## **Supporting Information**

## A novel AgNPs-based colorimetric sensor for rapid detection of Cu<sup>2+</sup> or Mn<sup>2+</sup> via pH control

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Figure S1. FT-IR spectra of  $Na_4P_2O_7$  (a) and  $P_2O_7^{4-}$ -AgNPs (b).



**Figure S2.** Influence of  $P_2O_7^{4-}$  concentration in the AgNPs-based detection systems on the sensing effect of Cu<sup>2+</sup> or Mn<sup>2+</sup>. (a): Photographic image and corresponding plot of  $A_0/A$  (A is the absorbance value at 414 nm in the UV-vis spectra of the detection systems incubated with 10 µM of Cu<sup>2+</sup>, and  $A_0$  is that of the detection systems without Cu<sup>2+</sup>) of the detection systems with different  $P_2O_7^{4-}$  concentrations at pH 1.9. (b) Photographic image and corresponding plot of  $A_0/A$  (A is the absorbance value at 395 nm in the UV-vis spectra of the detection systems incubated with 10 µM of Mn<sup>2+</sup>, and  $A_0$  is that of the detection systems without Mn<sup>2+</sup>) of the detection systems with different  $P_2O_7^{4-}$  concentrations at pH 12.0. The incubation time is 10 min. The HPMC concentration in the detection systems is 50 mg/L.



**Figure S3.** Influence of HPMC concentration in the AgNPs-based detection systems on the sensing effect of Cu<sup>2+</sup> or Mn<sup>2+</sup>. (a) Photographic image and corresponding plot of  $A_0/A$  (A is the absorbance value at 414 nm in the UV-vis spectra of the detection systems incubated with 10 µM of Cu<sup>2+</sup>, and  $A_0$  is that of the detection systems without Cu<sup>2+</sup>) of the detection systems with different HPMC concentrations at pH 1.9. (b) Photographic image and corresponding plot of  $A_0/A$  (A is the absorbance value at 395 nm in the UV-vis spectra of the detection systems incubated with 10 µM of Mn<sup>2+</sup>, and  $A_0$  is that of the detection systems without Mn<sup>2+</sup>) of the detection systems with different HPMC concentrations at pH 12.0. The incubation time is 10 min. The P<sub>2</sub>O<sub>7</sub><sup>4-</sup> concentration in the detection systems is 500 µM.



**Figure S4.** Influence of the incubation time between the detection system and  $Cu^{2+}$  (0.2 µM) at pH 1.9 (a) or between the detection system and  $Mn^{2+}$  (5.0 µM) at pH 12.0 (b) on the  $A/A_0$  values. *A* is the absorbance value at 414 nm or 395 nm in the UV-vis spectra of the detection systems incubated with 0.2 µM of  $Cu^{2+}$  or 5 µM of  $Mn^{2+}$ , and  $A_0$  is that of the detection systems without  $Cu^{2+}$  or  $Mn^{2+}$ . The  $P_2O_7^{4-}$  concentration in the detection systems is 50 mg/L.



**Figure S5.** Influence of pH values on the UV-vis absorption of the detection systems containing 0.5  $\mu$ M of Cu<sup>2+</sup> (a) and 5.0  $\mu$ M of Mn<sup>2+</sup> (b). The inset shows the photographic image of the corresponding solutions. The P<sub>2</sub>O<sub>7</sub><sup>4-</sup> concentration in the detection systems is 500  $\mu$ M. The HPMC concentration in the detection systems is 50 mg/L. The incubation time is 10 min.



**Figure S6.** Change in UV-vis absorption of AgNPs dispersions without  $Cu^{2+}$  at pH 1.9 (a) and without  $Mn^{2+}$  at pH 12.0 (b) compared with the control (pH 9.0) during storage at room temperature within 30 min. The P<sub>2</sub>O<sub>7</sub><sup>4-</sup> concentration in the detection systems is 500  $\mu$ M. The HPMC concentration in the detection systems is 50 mg/L. The incubation time is 10 min.

(a) Concentration of $Cu^{2+}$ (lake water)			Concentration of $Cu^{2+}$ (tap water)			
Blank	0.05µM	0.1µM	Blank	0.05µM	0.1µM	
(b) Concentration of $Mn^{2+}$ (lake water) Concentration of $Mn^{2+}$ (tap wate						
(b)Concen	tration of Mn <sup>2</sup>	+ (lake water)	Concentr	ration of Mn <sup>2+</sup>	(tap water)	
(b)Concen Blank	tration of Mn <sup>2</sup> 0.5µM	+(lake water) 1µM	Concentr Blank	ation of Mn <sup>2+</sup> 0.5µM	(tap water) 1µM	
(b)Concen Blank	0.5µM	<sup>+</sup> (lake water)	Concentr Blank	o.5μM	(tap water) 1µM	
(b)Concen Blank	utration of Mn <sup>2</sup>	+ (lake water)	Concentr	ation of Mn <sup>2+</sup>	(tap water) 1µM	
(b)Concen Blank	tration of Mn <sup>2</sup>	<sup>+</sup> (lake water) 1μΜ	Concentr	ation of Mn <sup>2+</sup> 0.5µM	(tap water) 1µM	
(b)Concen Blank	0.5µM	<sup>+</sup> (lake water)	Blank	ation of Mn <sup>2+</sup> 0.5µM	(tap water) 1µM	

Figure S7. Detection of  $Cu^{2+}$  (a) or  $Mn^{2+}$  (b) in real water samples by our developed colorimetric method.

Potential interfering ions of Cu <sup>2+</sup> detection	Tolerance ratios (compared to $5 \times 10^{-8}$ M) <sup>a</sup>		
Ni <sup>2+</sup> , Zn <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> ,CO <sub>3</sub> <sup>2-</sup>	100000		
Ba <sup>2+</sup> , Cd <sup>2+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Fe <sup>2+</sup> , Mn <sup>2+</sup> , Co <sup>2+</sup>	10000 1000 100		
$Hg^{2+}, Pb^{2+}, Cr^{3+}$			
Cr(VI)			
Potential interfering ions of Mn <sup>2+</sup>	Tolerance ratios (compared to $5 \times 10^{-7}$		
detection	M) <sup>b</sup>		
Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> ,CO <sub>3</sub> <sup>2-</sup>	1000		
$Co^{2+}, Cr^{3+}$	500		
$A^{1^{3+}}$ Fe <sup>3+</sup> Cr(VI)	200		
	200		
Cu <sup>2+</sup>	200 150		
$Cu^{2+}$ $Cd^{2+}$ , $Hg^{2+}$ , $Ni^{2+}$ , $Zn^{2+}$	200 150 100		
$Cu^{2+}$ $Cd^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}$ $Ba^{2+}, Pb^{2+}$	200 150 100 50		

Table S1. Influence of potential interfering ions on the detection of  $Cu^{2+}$  or  $Mn^{2+}$ 

<sup>a</sup>The limit of detection of  $Cu^{2+}$  is  $5 \times 10^{-8}$  M by the naked eyes;

 $^b The limit of detection of <math display="inline">Mn^{2\scriptscriptstyle +}$  is  $5 \times 10^{\text{--}7}\,M$  by the naked eyes.

Method	Probe	Targe t	LOD	Selectivity	Ref.
Colorimetry	Starch-AgNPs	Cu <sup>2+</sup>	0.632µM	Good	16
Colorimetry	Dopamine-AgNPs	Cu <sup>2+</sup>	0.05µM	Good	6
Colorimetry	P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> -AgNPs	Cu <sup>2+</sup>	2nM	Good	This work
Colorimetry	$P_3O_{10}^{5}$ - AgNPs	$Mn^{2+}$	0.05µM	Good	13
Colorimetry	L-tyrosine-AgNPs	Mn <sup>2+</sup>	16 nM	Not good	18
Colorimetry	P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> -AgNPs	$Mn^{2+}$	20nM	Good	This work

**Table S2.** Comparison of  $Cu^{2+}$  or  $Mn^{2+}$  detection using AuNPs or AgNPs-based systems.