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Supporting information

A novel and ultrasensitive yellow to taupe brown colorimetric sensing and removal method for Hg(II) based on thermosensitive poly (N-isopropyl acrylamide) stabilized silver nanoparticles

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The experimental details of Hg^{2+} detection

The AgNPs stabilized by PNIPAm were used for colorimetric determination of Hg^{2+} . First, the effects of various factors on Hg^{2+} colorimetric detection, including the concentration of AgNPs, the pH value and the concentration of Hg^{2+} were examined. In order to examine the effect of AgNPs concentration for Hg^{2+} detecting, 1.1×10^{-4} M Hg^{2+} solutions were added into the mixture of 0.17-1.44 mg/mL PNIPAm and 5.0×10^{-8} - 4.3×10^{-7} M AgNPs solutions, respectively. After the colorimetric detection systems were stable, the color change and adsorption spectra of solutions were recorded by a digital camera and a UV-vis spectrophotometer.

To study the Hg^{2+} detection by AgNPs/PNIPAm under the circumstance of different pH value, the mixed solutions (3.0×10^{-7} M AgNPs and 1.10×10^{-4} M Hg^{2+} solution) were implemented in a pH range of 3.24–9.94. And the pH value of dye solution was adjusted by $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl and $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution. Finally, the color change and adsorption spectra of solutions were recorded by a digital camera and a UV-vis spectrophotometer.

For Hg^{2+} sensing, 3.0×10^{-7} M AgNPs/PNIPAm solution was mixed with 0 to 1.10×10^{-4} M Hg^{2+} solution. After equilibrating at room temperature for 2 min, the color change and the UV-vis absorption spectra of the solution were recorded. All experiments were performed in triplicate.

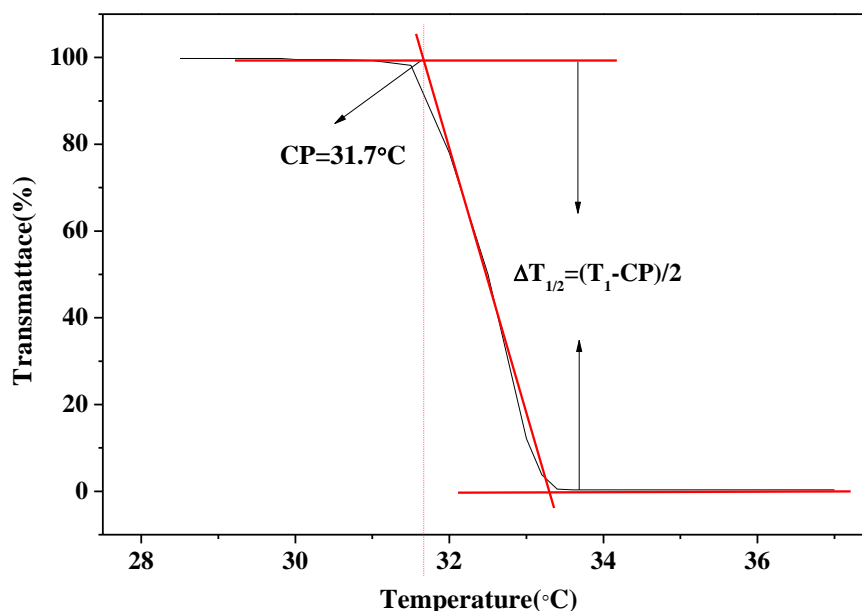


Fig. S1 The typical curve of temperature effect on the light transmittance of the aqueous solution of PNIPAm.

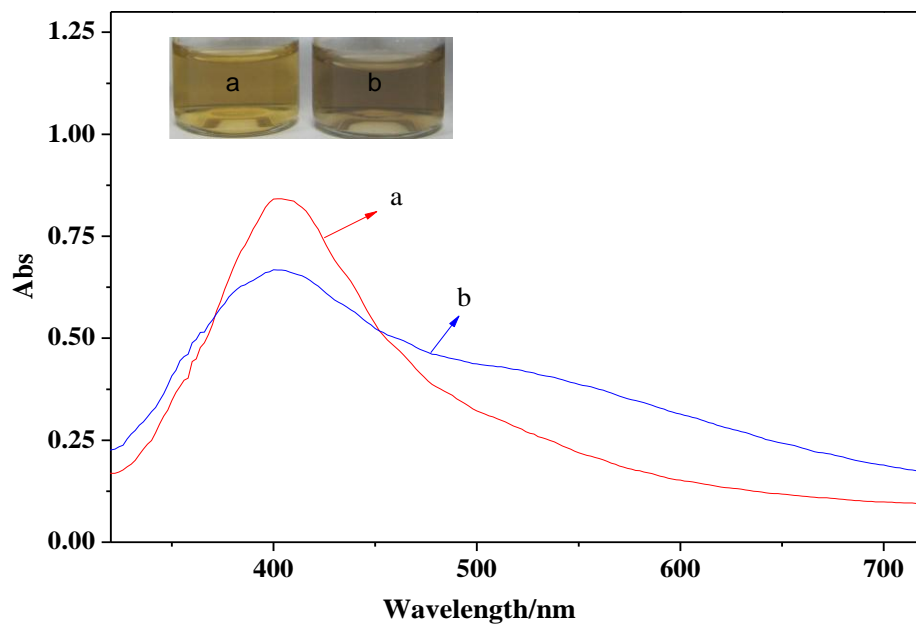


Fig. S2 Adsorption spectra and photographs (inset) of (a) the mixture of 4.3×10^{-7} M AgNPs and 1.44 mg/mL PNIPAM; (b) 1.10×10^{-4} M Hg^{2+} was added into the mixture of 4.3×10^{-7} M AgNPs and 1.44 mg/mL PNIPAM with a yellow to taupe brown color change.

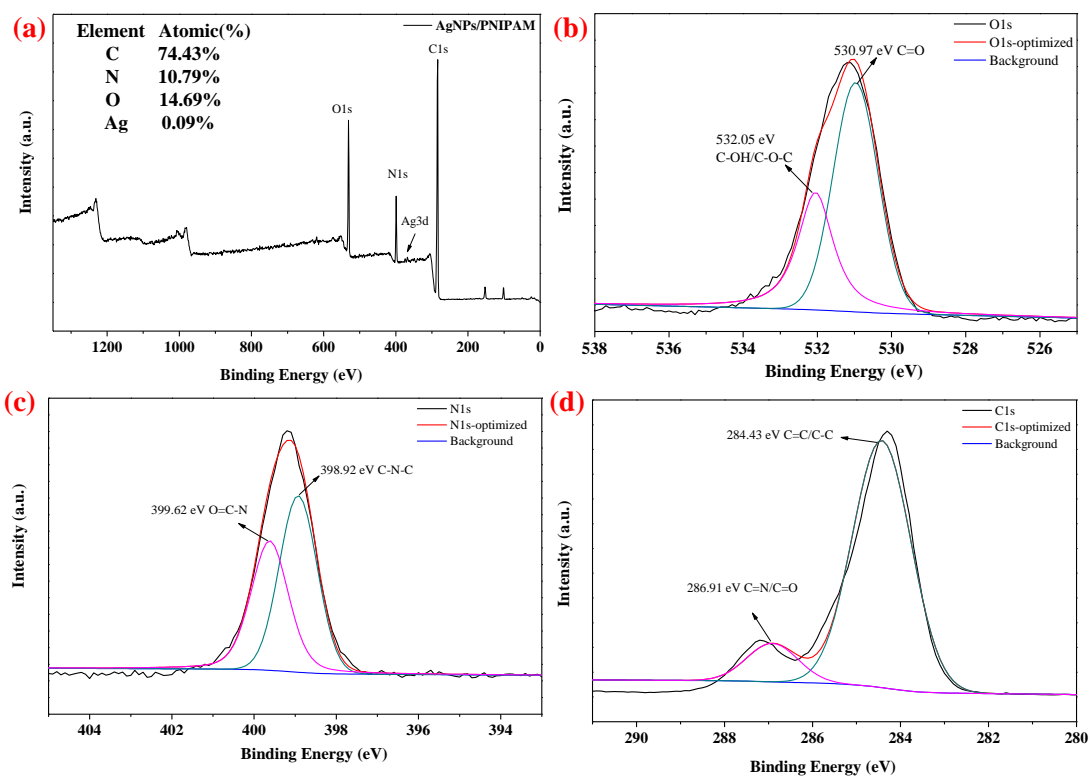


Fig. S3 Full-XPS spectra and C 1s, N 1s and O 1s high-resolution XPS (HRXPS) spectra AgNPs/PNIPAM.

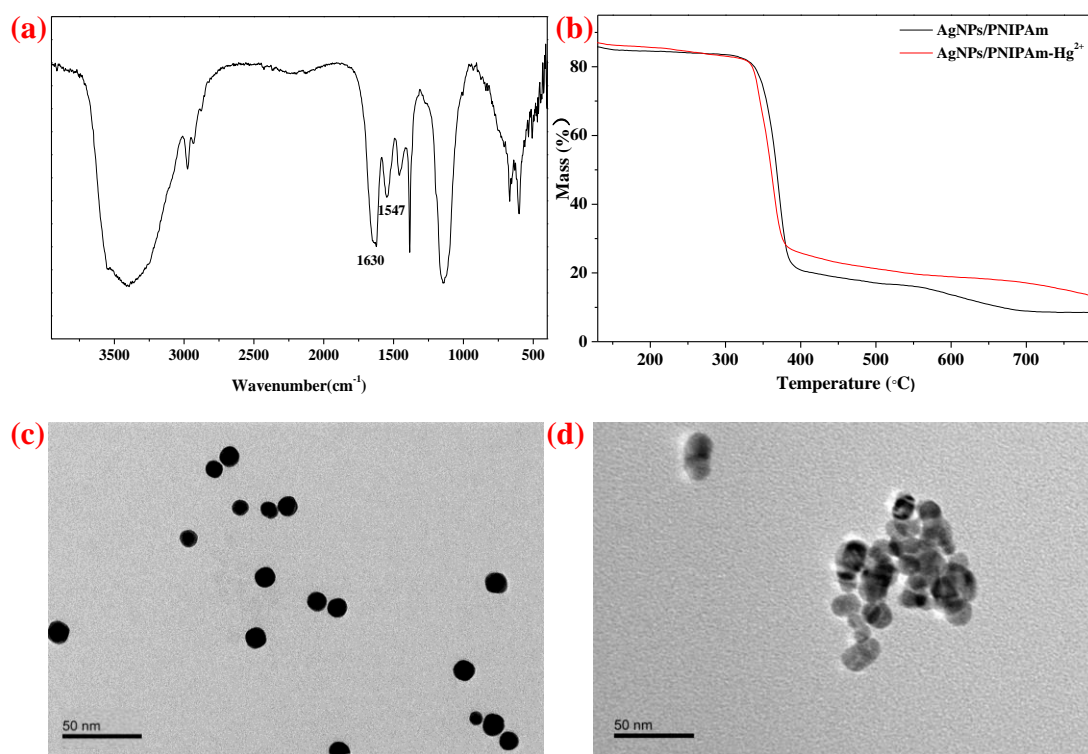


Fig. S4 (a) FTIR spectra of AgNPs/PNIPAm; (b) TGA curves of AgNPs/PNIPAm and AgNPs/PNIPAm-Hg²⁺; TEM images of (c) AgNPs/PNIPAm and (d) pure AgNPs at room temperature after five days.

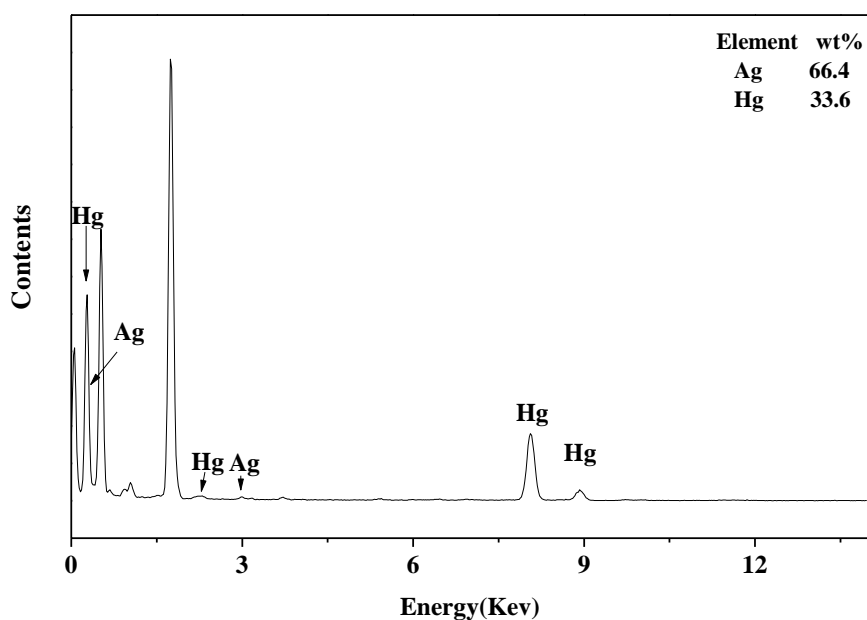


Fig. S5 EDS spectrum of the product of the reaction between the AgNPs and Hg²⁺.

Table S1 Zeta Potential (mV) of pure AgNPs, AgNPs/PNIPAm and sensor in the presence of Hg²⁺ by dynamic light scattering

	AgNPs	AgNPs/PNIPAm	AgNPs/PNIPAm-Hg ²⁺
Size (nm)	49.82	65.31	90.64
Zeta Potential (mV)	-21.7	-22.3	-23.7

Table S2. Comparison of LOD for Hg²⁺ detection of this work with other reported methods.

Method	Materials	Detection limit	Linear range (μM)	Ref.
Colorimetry	GO-Ag nanocomposite	590 nM	5–75	1
Colorimetry	lignin –AgNPs	23 μM	50–450	2
Colorimetry	Carrageenan-AgNPs	1 μM	1–100	3
Colorimetry	citrate-AgNPs	1.8 μM	0.1–5	4
Colorimetry	p-PDA capped AgNPs	800 nM	1–9.1	5
Colorimetry	Ag@GO	338 nm	50-200	6
Colorimetry	SG/AgNPs	5 μM	5-75	7
Colorimetry	AgNPs	2.2 μM	10-100	8
Colorimetry	AgNPs/PNIPAm composite	75 nM	0.05–27.3	This work

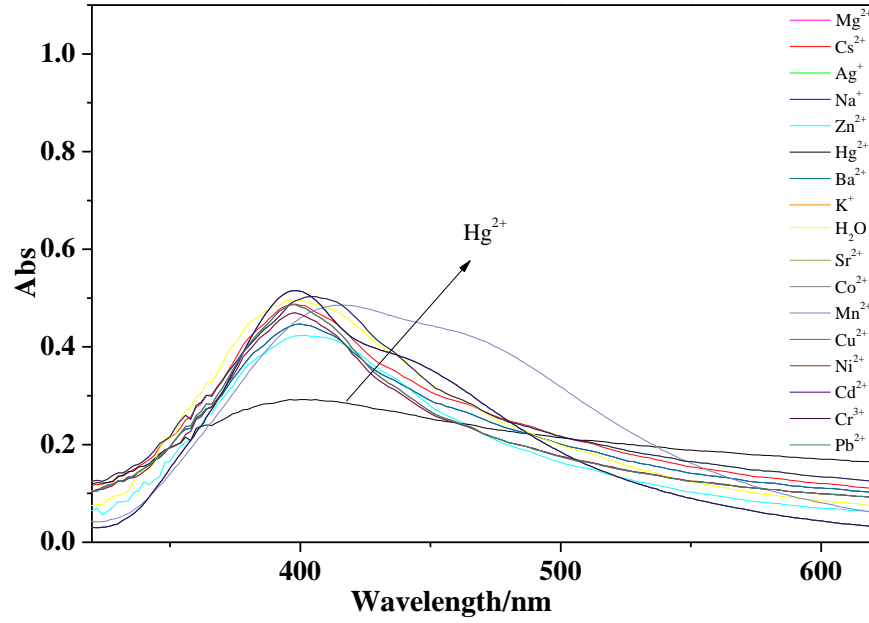


Fig. S6 Adsorption spectra of 2.0×10^{-7} M AgNPs with Hg^{2+} and other metal ions (1.10×10^{-4} M) in the presence of 0.67 mg/mL PNIPAm.

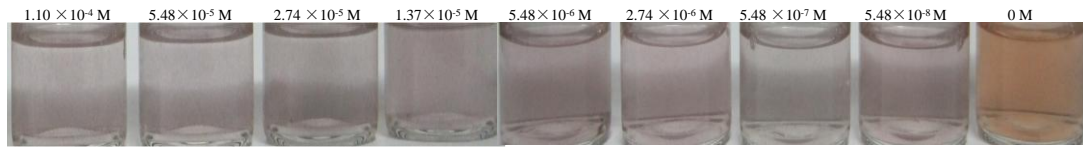


Fig. S7 Photo of 3.0×10^{-7} M AgNPs and 1.0 mg/mL PNIPAm with different concentrations of Hg^{2+} range of 0- 1.10×10^{-4} M in tap water.

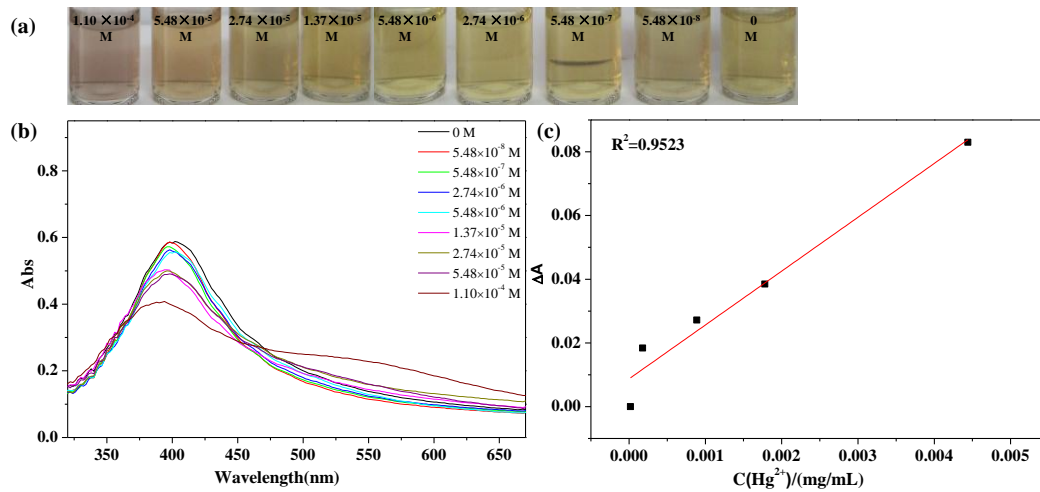


Fig. S8 (a) Photographs and (b) UV-vis adsorption spectra of 3.0×10^{-7} M AgNPs and 1.0 mg/mL PNIPAm with different Hg^{2+} concentrations range of 0- 1.10×10^{-4} M in drinking water. (c) The values of ΔA at 400 nm against the Hg^{2+} concentration range in 5.48×10^{-8} - 1.10×10^{-4} M.

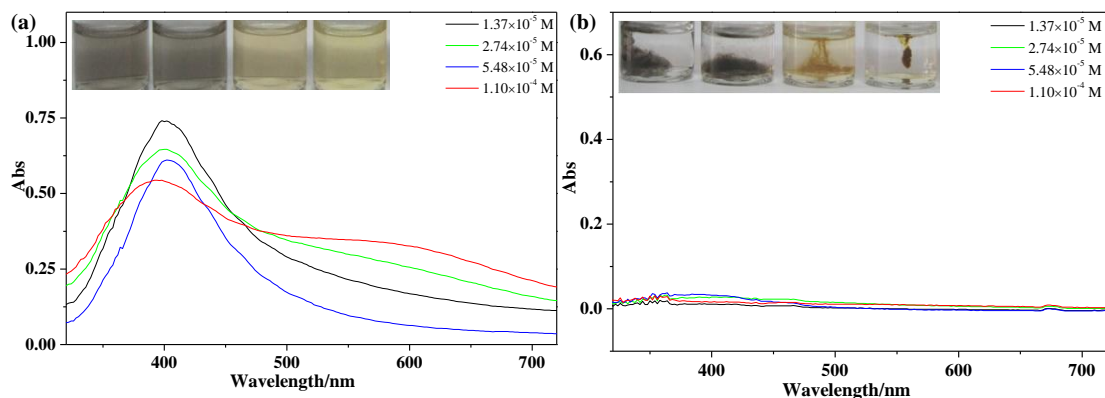


Fig. S9 Colorimetric detection and adsorption of different concentrations Hg^{2+} in ultrapure water: UV-vis adsorption spectra and photographs (inset) of 3.0×10^{-7} M AgNPs at (a) room temperature and (b) 45°C .

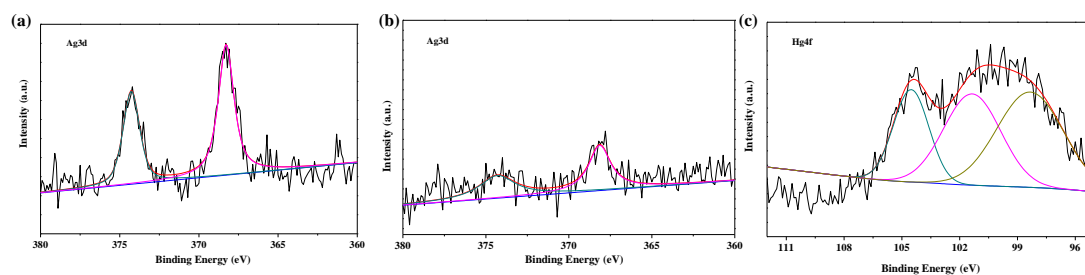


Fig. S10 (a) High-resolution Ag 3d XPS spectra of AgNPs/PNIPAm in the absence of Hg^{2+} and high-resolution (b) Ag 3d and (c) Hg 4f XPS spectra of AgNPs/PNIPAm in the presence of Hg^{2+} .

Notes and references

1. A. A. M. Noor, P. Rameshkumar, N. M. Huang and L. S. Wei, *Microchim. Acta*, 2016, **183**, 597-603.
2. T. Xin, Z. K. Zhou, L. Gang, B. Shen, P. D. Kang, L. Jian, L. Qi and F. X. Pei, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16147-16155.
3. K. B. Narayanan and S. S. Han, *Carbohydr. Polym.*, 2017, **160**, 90-96.
4. S. K. Kailasa, M. Chandel, V. N. Mehta and T. J. Park, *Spectrochim. Acta, Part A*, 2018, **195**, 120-127.
5. S. Bothra, J. N. Solanki and S. K. Sahoo, *Sensors & Actuators B Chemical*, 2013, **188**, 937-943.
6. K. Z. Kamali, A. Pandikumar, S. Jayabal, R. Ramaraj, N. L. Hong, B. H. Ong, C. S. D. Bien, Y. Y. Kee and N. M. Huang, *Microchim. Acta*, 2016, **183**, 369-377.
7. P. Rameshkumar, P. Viswanathan and R. Ramaraj, *Sensors & Actuators B Chemical*, 2014, **202**, 1070-1077.
8. K. Farhadi, M. Forough, R. Molaei, S. Hajizadeh and A. Rafipour, *Sensors & Actuators B Chemical*, 2012, **161**, 880-885.