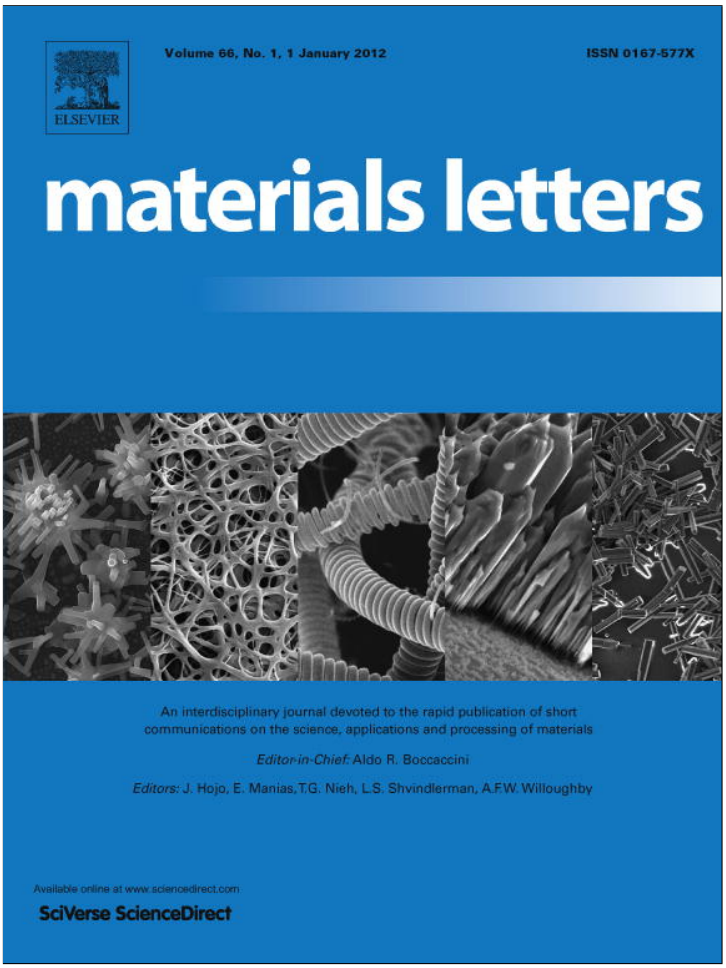

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Protein adsorption on gold nanoparticles supported by a layered double hydroxide

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ABSTRACT

A composite of gold nanoparticles loaded on a layered double hydroxide (AuNPs-LDH) was prepared by in situ reduction method, and its adsorption for hemoglobin (Hb), bovine serum albumin (BSA) and lysozyme (LYZ) were investigated. The results show that AuNPs-LDH composite exhibits the different adsorption capacities, and a significantly higher adsorption for Hb was observed. The effects of concentration, pH, and ionic strength of the protein solution on adsorption were examined. The pseudo second order kinetic model was used to simulate the adsorption process of Hb onto the AuNPs-LDH composite. Furthermore, the AuNPs-LDH composite does not deactivate during the adsorption process, and can be easily separated from the reaction system. The results indicate that AuNPs-LDH can be used as an attractive regenerative and recyclable adsorbent for protein.

1. Introduction

Protein adsorption on solid surfaces has attracted attention due to its scientific importance and application in many areas, such as interfacial engineering, materials science, and biomedicine [1,2]. However, the mechanism of binding proteins to surfaces is poorly understood and the interactions seem less specific [3]. Recently, gold nanoparticles (AuNPs) have become prevalent in adsorption and bioseparation. Compared with the conventional micrometer-sized adsorbents, AuNPs have many superior characteristics [4]. However, the aggregation of AuNPs largely restricts their application [5,6]. Therefore, immobilization and dispersing AuNPs on an inorganic support should be a good approach to resolve these problems.

Layered double hydroxides (LDHs) are a class of inorganic layered materials which can be described by the formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ (M^{II} and M^{III} are divalent and trivalent metals respectively, and A^{n-} a n-valent anion). The properties of LDHs make them attractive candidates as catalyst precursors [7,8], ion exchangers and absorbents [9,10]. This inspires us to take the challenge of dispersing AuNPs on LDH, which exhibit the following advantages: LDHs provide a microenvironment for AuNPs, and result in a higher dispersion AuNPs which could suppress AuNPs aggregation. Especially, LDHs possess good biocompatibility, facile manipulation and low-cost. Although AuNPs in the layered materials have been prepared, and protein adsorption on smectite layered complex has been reported [11], it is still an important task to research the selective adsorption protein on AuNPs supported by LDHs.

In this work, AuNPs supported by MgAl-LDH (AuNPs-LDH) has been synthesized by in situ reduction method. It displayed a superior adsorption for hemoglobin (Hb) relative to bovine serum albumin (BSA) and lysozyme (LYZ), as a result of its high specific surface area and high dispersing AuNPs. The adsorption process of Hb onto AuNPs-LDH can be described by the pseudo second order kinetic model. Moreover, it suggested that AuNPs bind tightly to LDH that can be recovered and reused multiple times. On the basis of the advantages of simplicity, high selectivity, and good reproducibility, the AuNPs-LDH composite may be used as a potential adsorbent for protein.

2. Experimental

2.1. Preparation of the AuNPs-LDH composite

MgAl-LDH precursor was synthesized by the hydrothermal method reported previously [12]. Then the LDH was suspended in 200 mL of $HAuCl_4$ (10 mg/mL) aqueous solution. The reaction was stirred at room temperature, and the solution of 0.8 g sodium borohydride dissolved in 25 mL ice decarbonated water was added. The resulting gel was aged under a nitrogen atmosphere at room temperature for 24 h. The obtained precipitation (denoted as AuNPs-LDH) was filtered, washed extensively with deionized water and dried overnight at 60 °C.

2.2. Adsorption experiments

A series of 50 mL aqueous solution of Hb, BSA and LYZ were added to the Erlenmeyer flask respectively and 0.15 g AuNPs-LDH powder was dispersed thoroughly in the solution. The flasks were then placed

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in a water bath and gently shaken for 500 min. Standard calibration curves of proteins were respectively obtained by means of UV–vis spectrophotometer. The amount of proteins adsorbed by AuNPs-LDH was calculated by the difference between the initial and equilibrium concentrations, per kilogram of LDH adsorbent.

3. Results and discussion

3.1. Characterization of the AuNPs-LDH composite

As shown in Fig. 1A, pristine LDH and AuNPs-LDH display the characteristic (003), (006), (012) and (110) reflections corresponding to hydrotalcite-like materials. As for AuNPs-LDH, the reflection of Au (111), (200) and (220) confirms that crystalline Au phase is formed. The basal reflection (003) of AuNPs-LDH does not shift to a lower 2θ angle compared with that of LDH. This may indicate that AuNPs mainly located on the surface of LDH. SEM image of AuNPs-LDH (Fig. 1B) shows the flat, well-defined hexagonal basal platelets, with fairly large crystal sizes ranging of 1–2 μm. HRTEM micrograph (Fig. 1C) further reveals that AuNPs with spherical morphology are arranged on LDH support, having average sizes in the range of 2–3 nm.

Fig. 1D displays the N_2 adsorption-desorption isotherm and the corresponding pore size distribution curve for the AuNPs-LDH sample. The AuNPs-LDH composite exhibits a typical isotherm with a H3-type hysteresis loop ($P/P_0 > 0.4$), indicating the presence of mesopores. The composite has a wide distribution of pore size (1.8–124 nm, maximum at 34.3 nm), and a specific surface area ($52.70\ m^2 \cdot g^{-1}$) was obtained.

3.2. Adsorption thermodynamics

3.2.1. Adsorption capacities for Hb, BSA and LYZ by the AuNPs-LDH composite

The adsorption capacities of AuNPs-LDH composite for Hb, BSA and LYZ with the different concentrations were shown in Fig. 2A. It was found that the adsorption capacities of AuNPs-LDH for proteins increased gradually upon increasing the original concentration. With increasing the original total concentration, the adsorption capacity for Hb could be up to 42.5 mg/g, whereas the adsorption capacities for BSA and LYZ were only about 0.58 mg/g and 0.19 mg/g, respectively. Therefore, the adsorption capacity of AuNPs-LDH for Hb is significantly larger than that for BSA and LYZ.

To verify that the different adsorption of AuNPs-LDH is related to AuNPs, a comparison study was carried out (Fig. 2B). It can be seen that the adsorption amount for Hb by the LDH precursor was significantly lower than that of AuNPs-LDH composite. Meanwhile, no significant different adsorption was observed among Hb, BSA and LYZ, indicating that the difference in adsorption capacity in Fig. 2A is related to the AuNPs dispersed by LDH. Therefore, the introduction of AuNPs modified the protein adsorption of LDH, showing a higher adsorption capacity for Hb. One possible explanation is that the adsorption characteristics of proteins are influenced by their amino acid compositions and sequences [13]. Compared with BSA and LYZ, Hb contains more free –SH groups which can form a covalently link to

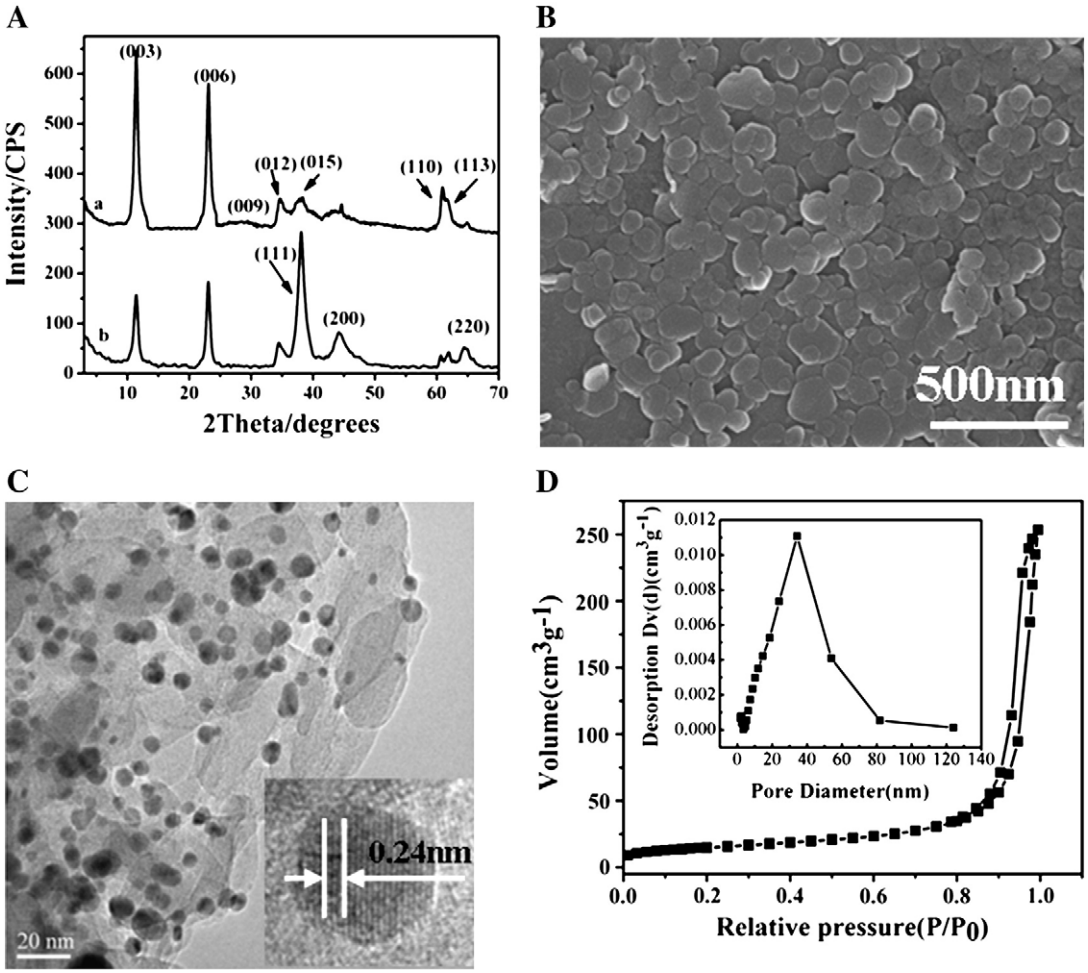

Fig. 1. (A) Powder XRD patterns for MgAl-LDH (a) and AuNPs-LDH (b); (B) SEM image of AuNPs-LDH; (C) TEM image of AuNPs; (D) N_2 sorption isotherms and pore size distribution of the AuNPs-LDH composite.

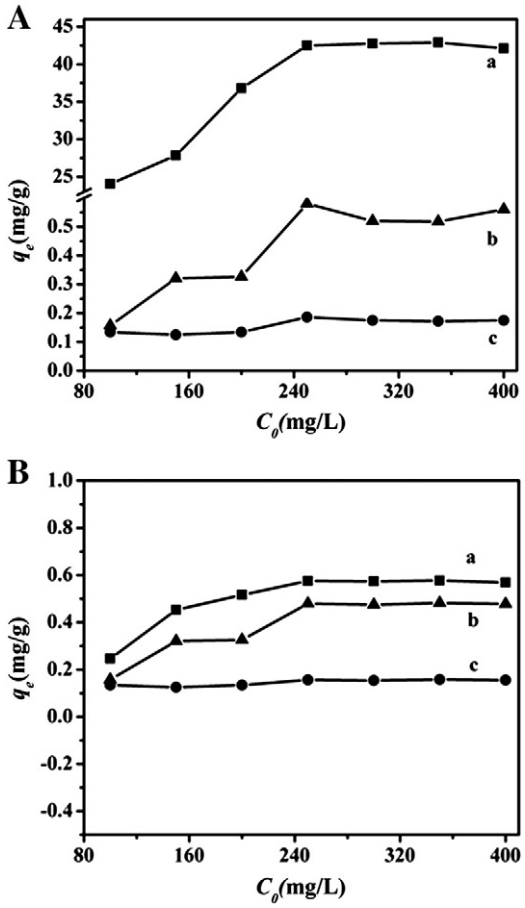

Fig. 2. Adsorption of Hb (a), BSA (b) and LYZ (c) with the different concentrations by (A) AuNPs-LDH and (B) MgAl-LDH.

AuNPs, accounting for a stronger adsorption onto the AuNPs-LDH composite. Also, LDHs provide a supporting material for AuNPs, which result in a dispersed AuNPs with a higher specific surface area and a significantly larger adsorption capacity for protein.

3.2.2. Influence of pH and ionic strength on Hb adsorption

The AuNPs-LDH composite exhibits a stronger adsorption for Hb than for BSA and LYZ, so the following section will be focused on Hb adsorption by AuNPs-LDH. The pH dependence of adsorption capacity is plotted in Fig. S1, and exhibits a maximum at its isoelectric points. Similar pH dependence of protein adsorption on inorganic support was also reported [14]. The effect of ionic strength on Hb adsorption by AuNPs-LDH is shown in Fig. S2. It can be seen that the amount of protein adsorbed decreases with increasing ionic strength of the solution. Therefore, it is suggested that the surface charge of protein and the charge of AuNPs-LDH may be a complementary interaction for the adsorption to occur.

3.3. Adsorption kinetics

To evaluate the adsorption of AuNPs-LDH to Hb, kinetic studies are also needed. The Lagergren's first order kinetic model (Eq. (1)) and the Ho's pseudo second order model (Eq. (2)) were used respectively to simulate the kinetic process.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (1)$$

$$t/q_t = t/q_e + 1/k_2 q_e^2 \quad (2)$$

Table 1
Adsorption kinetic parameters of Hb by the AuNPs-LDH composite.

Model	$K\times10^3$	q_e	$q_{e,exp}$	R^2
Lagergren's first order kinetic model	60.61	42.5334	40.50	0.931
Ho's pseudo second order model	5.018	42.2865		0.997

Where q_t and q_e (mg/g) are the amounts of protein adsorbed per unit mass of the adsorbent at time t and at equilibrium, respectively. k_1 (min^{-1}) is the first order rate constant of adsorption and k_2 (g/mg·min) is the second order rate constant. The parameters of the two equations were calculated in Table 1 and the fitting curves were shown in Fig. 3. It is observed that the calculated amount of equilibrium adsorption capacity is similar to the actual tested adsorption capacity. The pseudo second order equation appeared to be the best-fitting model ($R^2 > 0.99$). Therefore, the pseudo second order kinetic model is more suitable to describe the kinetics adsorption of Hb onto the AuNPs-LDH.

3.4. The regeneration and reversibility

An important advantage of the adsorbent is its recycling and regeneration. So the regeneration of AuNPs-LDH was performed by elution the composite with the distilled water, the solution of EDTA (50 mmol/L) and NaCl (0.5 mol/L), respectively. The procedure was repeated five cycles and the adsorption capacities of Hb were measured (Fig. S3). It was shown that the adsorption was almost not changed with five cycles, indicating that AuNPs-LDH does not deactivate during the adsorption process of Hb.

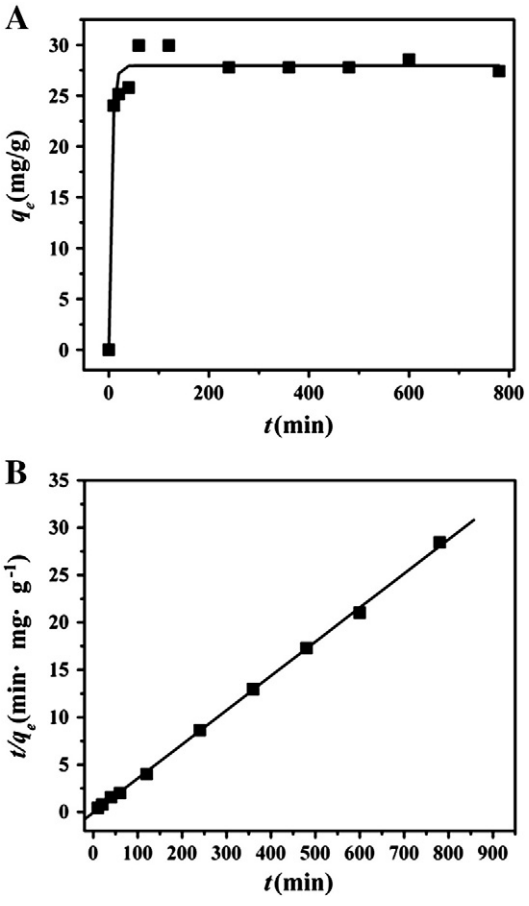

Fig. 3. The kinetic plots for the adsorption of Hb by (A) the Lagergren's first order kinetic model and (B) the Ho's pseudo second order model.

Furthermore, the AuNPs-LDH sample after adsorption was recovered and characterized by SEM and TEM (Figs. S4, S5). It shows that the composite microstructure keep intact. Meanwhile, the composite can be easily separated from the reaction system due to its particle size. The results thus indicate that AuNPs-LDH can be used as an attractive regenerative and recyclable adsorbent for protein.

4. Conclusions

Very small and stable gold nanoparticles (AuNPs) were successfully loaded on MgAl-LDH using in situ reduction method. TEM showed that AuNPs could be well dispersed in AuNPs-LDH composite. The introduction of AuNPs modified the protein adsorption of LDH, showing a higher adsorption capacity for Hb. The kinetic studies indicate that the pseudo second order model is more suitable to simulate the adsorption process. The regeneration and reversibility experiments revealed that AuNPs-LDH does not deactivate during the adsorption process. On the basis of the advantages of simplicity, specific adsorption for Hb and good reproducibility, the AuNPs-LDH composite may have great potentials in protein adsorption.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.matlet.2012.02.121.

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