Interfaces*, 2011, **3**, 183.
- 10 M. Liu, Z. Wang, S. Zong, H. Chen, D. Zhu, L. Wu, G. Hu and Y. Cui, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7371.
- 11 A. Alizadeh, M. M. Khodaei, Z. Hamidi and M. Bin Shamsuddin, *Sens. Actuator B-Chem.*, 2014, **190**, 782.
- 12 H. Y. Qiao, M. L. Hong, X. Tian, L. J. Huang and X. Chu, *Anal. Sci.*, 2013, **29**, 991.
- 13 F. Z. Wang, Y. G. Wu, S. S. Zhan, L. He, W. T. Zhi, X. X. Zhou and P. Zhou, *Aust. J. Chem.*, 2013, **66**, 113.
- 14 Z. H. Qing, X. X. He, K. M. Wang, Z. Zou, X. Yang, J. Huang and G. P. Yan, *Anal. Methods*, 2012, **4**, 3320.
- 15 S. S. Zhan, Y. G. Wu, L. He, F. Z. Wang, X. J. Zhan, P. Zhou and S. Y. Qiu, *Anal. Methods*, 2012, **4**, 3997.
- 16 C. K. Wu, C. Xiong, L. J. Wang, C. C. Lan and L. S. Ling, *Analyst*, 2010, **135**, 2682.
- 17 Z. Zhu, Y. Su, J. Li, D. Li, J. Zhang, S. Song, Y. Zhao, G. Li and C. Fan, *Anal. Chem.*, 2009, **89**, 7660.