

Supporting Information For
Imprinted Photonic hydrogel pillars for self-reporting
water treatment of heavy metal ions

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1. Silica colloidal crystal preparation

The highly uniform silica colloidal microspheres were based on the Stöber method and improved by Zhang T's work^{1, 2}. Briefly, 6.25ml ammonia hydroxide and 60ml anhydrous ethanol were mixed in a 100ml flask, stirred intensively with a magnetic beater at 298K keeping the speed of 1000rpm. And then 2ml tetraethoxysilane (TEOS) was added. What the most important point is that the mixed solution should be stirred at the speed of 1000rpm for 120 seconds first and then at the speed of 400rpm for 24 hours. The colloidal particles were obtained by centrifugation and ultrasonic cleaning 4 times with anhydrous ethanol to remove impurities in the colloidal particles. The pretreatment SiO₂ particles were diluted by anhydrous ethanol to a weight concentration of 0.7% and then transferred into clean 10ml vials. About 7 days later, when ethanol evaporated, silica colloidal crystal templates were formed on the inner surface of the vials shown in Figure S1.

2. Preparation of the hydrogel pillars.

A schematic diagram of the synthesis procedure is shown in Scheme 1. First, the monomer solution was filled into the two kinds of glass vials: one is assembled with PC layer and the other one is not. In this way, we synthesized hydrogel pillars with/without PC structure. The monomer solution is consist of 1wt% of 3-Sulfopropyl methacrylate potassium salt, 9wt% of acrylamide, 0.01wt% of Bis-acrylamide and 10⁻⁵wt% of N,N,N',N'-Tetramethylethylenediamine which the total weight of the solution is 8g. And 40μL ammonium persulfate (10wt%) and 72μL Glycidyl methacrylate were also added into the solution. After 60min when polymerization reaction finished,

heavy metal ions coordination with pentaethylenehexamine which mole ratio is 1:2 were added into the vials. This is aim to form the IPN structure with polyacrylamide as well as building the imprinted cavities. To prepare samples without imprinted ions, the pentaethylenehexamine solution without target ions was filled into the vials with polyacrylamide. These closed vials were put into the oven at 323K for 4 hours. This step was to induce the formation of interpenetrating polymer network. At last, vials would be removed by scraping softly and photonic crystal on the surface of the hydrogel was carved by hydrofluoric acid (1.5wt%). For recyclability testing, heavy metal ions were eluted from the adsorbed hydrogel with 0.1M HAc changing every 30min for 4 times. And the eluted hydrogels were washed with 0.5M pH 7 EDTA solution and deionized water, and used again for adsorption study.

3. FTIR Analysis

FTIR spectra of the imprinted PC hydrogel are shown in Figure S2. As shown in Fig. S2a, the peak at 3443.32 cm^{-1} is related with the dissociative $-\text{NH}_2$ stretching vibration. The absorption at 2925.34 cm^{-1} arises from the $-\text{CH}_2-$ anti-symmetric stretching. The absorption at 1646.50 cm^{-1} is caused by carbonyl group³.

The absorption bands in Fig.S2a at 3201.47 cm^{-1} is related with the association-bonded $-\text{NH}_2$ stretching vibration which doesn't exist in Fig. S2b. This adsorption peak is caused by the formation of the IPN between polyacrylamide and PEHA. The complexing function group $-\text{NH}_2$ which has been proved possessing high complexing constant with various heavy metal ions is successfully grafted on the hydrogel. In this work, PAM serves as wall materials the properties of low costing and easy

preparation and $-\text{NH}_2$ acts as adsorption function group which can adsorb many kinds of toxic ions with a high quantity⁴.

4. Calculation of Adsorption Capacity

According to the Lambert-Beer's Law, it can be drawn the relationship between the light adsorption and density of the heavy metal ions solution. In a certain concentration scope, intensity of adsorption peak of the solution is in direct proportion to the concentration and in this way the unknown density could be calculated by diluted proper multiples.

5. Method to determine Pb(II) ion

Xylenol Orange disodium salt (XO) was chosen as the color developing agent for Pb(II) ion. First, pH=6.0 buffer solution of HAc and NaAc, 1.0g/L XO solution and 10mg/L lead ion solution were prepared. Second, 0.5ml, 1.0ml, 1.5ml, 2.0ml, 2.5ml, 3.0ml, 3.5ml, 4.0ml, 4.5ml and 5.0ml of 10mg/L lead ion solution were separately filled into 10 10ml volumetric flasks which formed the lead ion standard solution from 0.5mg/L to 5mg/L. And last, 0.5ml XO solution and 1ml buffer solution were filled into the volumetric flasks. All the volumetric flasks were metered volume with DI water. These ten samples were measured the adsorption peaks by the Quawell ultraviolet spectrophotometer.

6. Methods to measure the adsorption capacity

Method to determine Cu(II) ion. Sodium diethyldithiocarbamate (DDTC) was chosen as the color developing agent for Cu(II) ion. First, 54mg/L DDTC solution and 10mg/L Cu(II) ion solution were prepared. Second, 0.5ml, 1.0ml, 1.5ml, 2.0ml, 2.5ml.

3.0ml, 3.5ml, 4.0ml, 4.5ml and 5.0ml of 10mg/L Cu(II) ion solution were separately filled into 10 10ml volumetric flasks which formed the Cu(II) ion standard solution from 0.5mg/L to 5mg/L. The third step was to add 3ml DDTC solution into the volumetric flasks. And then the solutions were adjusted to pH=9 with ammonia. At last, the volumetric flasks were metered volume with DI water. These ten samples were measured the adsorption peaks by the Quawell ultraviolet spectrophotometer.

Method to determine Zn(II) ion. Zincon monosodium salt (ZCN) was chosen as the color developing agent for Zn(II) ion. First, 1.0g/L (the solvent was ethanol), pH=9.0 borate buffer solution (potassium chloride, boric acid and sodium hydroxide) and 10mg/L Zn(II) solution were prepared. Second, 0.5ml, 1.0ml, 1.5ml, 2.0ml, 2.5ml, 3.0ml, 3.5ml, 4.0ml, 4.5ml and 5.0ml of 10mg/L Zn(II) ion solution were separately filled into 10 10ml volumetric flasks which formed the Zn(II) ion standard solution from 0.5mg/L to 5mg/L. Second, 2.0ml buffer solution and 1.0ml ZCN solution were added into the volumetric flasks. At last, the volumetric flasks were metered volume with DI water. These ten samples were measured the adsorption peaks by the Quawell ultraviolet spectrophotometer.

Method to determine Ag(I) ion. Dithizone-CTMAB (DTZ-CTMAB) solution was chosen as the color developing agent for Ag(I) ion. First, DTZ-CTMAB (0.5g/L DTZ and 1.0g/L CTMAB) and 40mg/L Ag(I) ion nitric acid solution were prepared. Second, 0.5ml, 1.0ml, 1.5ml, 2.0ml, 2.5ml, 3.0ml, 3.5ml, 4.0ml, 4.5ml and 5.0ml of 40mg/L Ag(I) ion solution were separately filled into 10 10ml volumetric flasks which formed the Ag(I) ion standard solution from 2.0mg/L to 20.0mg/L. At last, all

the volumetric flasks were metered volume with pH=1 nitric acid solution. These ten samples were measured the adsorption peaks by the Quawell ultraviolet spectrophotometer.

Method to determine Ni(II) ion.

We take Ni(II) for example. In this experiment, we used Dimethylglyoxime (DMGO) as the color developing agent for Ni(II). First, 1.0mol/L NaOH solution, 3wt% APS solution and 0.1wt% DMGO solution were prepared. Second, 0.2ml, 0.4ml, 0.6ml, 0.8ml, 1.0ml, 1.2ml, 1.4ml, 1.6ml, 1.8ml and 2.0ml of 10mg/L Ni(II) ion solution were separately filled into 10 10ml volumetric flasks which formed the Ni(II) ion standard solution from 0.2mg/L to 2.0mg/L. Second, 0.1ml NaOH solution and 0.3ml APS solution and 1.5ml MDGO solution were added into the volumetric flasks. At last, the volumetric flasks were metered volume with DI water. These ten samples were measured the adsorption peaks by the Quawell ultraviolet spectrophotometer.

Figure S3 shows the linearity of Pb(II), Cu(II) Zn(II) and Ag(I) ions. The limit of detection (LOD) of Pb(II) ions is 1.0~3.5mg/L and Cu(II) ions is 0.5~5.0mg/L. The equation is proper for Zn(II) ions ranged from 0.5~4.0mg/L and Ag(I) ion is 10.0~20.0mg/L. On the basis of the linear equation, concentration of the residual solution could be obtained. However, all the solutions to be examined would be diluted to proper concentration to match the LOD.

Figure S6a and S6b show that the adsorption capacity and time profile were similar to the trend of Pb(II) ion. It is concluded that the PC structure would improve the adsorption efficiency of the hydrogels in adsorbing Ni(II) ion.

7. Experiments data on Ag(I) target ion

When the prepared hydrogel was soaked in Ag⁺ solution, the hydrogel would turn into

brown after 6h shown in figure S4a. The SEM image of the brown hydrogel in Figure S4b describes that there are many particles with the size of 20 nm in the hydrogel.

8. Experiments data on Ni(II) target ion

The results on Pb(II), Cu(II) and Zn(II) all showed the same trend in the adsorption capacity and time profile experiments. It can be predicted that adsorption capacity and time profile experiments of Sn(II), Mn(II), Co(II) and Ni(II) ions were similar with Pb(II), Cu(II) and Zn(II). We take Ni(II) for example. The results are shown in Figure S5.

9. Experiments on regeneration

The hydrogel pillar was firstly immersed in pH 7.0 water at 298K for 2h and then it was removed to 1200 mg/L Pb(II) ion solution immersing 6h. In the second process, desorption was conducted by soaking the adsorbed hydrogel in 0.1M of HAc solution changing every 30min for 4 times and soaking it 0.5M pH 7 EDTA solution. And then the hydrogels were washed repeatedly by DI water. To learn the repeatability of this imprinted photonic hydrogel, the above two steps were conducted twice.

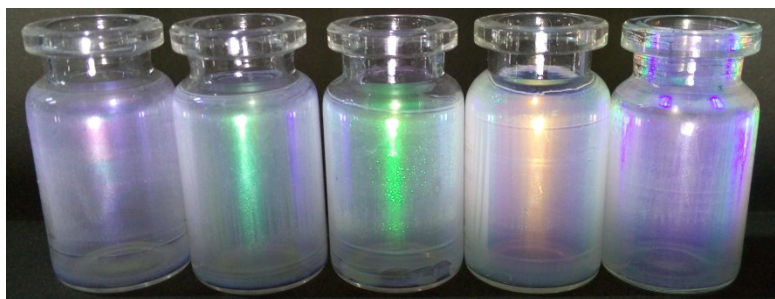


Figure S1. Image of the PC structure on the inner surface of vials. The wavelengths of reflection peak from left to right in turn were 451, 495, 520, 590 and 610nm.

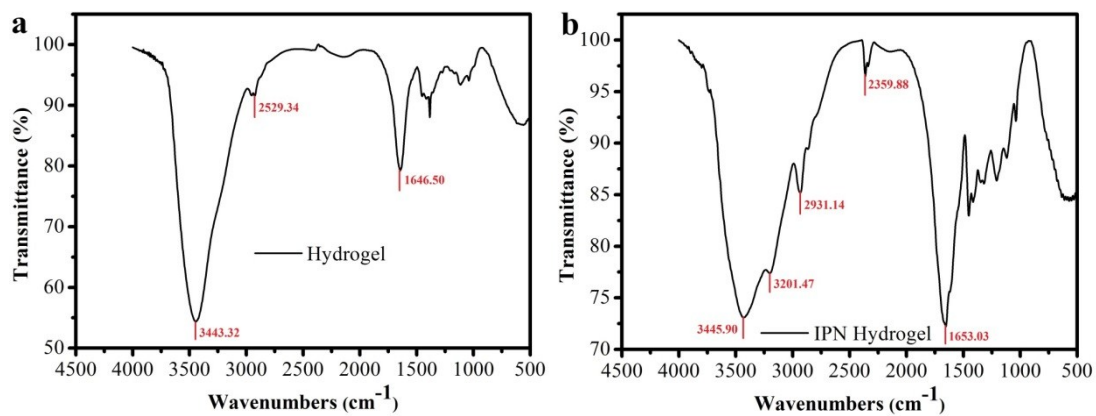
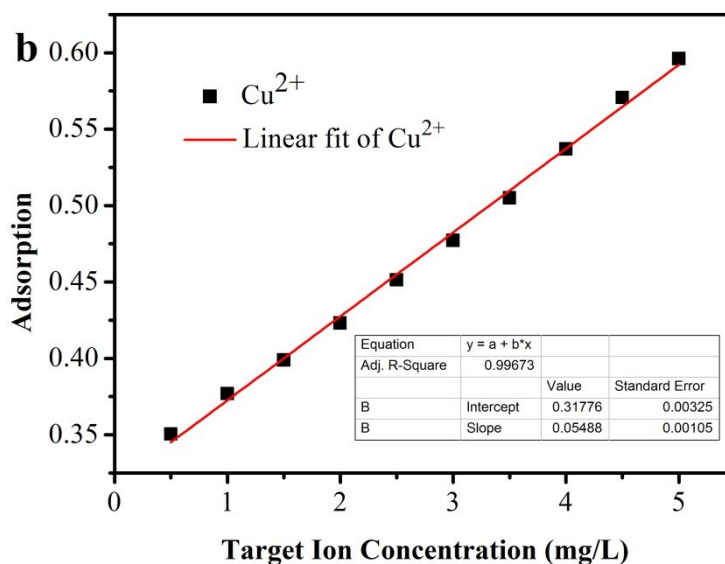
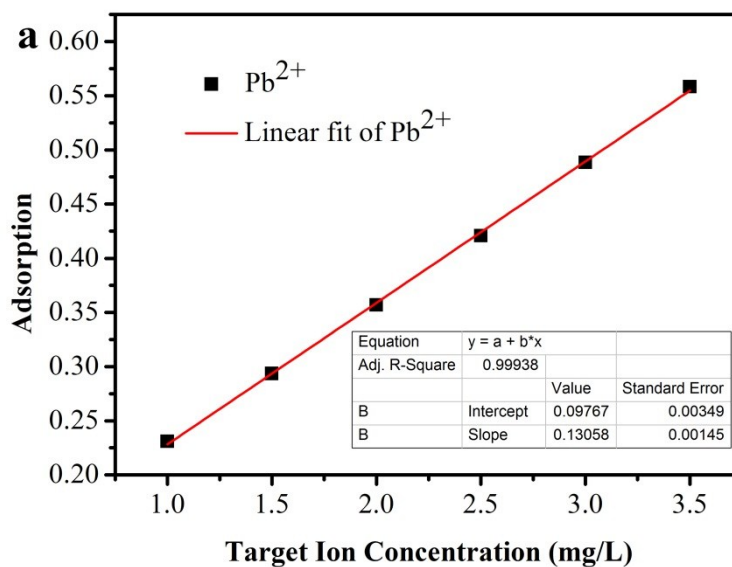


Figure S2. FTIR spectra of a) PAM hydrogel and b) IPN PAM and PEHA hydrogel.



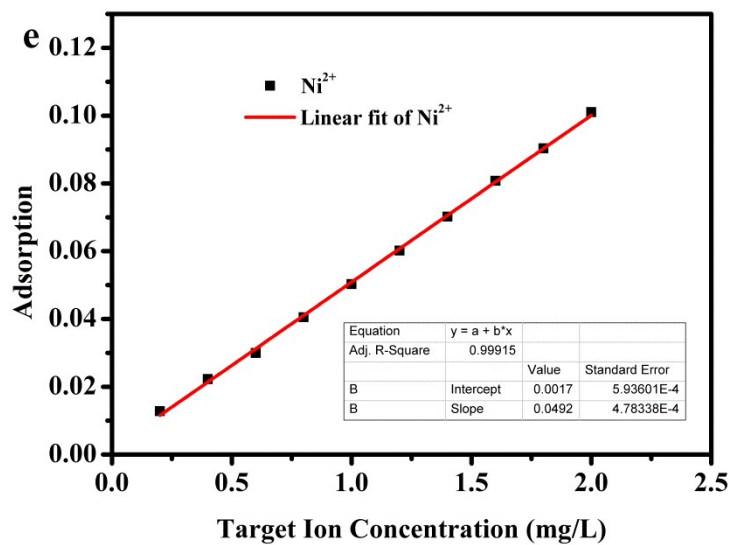
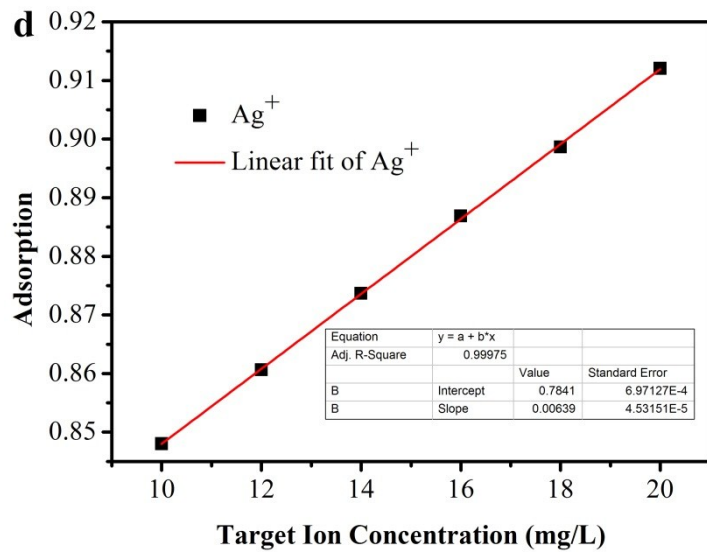
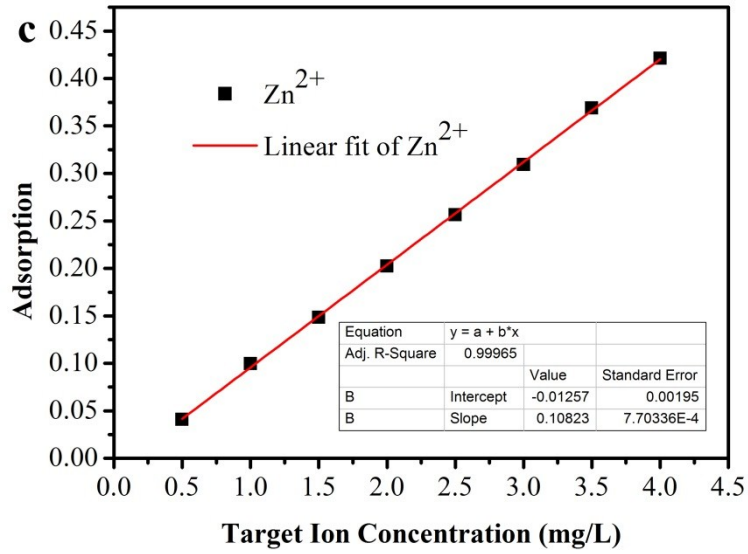


Figure S3. Linear fits of the concentration and adsorption of a) Pb(II), b) Cu(II), c) Zn(II), Ag(I) ions and Ni(II) ions.

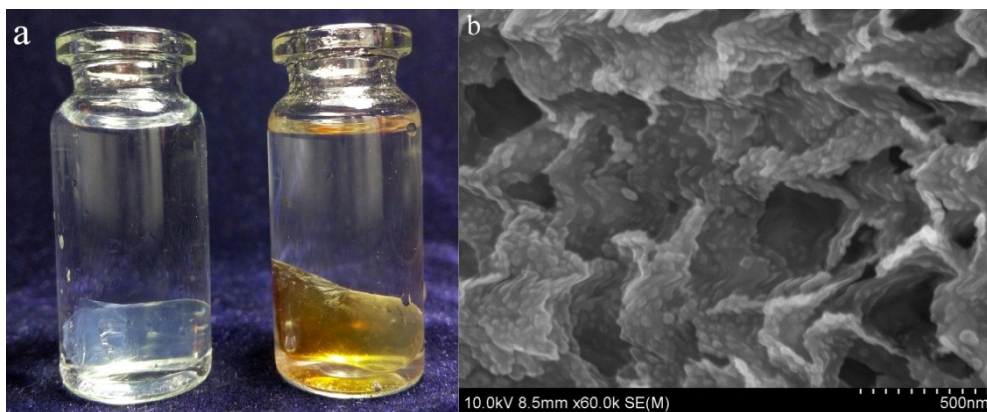


Figure S4. a) Image of the hydrogel turns from colorless to brown after soaking in Ag(I) ion solution and b) SEM image of the hydrogel. The concentration of Ag(I) ion solution is 900 mg/L and soaked in it for 5h.

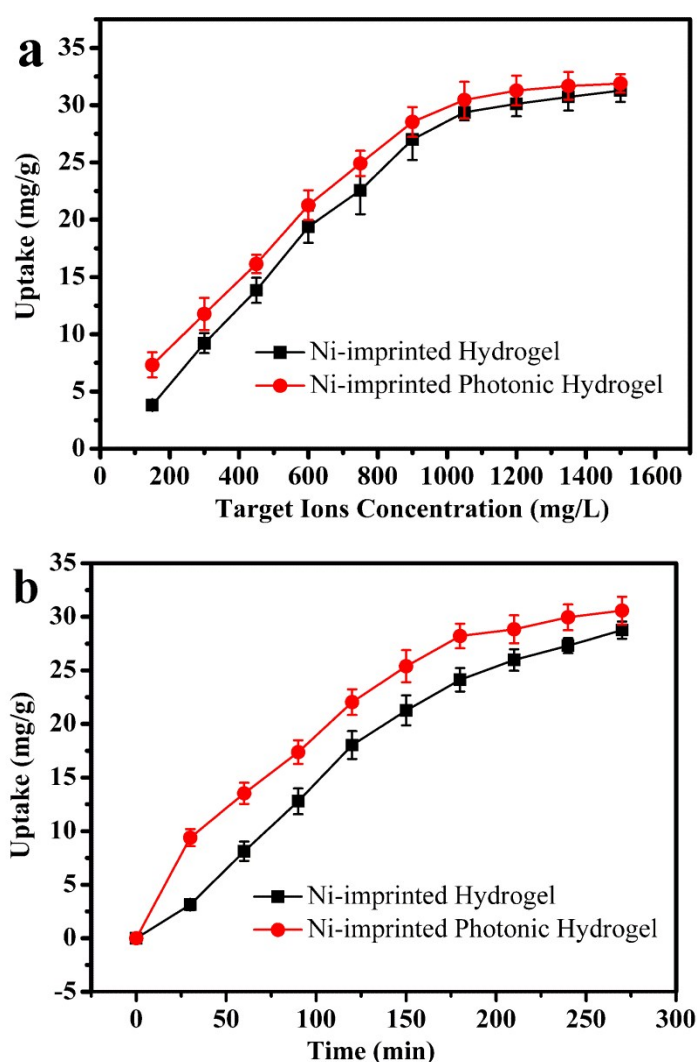


Figure S5. a) Equilibrium adsorption of Ni(II) with various target ion concentrations of imprinted photonic hydrogel, imprinted hydrogel, photonic hydrogel and hydrogel and b) time profile of Ni(II) ions removal by use of imprinted photonic hydrogel, imprinted hydrogel, photonic hydrogel and hydrogel soaking in 1050mg/L.

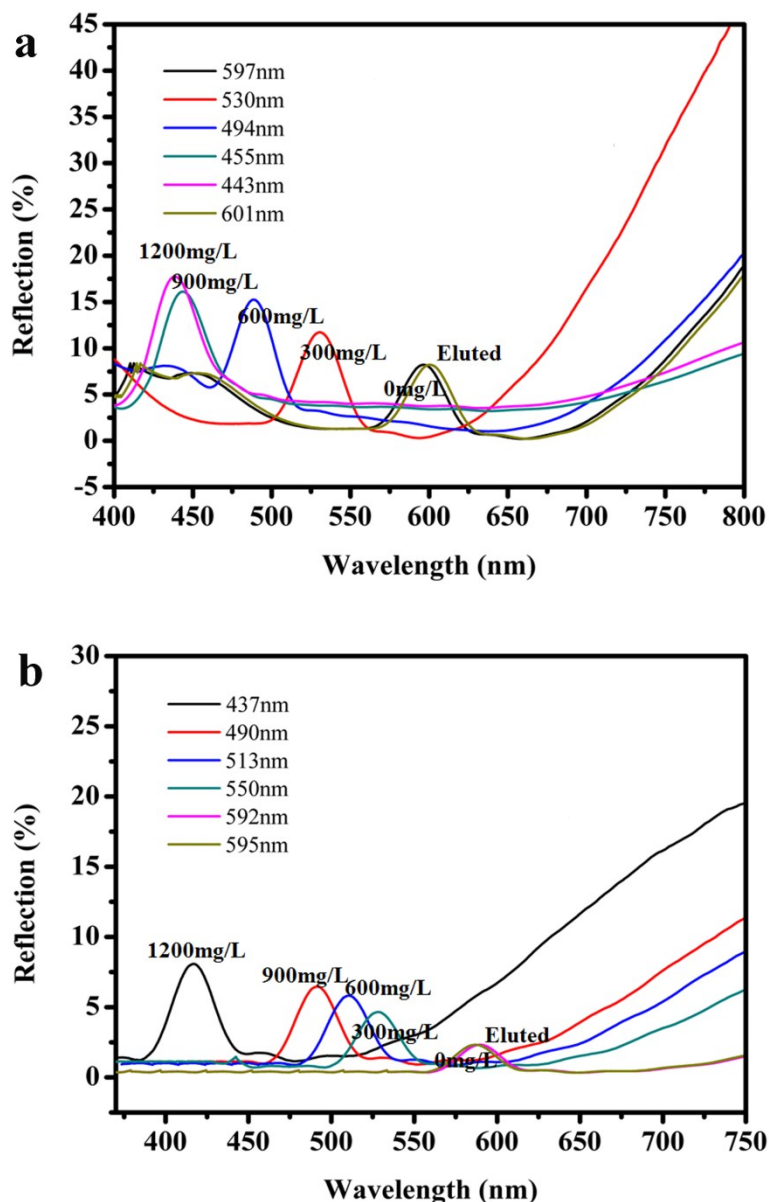


Figure S6. Reflection spectrums of a) Cu-imprinted PC hydrogel and b) Zn-imprinted PC hydrogel adsorbing target ions in the concentration of 0, 300, 600, 900, 1200mg/L and eluted condition

References

1. Stöber, W.; Fink, A.; Bohn, E., Controlled growth of monodisperse silica spheres in the micron size range. *Journal of colloid and interface science* **1968**, *26*, (1), 62-69.
2. Zhang, T.; Zhang, Q.; Ge, J.; Goebel, J.; Sun, M.; Yan, Y.; Liu, Y.-s.; Chang, C.; Guo, J.; Yin, Y., A self-templated route to hollow silica microspheres. *The Journal of Physical Chemistry C* **2009**, *113*, (8), 3168-3175.
3. Barati, A.; Moghadam, E. A.; Miri, T.; Asgari, M., Rapid Removal of Heavy Metal Cations by Novel Nanocomposite Hydrogels Based on Wheat Bran and Clinoptilolite: Kinetics, Thermodynamics, and Isotherms. *Water, Air, & Soil Pollution* **2014**, *225*, (9), 1-18.

4. Huang, S.-H.; Chen, D.-H., Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent. *Journal of hazardous materials* **2009**, *163*, (1), 174-179.