Preparation of Magnetic Carbon Nanotubes with Hierarchical Copper Silicate Nanostructure for Efficient Adsorption and Removal of Hemoglobin

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Abstract

The controllable synthesis of materials with the desired structure and dimensionality is of great significance in material science. In this work, the hierarchical CNTs/Fe₃O₄@copper silicate(CNTs/Fe₃O₄@CuSilicate) composites was synthesized *via* a simple chemical conversion route by using CNTs/Fe₃O₄@SiO₂ nanocables as template. Firstly, magnetic CNTs composites (CNTs/Fe₃O₄) were synthesized by the high temperature decomposition process using the iron acetylacetonate as raw materials. Then a layer of SiO₂ can be easily coated on the magnetic CNTs by the stöber method, which were then converted into CNTs/Fe₃O₄@CuSilicate composites by hydrothermal reaction between the silica shell and copper ions in alkaline solution. The resulting CNTs/Fe₃O₄@CuSilicate composites hold merits such as magnetic responsivity, good dispersibility, and large specific surface area. Moreover, the CNTs/Fe₃O₄@copper silicate composites have strong affinity toward bovine hemoglobin(BHb), which were successfully applied to convenient, efficient, and fast removal of abundant proteins(HHb and HSA) in human blood.

Introduction

With the increasing need for purified proteins in applications ranging from diagnostics to therapeutics, the development of efficient methods for the separation and purification of recombinant proteins has aroused great interest in proteomics [1]. Currently, immobilized metal affinity chromatography (IMAC) is the most frequently

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used method for the separation of His-tagged proteins from a matrix containing other undesirable biological elements[2, 3]. However, this technique has limitations including the need for pre-treatment on removing the cell debris and fouling components. In order to circumvent these limitations, several separation systems based on magnetic nanomaterials have been developed, such as nitrilotriacetic acid (NTA)[4] or polymer brush-modified magnetic nanoparticles[5], Au–Ni–Au triblock nanorods[6], Ni/NiO core–shell nanoparticles[7], $\text{Fe}_2\text{O}_3/\text{SiO}_2$ core–shell microspheres decorated with NiO nanoparticles[8]. However, these systems, still suffer from drawbacks such as complicated synthesis procedures, limited surface area as well as low metal ion intensity. Therefore, it is necessary to develop new approaches to fabricate magnetic materials for proteins with appropriate magnetic properties.

To overcome these problems, the well-designed hierarchical magnetic metal silicate nanomaterials have emerged as powerful candidates for meeting the above mentioned requirements. Metal silicates have attracted significant interest due to exhibit much higher stability in various chemical and physical environments, and they are widely used in adsorption, separation, and catalytic fields[9,10]. The hierarchical metal silicate architectures assembled from nanoscale units can avoid aggregation while maintaining high metal ion density, which greatly favors enhancing protein binding capacity. For example, Liu etc have synthesized $\text{Fe}_3\text{O}_4@\text{Ni}_x\text{SiO}_y$, which provides a convenient means of purifying His-tagged proteins[11]. Wang etc have fabricated the yolk–shell nanostructured $\text{Fe}_3\text{O}_4@\text{NiSiO}_3$ by a facile sol–gel and hydrothermal method. The outer shell of nickel silicate could provide for a selective adsorption of His-tagged protein from the mixed-protein solutions[12]. However, these works are only limited to the zero materials(spheres). Compared to metal silicate nanospheres, one-dimensional metal silicate nanomaterials have better mechanical strength, higher specific surface areas and shorter diffusion path for mass transportation, and are thereby more suitable for adsorption. Thus, synthesizing such one-dimensional metal silicate nanomaterials has been highly desired. Song and his co-workers have

synthesized hierarchical double-walled copper/nickel/magnesium silicate hollow nanofibers and their application as an efficient and reusable adsorbents for the removal of dye[13-15]. More recently, Song etc have designed a magnetic magnesium silicate nanotubes by a well-controlled programmed synthesis, and they showed very good adsorption properties for Pb(II) and Cd(II)[16]. Although great progress has been achieved in removing the hazardous substances, few reports were reported to adsorb and separate the proteins using the one dimensional metal silicate materials. Furthermore, combining the one dimensional metal silicate materials with magnetism may help for protein separation with the external magnetic field.

In this regards, the hierarchical CNTs/Fe₃O₄@copper silicate composite was synthesized via a simple *in situ* chemical conversion route by using CNTs/Fe₃O₄@SiO₂ nanocable as template. Owing to the high copper density on the surface and the response toward an assistant magnet, these materials could be applied to selectively bind and magnetically separate HHb and HSA from diluted human blood. To the best of our knowledge, this kind of magnetic one-dimensional hierarchical copper silicate structure has not been reported before. When used as protein adsorbent, the hierarchical CNTs/Fe₃O₄@copper silicate (CNTs/Fe₃O₄@CuSilicate) composite exhibited excellent protein adsorption capability.

2. Experimental Section

2.1 Chemicals

Multiwalled CNTs (MWCNTs) with a mean diameter of 60–100 nm were provided by the Shenzhen Nanotech Port Co. Ltd. Iron(III) acetylacetonate (Fe(acac)₃, 99%) was purchased from Acros. Triethylene glycol (TREG, 99%) was from Aldrich. Tetraethoxysilane (TEOS, 95%) was obtained from the Alfa Aesar Chemical Company, which was used directly without further purification. Copper chloride hydrate (CuCl₂·2H₂O), ammonia solution (28–30%), water and ethanol were used for

all experiments. Other chemical reagent were purchased from shanghai chemical reagent company.

2.2 Synthesis of CNTs/Fe₃O₄ composites:

CNTs/Fe₃O₄ composites were fabricated according to the literature with minor modification [15]. In a typical procedure, 400 mg Fe(acac)₃ and 100 mg MWCNTs were added to 60 mL TREG and ultrasonicated for 10 min. The resulting mixture was then heated to 278 °C under N₂ protection and kept at reflux for 30 min. After cooling to room temperature, the obtained composites were magnetically separated by a magnet and washed with ethanol for several times and dried at 60 °C in vacuum.

2.3 Synthesis of CNTs/Fe₃O₄@SiO₂ composites:

The synthesis procedure is based on the stöber method. In a typical procedure, 30 mg CNTs/Fe₃O₄ composites were added to 250 mL three-neck round flask containing 95 mL ethanol and 5 mL water. The mixture was sonicated for 50 min. Then 0.5 mL TEOS was slowly added to the above solution in 30 min under mechanical stirring. After kept stirring for 6 h, the precipitates were separated by a magnet and washed with ethanol and water for 5 times and dried at 60 °C in vacuum.

2.4 Synthesis of CNTs/Fe₃O₄@CuSilicate composites :

In a typical procedure, 50 mg CNTs/Fe₃O₄@SiO₂ nanotubes, 1 mmol CuCl₂·H₂O, 10 mmol NH₄Cl and 1 mL NH₃·H₂O (28 %) were dissolved in 40 ml DI water and ultrasonicated for 10 min, and then the reaction solution was poured into a Teflon-lined autoclave with volume of 50 mL. The oven was heated to 140 °C and kept at that temperature for 12 h. After cooling to room temperature, precipitates were collected as CNTs/Fe₃O₄@CuSilicate by centrifugation and washed with ethanol for five times, and then dried at 60 °C for 3 h.

2.5 Instrumentation

The data of UV-vis adsorption were obtained by using UV-2450 spectrophotometer (Shimadzu, Japan). The crystal structure of nanoparticles was determined by X-ray diffractometer (XRD). The XRD pattern of each sample was recorded with a

Shimadzu (Japan) D/Max-2500 diffractometer, using a monochromatized X-ray beam with nickel-filtered $\text{Cu K}\alpha$ radiation. The XRD patterns were collected in the range of $5^\circ < 2\theta < 80^\circ$ with a dwelling time of 2s and a scan rate of $6.0^\circ/\text{min}$. The substance is automatically searched by using JCPDS-International Center for Diffraction Data. The morphology and microstructures of the samples were characterized by scanning electron microscopy (SEM, JEOL-4800), transmission electron microscopy (TEM, JEOL-1011) and high-resolution transmission electron microscopy (HR-TEM) (FEI Tecnai T200). The nitrogen adsorption-desorption isotherms were measured on a Quantachrome Autosorb AS-1 instrument. The magnetic properties were collected using vibrating sample magnetometry (VSM, MicroSense EV7) at room temperature. XPS of the Copper silicate state was measured using Physical Electronics PHI 5600 XPS spectrophotometer with monochromatic Al K (1486.6 eV) excitation source.

3. Results and Discussion

The fabrication process for $\text{CNTs/Fe}_3\text{O}_4\text{@CuSilicate}$ is depicted in Scheme 1. Magnetite nanoparticles/carbon nanotubes (denoted as $\text{CNT/Fe}_3\text{O}_4$) composites were firstly fabricated in one-pot procedure through a solvothermal method[17]. A thin layer of SiO_2 was then coated onto the $\text{CNT/Fe}_3\text{O}_4$ to produce $\text{CNT/Fe}_3\text{O}_4\text{@SiO}_2$ nanocable, which were then converted into the hierarchical $\text{CNTs/Fe}_3\text{O}_4\text{@CuSilicate}$ composites by hydrothermal reaction between the silica shell and copper ions in alkaline solution.

Scheme 1. Schematic illustration of synthesis of hierarchical structured
CNTs/Fe₃O₄@CuSilicate composites

The morphologies and structural features of the prepared materials can be observed from the SEM and TEM images (Fig. 1). Fe₃O₄ nanoparticles with an average diameter of 8 nm were uniformly distributed on the surface of the CNTs. Functionalizing the assembled nanostructures stabilizing with a layer of hydrophilic polyol molecules, these CNTs/Fe₃O₄ nanocomposites are highly water-dispersed, which is beneficial for SiO₂ coating[18]. Using tetra-ethoxysilane (TEOS) as the silica source, a SiO₂ layer was successfully coated on the CNT/Fe₃O₄ nanocomposites. As shown in Fig. 1(d-f) , and a SiO₂ layer with thickness of 31 nm was coated on the CNT/Fe₃O₄ nanocomposites . When the amount of TEOS was increased from 300 uL to 500 uL, the thickness of silica layer for the CNT/Fe₃O₄@SiO₂ nanocomposites can be increased to 50 nm(Fig. 1(g-i)). From which it can be confirmed that the thickness of the silica layer can be readily controlled by changing the TEOS amount. It can be seen that the surface of CNT/Fe₃O₄@SiO₂ nanocomposites exhibit smoother than that of the CNT/Fe₃O₄ nanocomposites, which fully prove that the successful deposition and growth of the silica layer on the CNT/Fe₃O₄ composites. Additionally, no aggregates of the silica spheres are visible in the FSEM and TEM images. These results suggest that the CNT/Fe₃O₄@SiO₂ nanocomposites were successfully synthesized.

Fig. 1 SEM images of CNTs/Fe₃O₄ (a), TEM images of CNTs/Fe₃O₄ (b,c); SEM images of CNTs/Fe₃O₄@SiO₂(0.3 mL TEOS, (d)), TEM images of CNTs/Fe₃O₄@SiO₂(0.3 mL TEOS, (e,f)); SEM images of CNTs/Fe₃O₄@SiO₂(0.5 mL TEOS, (g)), TEM images of CNTs/Fe₃O₄@SiO₂(0.5 mL TEOS, (h, i)).

Hydrothermal reaction with CuCl₂ and NH₃ H₂O is driven by the interfacial reaction between Cu²⁺ ions and the silicate anions, CuSilicate nanograins are grown readily around the surface of the SiO₂ layer to form the CuSilicate shell[19-22]. Herein, the SiO₂ layer serves not only as the precursor for the CuSilicate shell but also as a protector for the CNT/Fe₃O₄. After the hydrothermal reaction, a single nanocomposites composed of many nanotubes can be clearly observed (Fig. 2). Most of the nanotubes stand on the surface of the nanocomposites and the mean diameter of the nanotubes is about 2 nm with a narrow size distribution. Many holes can be seen on the shell surface due to the open ends of the nanotubes, which endowed the CNT/Fe₃O₄@CuSilicate composites with more BET surface, this will be verified by the following BET test. In addition, the thicknesses of the copper silicate shells of these CNT/Fe₃O₄@CuSilicate core-shell nanocomposites can be readily tuned by the SiO₂ layer thickness of the CNT/Fe₃O₄@SiO₂ in the hydrothermal reaction. From the SEM and TEM image of Fig. 2, it can be observed that the copper silicate shells of the CNT/Fe₃O₄@CuSilicate composites are mainly dependent on the SiO₂ layer

thicknesses of the CNT/Fe₃O₄@SiO₂ templates. Fig. 2(b, c) shows the TEM image of the CNT/Fe₃O₄@CuSilicate using the CNT/Fe₃O₄@SiO₂ with ~30 nm SiO₂ layer thickness as templates. It can be seen that the thickness of the copper silicate shells for the resulting nanocable is ~60 nm. When using the CNT/Fe₃O₄@SiO₂ with ~60 nm SiO₂ layer thickness and keeping other experimental parameters fixed, the shell thickness of the copper silicate shell was increased to ~100 nm. These results are also in accordance with previous work [23].

Fig. 2 SEM images of CNTs/Fe₃O₄@CuSilicate (0.3mL TEOS; a), TEM images of CNTs/Fe₃O₄@CuSilicate (0.3 mL TEOS, (b, c)), SEM images of CNTs/Fe₃O₄@CuSilicate (0.5 mL TEOS, (d)), TEM images of CNTs/Fe₃O₄@CuSilicate (0.5mL TEOS, (e, f)).

Fig. 3 XRD diffraction patterns of the as-prepared CNTs/Fe₃O₄ (a), CNTs/Fe₃O₄@SiO₂ (b), and CNTs/Fe₃O₄@CuSilicate (c).

The XRD patterns of the as-synthesized CNTs/Fe₃O₄, CNTs/Fe₃O₄@SiO₂ and CNTs/Fe₃O₄@CuSilicate are shown in Fig. 3. Fig. 3a shows the XRD pattern of the CNTs/Fe₃O₄ particles, the diffraction peaks of as-received Fe₃O₄ at 30.00°, 35.48°, 43.14°, 53.44°, 57.04°, and 62.58° were observed. The positions and relative intensities of these CNTs/Fe₃O₄ related new peaks match well with the (220), (311), (400), (422), (511), and (440) planes of the standard XRD data for the cubic spinel crystal structure of bulk magnetite. The diffraction peaks of MWCNTs at 25.98° and 42.78° could be attributed to the graphite structure (002) and (100) planes of the MWNTs[24]. As calculated by Scherrer's formula, the average crystallite size of the magnetite crystals was about 8 nm. For the XRD spectrum of CNTs/Fe₃O₄@SiO₂ (Fig. 3b), the major peaks are similar to the pristine CNTs/Fe₃O₄ particles (Fig. 2a), revealing that the core-shell composites consist of the CNTs/Fe₃O₄ component, and the obvious broad peaks at 22° for the SiO₂ is observed, indicating the SiO₂ layer is amorphous. Fig. 3c shows the XRD pattern of the CNTs/Fe₃O₄@CuSilicate composite in which the diffraction peaks assigned to the magnetite can be clearly visible. All weak diffraction peaks of XRD pattern can be clearly indexed to copper silicate (JCPDS card no. 32-0346). It confirms the formation of magnetite-copper silicate composites. The apparent broadening and overlapping of all these peaks indicated that the as-prepared copper silicates were composed of nanoscale crystals.

Fig. 4 XPS pattern of the CNTs/Fe₃O₄@CuSilicate composite.

Fig. 5 N₂ adsorption–desorption isotherms of CNTs/Fe₃O₄@CuSilicate composites.

Inset: pore size distributions.

X-ray photoelectron spectroscopy (XPS) (Fig. 4) was performed to analyze the chemical and oxidation states of the CNTs/Fe₃O₄@CuSilicate composites. All peaks on XPS curve for the composites are ascribed to Cu, Si, O, N and C. No other peaks can be observed. The peaks at 934.3 and 955.2 eV can be addressed to the binding energy of Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, which fully indicates that copper ion was existed in the final product [25]. As shown in Fig. 4c, the peaks of Si 2s and Si 2p could be observed, and the binding energy of Si 2p was 102.8 eV, which suggested that all samples were silicates rather than composites of SiO₂, because the binding energies of Si 2p in many silicates are 102~103 eV whereas that of the SiO₂ is higher(103.8 eV) [26]. The binding energies of Fe 2p_{1/2} and Fe 2p_{3/2} (Fig. 4d) were not found to be 723.9 and 710.4 eV, respectively, because the CNTs/Fe₃O₄ cores are coated with a shell thickness of CuSilicate layer above 10 nm. X-ray photoelectron spectroscopy (XPS) allows the characterization of surface composition with a detection depth limit of approximately 10 nm[27, 28]. Therefore, if the shell thickness exceeds this value, any encapsulated cargo will not be detected. The nitrogen adsorption-desorption isotherms (Fig. 5) at 77 K of the CNTs/Fe₃O₄@CuSilicate composites show type IV curves, suggesting cylindrical pores with narrow pore size distribution at 5.7 nm (Fig. 5 Inset)[29]. The Brunauer-Emmett-Teller (BET) surface

area and total pore volume were calculated to be about 453.2 m²/g and 0.65 cm³/g, respectively, due to the mesoporous and hollow structures.

Fig. 6 shows the hysteresis loop of typical magnetic CNTs/Fe₃O₄@CuSilicate with different thickness of CuSilicate layer composites measured by sweeping the external field at room temperature. No obvious remanence or coercivity is observed in the magnetization curve at room temperature, suggesting a superparamagnetic character. The saturation magnetization of CNTs/Fe₃O₄@CuSilicate(100 nm and 60 nm) are approximately 2.8, 4 emug⁻¹ respectively, and this fully illustrates the thickness of the metal silicate layers makes a difference on the magnetic properties of composites. Inset shows the corresponding magnified hysteresis loops at low applied magnetic fields. The obvious magnetic hysteresis loops ($H_c < 30$ Oe) were observed for the magnetic CNTs/Fe₃O₄@CuSilicate composites based on the field dependent magnetization plots in the inset of Fig. 6, which indicates that the products possessed superparamagnetic features at room temperature. Therefore, based on the combined VSM and above TEM, XRD, XPS results, the hierarchical copper silicate shell and superparamagnetic CNTs/Fe₃O₄ cores were successfully prepared, which can be easily separated from the reaction solution by applying an external magnetic field.

Fig. 6 Hysteresis loops of the magnetic CNTs/Fe₃O₄@ CuSilicate composites, TEOS 0.3mL (a), TEOS 0.5mL (b)

The CNTs/Fe₃O₄@CuSilicate composites were tested for the adsorption of BHb in 20 mM phosphate buffer (pH 8.0) by the batch experiment. Firstly, 1 mg of CNTs/Fe₃O₄@ CuSilicate was mixed with 5 mL of various concentrations of BHb solution (0.02–0.1 mg mL⁻¹). Then, the mixture was shaken at 25°C for 12 h, sufficient time to reach adsorption equilibrium. Analysis of Fig. 7 reveals that the BHb was effectively adsorbed. The BHb adsorption isotherm could be described by the Langmuir equation, Equation :

$$q = \frac{q_m c}{K_d + c}$$

where c (mg mL⁻¹) and q (mg g⁻¹) are the aqueous protein concentration and the amount of adsorbed protein at equilibrium, respectively. q_m (mg g⁻¹) is the maximum adsorption capacity and K_d (mg mL⁻¹) is the dissociation constant. By fitting the experimental data to the Langmuir equation, q_m and K_d are estimated to be 302.3 mg g⁻¹ and 0.20 mg mL⁻¹ respectively.

Fig. 7 Adsorption isotherm of BHb on CNTs/Fe₃O₄@CuSilicate in the solution containing 20 mM phosphate at pH 8.0.

Fig. 8 Curve a is the UV-vis spectrum of 0.4 mg mL⁻¹ of the BHb (A), BSA (B) BHb and BSA mixture (C) before adsorption by CNTs/Fe₃O₄@ CuSilicate. Curve b is the UV-vis spectrum of supernatant of BHb (A), BSA (B), BHb and BSA mixture (C) after adsorbed by CNTs/Fe₃O₄@CuSilicate. Curve c is the UV-vis spectrum of desorption solution of the adsorbed protein by CNTs/Fe₃O₄@CuSilicate in BHb (A), BSA (B), BHb and BSA mixture (C) using concentration of 0.2 g mL⁻¹ of dimethyl imidazole solution as the eluent. D is the recyclability of the CNTs/Fe₃O₄@ CuSilicate as the absorbent for BHb.

In addition, The single protein BHb (0.4 mg mL⁻¹) and BSA (0.4 mg mL⁻¹), a binary protein mixture containing 0.4 mg mL⁻¹ BHb and BSA respectively were incubated with CNTs/Fe₃O₄@CuSilicate composites for 6 h at room temperature. The adsorbed proteins could be eluted by dimethyl imidazole solution(0.2 g mL⁻¹). The protein concentration in the supernatant was analyzed using a UV-vis spectrophotometer at 280 and 406 nm for BSA and BHb respectively. As shown in Fig. 8, the absorption intensity of BHb at 406 nm revealed the efficient removal of BHb from the single BHb solution, and the binary BHb and BSA solution (Fig. 8A(b), C(b)), while the adsorption intensity of BSA exhibits a negligible decrease at 280 nm. Compared with

the absorption spectra of the single BHb and of binary protein solutions (BHb and BSA), an interesting phenomenon was observed. When BSA is considered as a competitive protein, the amount of adsorbed BHb is lower than that of single solution. This is mainly attributed to the interaction between BHb and BSA is relatively stronger than that of without competitive protein. The interaction between proteins has the negative effect on the adsorption of the BHb. The difference on the adsorption capacity of CNTs/Fe₃O₄@ CuSilicate composites towards BHb and BSA may be ascribed to the different histidine residues in the proteins. It is well known that the number of accessible histidine residues on BHb is 24, whereas there are only 2 histidine residues on the surface of BSA. The captured BHb on the CNTs/Fe₃O₄@ CuSilicate composites was released by the treatment of the composites with dimethyl imidazole solution (0.2 g mL⁻¹). Because the dimethyl imidazole has a strong metal chelating interaction with Cu²⁺, it resulted in the release of BHb protein from the CNTs/Fe₃O₄@CuSilicate composites. After complete desorption of His-tagged proteins, the CNTs/Fe₃O₄@CuSilicate composites could be reused after sonication in buffer to release the excess adsorbed dimethyl imidazole. The time of sonication was very important to improve the adsorption activity. Thus, the 30 minutes was selected for releasing the excess adsorbed dimethyl imidazole. Here, the CNTs/Fe₃O₄@CuSilicate composites were reused up to five times through the centrifugal separation and subsequent release of the captured protein. As shown in Fig. 8D, it reveals the reduction of BHb drops slightly after each cycle, and it decreased gradually in subsequent runs to 89% at run 5, indicating that the CNTs/Fe₃O₄@CuSilicate composites have excellent separation efficiency.

In order to further demonstrate the specific adsorption of CNTs/Fe₃O₄@CuSilicate composites to BHb and explore its application in the real samples (human blood), the mixtures of binary proteins BHb and BSA solution, diluted human blood were carried out by contacting CNTs/Fe₃O₄@CuSilicate composites. The supernatant solution and the desorption solution of CNTs/Fe₃O₄@CuSilicate composites from the adsorbent by

dimethyl imidazole solution (0.2 g mL^{-1}) were analyzed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). From the SDS-PAGE analysis (Fig. 9), it could be seen that the BHb band obviously faded while the BSA band nearly remained as original (lane 3) after treatment with the CNTs/Fe₃O₄@CuSilicate composites. The eluted solution from CNTs/Fe₃O₄@CuSilicate composites showed the BHb, BSA band, which demonstrated the specific absorption on his-tagged proteins (lane 4). This further demonstrated that most of the protein adsorbed by CNTs/Fe₃O₄@CuSilicate composites was BHb. Compared with that of the binary proteins mixture of BHb and BSA, the two bands between 10-fold human whole blood solution and adsorbed solution by the CNTs/Fe₃O₄@CuSilicate composites is not quite obvious, the reason can be explained as follows: The human blood consists of many kinds of proteins including HSA, HHb, the proteins interaction among HHb, HSA and other proteins in human blood will lead to the loss of the capacity adsorption on HHb, which is also verified by our previous work[30]. Consequently, the adsorbed solution by treatment with the CNTs/Fe₃O₄@CuSilicate composites was almost the same as that of the original diluted human blood band. However, it can still be observed that the HHb and HSA proteins were existed in the eluted solution from the adsorbed CNTs/Fe₃O₄@CuSilicate composites. This fully indicates that the CNTs/Fe₃O₄@CuSilicate composites can effectively remove the abundant proteins(HHb and HSA) in the real biological samples, which seriously hamper the detection of less abundant proteins that are often markers of diseases.

Fig. 9 SDS-PAGE analysis of adsorption by CNTs/Fe₃O₄@CuSilicate composites from solution. Lane 1, marker; lane 2, 0.6 mg ml⁻¹ of BHb and BSA binary solution; lane 3, remaining BHb and BSA solution after adsorption by CNTs/Fe₃O₄@CuSilicate composites; lane 4, the eluted BHb and BSA mixture by 0.2 g ml⁻¹ dimethyl imidazole solution; lane 5, 10-fold human whole blood; lane 6, remaining human whole blood solution after adsorption by CNTs/Fe₃O₄@ CuSilicate composites; lane 7, the eluted 10-fold human whole blood by 0.2 g ml⁻¹ dimethyl imidazole solution

4. Conclusions

We have demonstrated a facile method for the synthesis of hierarchical magnetic composites with copper silicate shells and superparamagnetic CNTs/Fe₃O₄ cores. Due to the high alterability of the SiO₂ coating thickness, the thickness of CuSilicate nanoneedles can be technically designed. In virtue of the unique structural features, these CNTs/Fe₃O₄@CuSilicate composites exhibit high adsorptive property with excellent cycling stability, which suggests their potential application in protein adsorption. Moreover, the CNTs/Fe₃O₄@CuSilicate composites was successfully employed to selectively bind and removal abundant proteins (HHb, HSA) from human blood samples. The good results demonstrated their potential in separation of His-rich proteins from biological samples. Meanwhile it has also high potential in other fields such as supports for noble metal catalysts and supercapacitors. Additionally, this strategy can be extended as a general method to prepare other magnetic metal silicate nanocables.

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