

Supporting Information for

Preparation and properties of ion-imprinted hollow particles for the selective adsorption of silver ions

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1. Effects of pH value on Ag⁺ absorption onto the Ag-IIPs

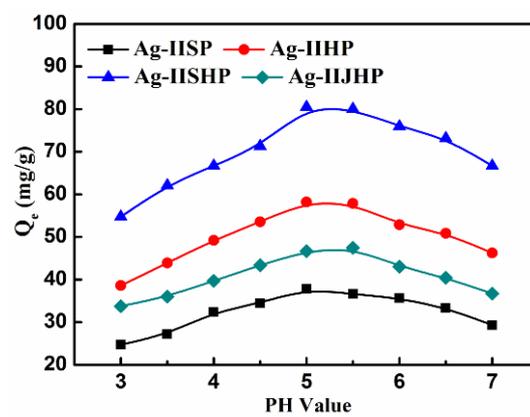


Figure S1 Effects of pH value on Ag⁺ absorption onto the Ag-IIPs

2 Effects of CTS and template Ag^+ content on Ag^+ absorption onto the Ag-IIPs

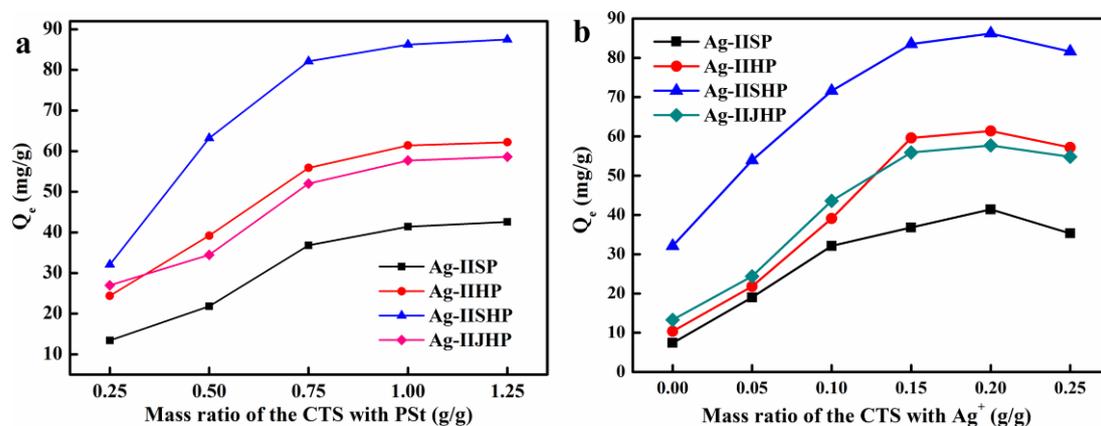


Figure S2 The effect of (a) CTS & (b) template Ag^+ content on Ag^+ absorption onto the Ag-IIPs

The Ag-IIPs were prepared by CTS and polymer particles in accordance with the mass ratio of 0.25:1, 0.5:1, 0.75:1, 1:1, and 1.25:1, and the Q_e values of the Ag-IIPs were measured as shown in Figure S2a. Along with the increasing CTS content in Ag-IIPs, the Q_e values of the Ag-IIPs increased gradually to saturation as a result of more binding sites for the Ag^+ . The growth rates of the Q_e were slower after the mass ratio was higher than 0.75:1. The epoxy groups in GMA were finite on the surface of polymer particles, so the redundant CTS were difficult to be introduced onto these particles. The redundant CTS were eliminated entirely by washing with 5% (wt) HAc aqueous solution. To avoid the waste, the mass ratio of CTS to polymer particles 1:1 was chosen as the optimal CTS content for the preparations of Ag-IIPs. In addition, the viscosity in system was too sticky due to high concentration CTS-HAc solution, and the resulting particles were difficult to separate. So the CTS concentration 0.5% (wt) was used to prepare the Ag-IIPs.

The Ag-IIPs were prepared by CTS and the template Ag^+ in accordance with the mass ratio of 1:0, 1:0.05, 1:0.10, 1:0.15, 1:0.20, and 1:0.25, and the Q_e values of the

Ag-IIPs were measured as shown in Figure S2b. Along with the increasing template Ag^+ content in Ag-IIPs, the Q_e values of Ag-IIPs increased first and decreased then, and the maximum Q_e values were observed when the mass ratio was 1:0.20. It was because more binding sites for the Ag^+ could be generated at the higher template Ag^+ content, but the overmany template Ag^+ tended to clutter and stack with excessive increase. The formation of binding sites would be obstructed by the steric hindrance effects originated from the cluttered template Ag^+ , and the elution of template Ag^+ would be more difficult too. So the binding sites were insufficient for the complex of CTS with Ag^+ at excessive template Ag^+ content. Conversely, the Ag-IIPs were often unable to exert efficient imprinting performance with limited binding sites for Ag^+ , and the nonselective adsorption would be fomented at lower template Ag^+ content. Therefore, the mass ratio of CTS to template Ag^+ 1:0.20 was chosen as the optimal template Ag^+ content for the preparation of the Ag-IIPs.

3 Reusability evaluations

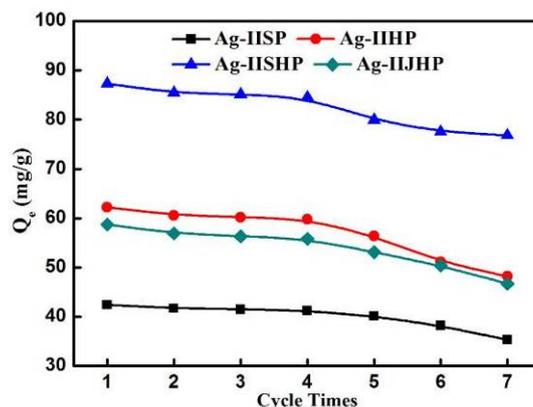


Figure S3 Reusability for Ag^+ adsorption onto the Ag-IIPs after seven reuse cycles

The reusability is a major factor for evaluating the practical application value of Ag-IIPs. The reuse cycles of Ag-IIPs were repeated seven times for Ag^+ adsorption in same adsorption and desorption conditions. Fortunately, all the Q_e values of Ag-IIPs were decreased with the increasing cycles as shown in Figure S3, but Ag-IIPs could be effectively regenerated for further utilization with only about 5% - 8% loss of initial adsorption capacity. Compared to the fresh Ag-IIPs, there were no significant changes on Ag^+ adsorption onto the Ag-IIPs used after seven times. So it was considered that the Ag-IIPs were capable of recycling favorably.

4 Adsorption isotherms

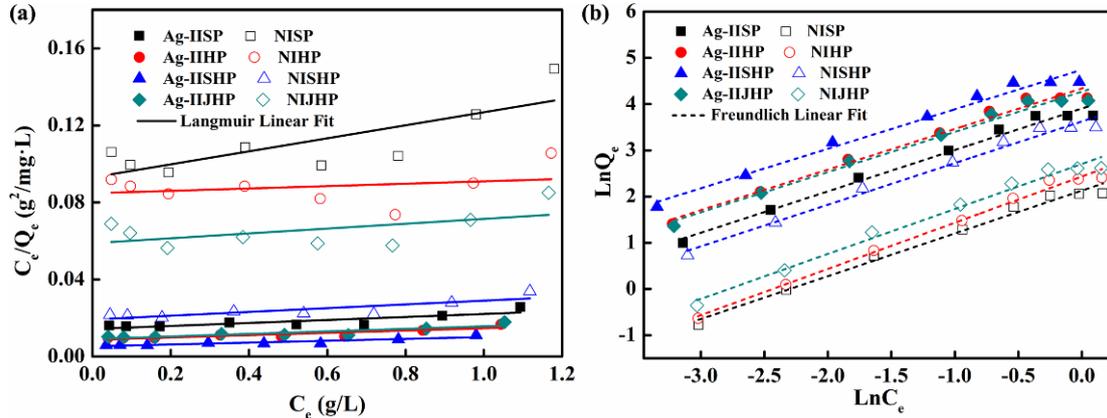


Figure S4 The linear fit of Langmuir and Freundlich isotherm models for Ag⁺ adsorption onto the Ag-IIPs and NIPs

The equilibrium adsorption isotherm is fundamental to describe the interaction between the adsorbate and the adsorbent, and is important on designing an adsorption system. The widely used Langmuir isotherm equation can be expressed by Eq. 1.

$$Q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \quad (1)$$

Where Q_e is the equilibrium adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), Q_m is the maximum adsorption capacity of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$), C_e is the equilibrium concentrations of Ag⁺ ($\text{mg} \cdot \text{L}^{-1}$) and k_L represents the Langmuir adsorption constant ($\text{L} \cdot \text{mg}^{-1}$), which is related to the energy of adsorption. The linear form for this mechanism is expressed in Eq.2. Values of k_L and Q_m are calculated from a plot of C_e/Q_e versus C_e (Figure S4a).

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{k_L Q_m} \quad (2)$$

The Langmuir isotherm model assumes monolayer adsorption onto a surface with a finite number of identical sites. To predict the favorability of an adsorption system, the Langmuir equation may also be expressed in terms of a dimensionless constant separation factor, R_L , defined as follows:

$$R_L = \frac{1}{(1 + C_m K_L)} \quad (3)$$

Where C_m is the maximal Ag^+ initial concentration of the solutions ($mg \cdot L^{-1}$), R_L indicates the favorability and adsorptivity of the adsorption system. It is considered to be a favorable adsorption process when the value is within the range 0 - 1.0.

The Freundlich isotherm model is an empirical equation based on the adsorption on heterogeneous surfaces. The equation can be expressed by Eq. 4.

$$Q_e = k_F C_e^{1/n} \quad (4)$$

Where Q_e is the equilibrium adsorption capacity of the adsorbent ($mg \cdot g^{-1}$), C_e is the equilibrium concentrations of Ag^+ ($mg \cdot L^{-1}$) and k_F represents the Freundlich adsorption constant ($mg \cdot g^{-1}$). It is considered to be a favorable adsorption process when the $1/n$ value is within the range 0.1 ~ 1.0. The linear form for this mechanism is expressed in Eq.5. Values of k_F and $1/n$ are calculated from a plot of $\ln Q_e$ versus $\ln C_e$ (Figure S4b).

$$\ln Q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (5)$$

5 Adsorption Kinetics

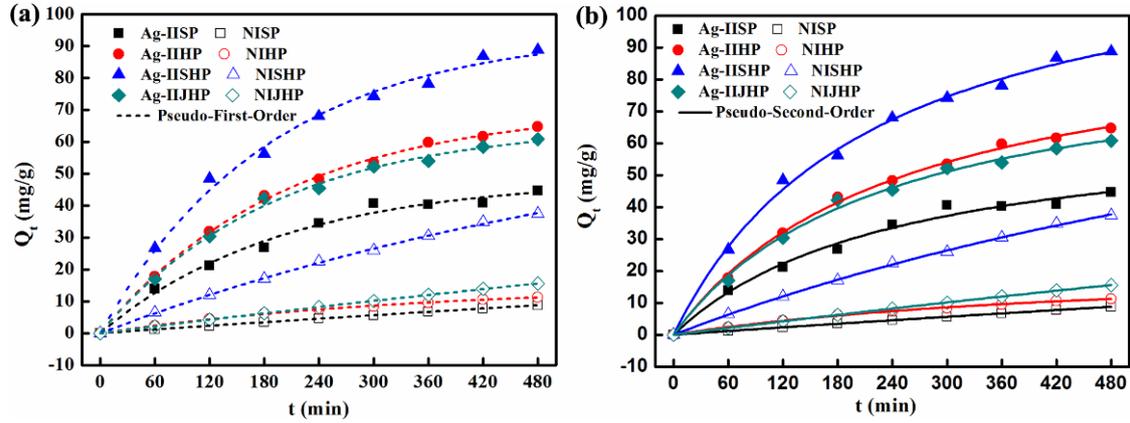


Figure S5 The nonlinear fit of Pseudo-first-order and Pseudo-second-order models for Ag^+ adsorption onto the Ag-IIPs and NIPs

The adsorption kinetics for Ag^+ adsorption onto the Ag-IIPs was investigated with the help of two kinetic models, namely the Lagergren pseudo-first-order model and pseudo-second-order model. The pseudo-first-order and pseudo-second-order models are expressed by the following Eq.6 & 7.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

Where Q_e and Q_t are the adsorption capacity of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium and at time t (min), k_1 ($\text{L}\cdot\text{min}^{-1}$) and k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order model. k_1 is calculated from the slope of the line plotted by $\ln(Q_e - Q_t)$ versus t , and k_2 is calculated from the slope and intercept of the line plotted by t/Q_t versus t , respectively.

Weber-Morris intra-particle diffusion model, which is widely used for adsorption, has been applied to investigate the mechanism for Ag^+ adsorption onto the Ag-IIPs. The intra-particle diffusion model is expressed by the following Eq.8.

$$Q_t = k_{\text{int}} t^{1/2} + C \quad (8)$$

Where Q_t is the adsorption capacity of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$) at time t (min), k_{int} is the the intra-particle diffusion rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$). C is the intercept, which is an indicator for expressing the boundary layer thickness. k_{int} and C are calculated from the slope and intercept of the line plotted by Q_t versus $t^{1/2}$, respectively.

6 Selectivity parameters

Distribution coefficients (K_d , $\text{mL}\cdot\text{g}^{-1}$) of Cu^{2+} and Zn^{2+} with respect to Ag^+ were calculated by Eq. 9.

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \quad (9)$$

Where K_d represents the distribution coefficient, C_0 , and C_e are the initial and equilibrium concentrations of Ag^+ ($\text{mg}\cdot\text{mL}^{-1}$), respectively. V is the volume of the adsorption solution (mL), and m is the adsorbent mass (g).

Selectivity coefficient (k) for the Ag^+ adsorption in the presence of interfering ions can be calculated by Eq. 10.

$$k = \frac{K_d(\text{imprinting ion})}{K_d(\text{interfering ion})} \quad (10)$$

Relative selectivity coefficient (k') can be defined as

$$k = \frac{k(\text{Ag-IIPs})}{k(\text{NIPs})} \quad (11)$$

All above coefficients provided an evaluation of the effect of ion-imprinting technology on selectivity.