A Highly Sensitive and Efficient Functionalized Magnetic Chemosensor for Cu\textsuperscript{2+} Removal

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Abstract

Fe\textsubscript{3}O\textsubscript{4} nanoparticles were covalently functionalized by N-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide (QTPA), and finally utilized to be magnetic chemosensor for sensitive and efficient Cu\textsuperscript{2+} removal in aqueous solution. Fourier FT-IR, TEM, XRD and XPS results showed that QTPA was bonded to the surface of Fe\textsubscript{3}O\textsubscript{4} nanoparticles. At room temperature, the magnetic chemosensor exhibited high removal efficiency towards Cu\textsuperscript{2+}.

Keywords: Fe\textsubscript{3}O\textsubscript{4} nanoparticles, functionalization, chemosensor, Cu\textsuperscript{2+} removal

1. Introduction

Copper is one of the biochemically essential metals that are required to maintain the normal structure, function and proliferation of cells. It is essential for life but also plays an important role in the maintenance of homeostasis in living organisms. The excessive of copper in the body can lead to many serious human afflictions, including neurodegenerative diseases, such as Menkes and Wilson diseases [1], Alzheimer’s disease [2], prion diseases [3] and amyotrophic lateral sclerosis [4]. In recent years, copper has been suspected to causing liver damage in children [5]. The measurement of copper in environmental and biological samples has become increasing important. The functional molecules have to be assembled on carriers of sufficiently small dimensions. And now an active area of research covered the use of related nanomaterials for the fabrication of chemosensors through anchoring or grafting of organic groups to the nanomaterials. The organic/inorganic hybrid materials also have attracted greater interests. Some sensors for Cu\textsuperscript{2+} have been developed [6-9]. Our group also reported a method for the detection of Cu\textsuperscript{2+} ions by
azide and terminal alkyne-functionalized gold nanoparticles in aqueous solutions using click chemistry [10]. Recently, Lee [11] and coworkers designed and synthesized a new fluorescence ligand N-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide, which was sensitive and selective for Cu\(^{2+}\) detection. In terms of fluorescent Cu\(^{2+}\) chemosensors, a quenching of fluorescence intensity was typically observed accompanied with Cu\(^{2+}\) binding.

Although the detection of Cu\(^{2+}\) has attracted more attention and developed quickly, the Cu\(^{2+}\) removal from the existed environment is still serious issue. Several literatures reported the use of chelating ligands functionalized onto silica for Cu\(^{2+}\) extraction and removal. For example, 5-formyl-3-(1’-carboxyphenylazo) salicylic acid was used for Cu\(^{2+}\) extraction from natural water [12]. 4-amino-3,5,6-trichloropicolinic acid has been used for divalent cations (Cu\(^{2+}\)) adsorption from aqueous solutions [13]. Quinolinol was immobilized on silica surface for enrichment of trace metal ions like Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Cr\(^{3+}\), Pb\(^{2+}\) and Hg\(^{2+}\) [14]. Hydroxyquinoline functionalized silica was reported for preconcentration of Cu\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\) and Cd\(^{2+}\) from seawater samples [15].

Herein, we report a highly sensitive and efficient method of functionalized magnetic chemosensor for Cu\(^{2+}\) removal from aqueous solutions. 8-chloroacetylaminoquinoline was synthesized and grafted onto the surface of Fe\(_3\)O\(_4\) nanoparticles, which could be used as Cu\(^{2+}\) chemosensor to bind Cu\(^{2+}\) ions.

2. Experimental section

**Materials**

8-aminoquinoline, chloroacetyl chloride, triethylamine were purchased from Sigma-Aldrich chemical Co. 3-aminopropyltriethoxysilane (APTES) were endowed by Dowcorning. Copper sulfate, potassium carbonate, ferric chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O, >98 %), ferrous chloride tetrahydrate (FeCl\(_2\)·4H\(_2\)O, >99 %), dichloromethane (DCM), ammonium hydroxide, ethanol, toluene, acetonitrile were obtained from Sinopharm Chemical Reagent Tianjing Co. Ltd.

**Characterization**

High-resolution transmission electron microscopy (HRTEM) images were obtained by means of a Tecnai 20 (FEI-Philips) instrument with a field emission gun operating at 200 kV. X-ray diffraction (XRD) measurements were carried out with a RIGAKU D/MAX-2400 with Cu K\(\alpha\) (40 kV) radiation. Fourier transform infrared (FT-IR) spectra were obtained using Spectrum One FT-IR spectrometer (Perkin Elmer) with a resolution of 4 cm\(^{-1}\). Proton nuclear magnetic resonance (\(^1\)H-NMR) spectra were recorded using a Bruker AV 400 spectrometer with TMS as the internal standard. X-ray photoelectron spectroscopy was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K\(\alpha\) radiation. In curve fitting, the line width for the Gaussian peaks was maintained constant for all components in a particular spectrum.

**Surface modification of Fe\(_3\)O\(_4\) nanoparticles**

8-chloroacetylaminoquinoline (CAAQ) was synthesized based on Lee’s method. 0.95 g of 8-aminoquinoline and 1 ml of triethylamine in 50 ml of DCM were mixed in a round flask for 30 min at 0 \(^0\)C. Then 0.6 ml of chloroacetyl chloride was added in dropwise. The mixture was magnetic stirred in darkness for 48 h at room temperature. The solvent was evaporated and the product was obtained. Then the crude product was further purified by column chromatography (silica gel, petroleum ether /
ethylacetate at 3:1. $^1$HNMR: (CDCl$_3$, 400 MHz): 7.7 (m, 1H), 10.7 (s, 1H, (CO)NH-quinoline), 8.4 (m, 1H), 8.6 (m, 1H), 8.9 (m, 1H), 4.5 (s, 2H, (CO)CH$_2$Cl).

APTES functionalized Fe$_3$O$_4$ nanoparticles were synthesized according to our previous report [16]. APTES surface modified Fe$_3$O$_4$ nanoparticles (2 g), K$_2$CO$_3$ (3 g), CAAQ (0.5 g) were added into 50 ml of CH$_3$CN. The mixture was refluxed for 12 h under nitrogen atmosphere with vigorous mechanical stirring. After reaction, the mixture was cool down to room temperature and magnetic separated. The N-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide (QTPA) functionalized Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$-QTPA) were washed with ethanol (2 × 50 ml) and distilled water (2 × 50 ml).

3. Results and discussion

The TEM image of QTPA functionalized Fe$_3$O$_4$ nanoparticles was showed in Fig. 1A. The particle size distribution was estimated from the measurement of the diameter of the shown particles. The average diameter of QTPA functionalized Fe$_3$O$_4$ nanoparticles was 38 ± 2 nm. The shapes of Fe$_3$O$_4$ NPs are spherical. Fig. 1B showed the XRD pattern of Fe$_3$O$_4$ nanoparticles. The diffraction peaks at 2$\theta$ = 18.8°, 30.2°, 35.2°, 43.1°, 53.6°, 57.5°, 62.4° and 74.2° can be assigned to the (111), (2 20), (311), (400), (422), (511), (440) and (533) planes of Fe$_3$O$_4$, respectively.

FT-IR spectra of Fe$_3$O$_4$-APTES and Fe$_3$O$_4$-QTPA nanoparticles were presented in Fig. 2. The peak at 579 cm$^{-1}$ corresponded to the Fe-O vibration of the magnetite phase. In Fig. 2A, the peak at 1002, 1630, 2926, 3446 cm$^{-1}$ should be ascribed to Si-O stretching vibration, C-N inflective vibration, C-H asymmetric stretching and N-H stretching vibration, respectively. From Fig. 2B, we can see that the new peaks appear at, 1540, 1679, 1485, 1272, 827, 1679, 1594 and 1540 cm$^{-1}$ compared to the Fe$_3$O$_4$-APTES nanoparticles. These peaks may be attributed to N-H inflective, N-C=O vibration, C-H stretching, benzene ring vibration and NH-CH$_2$ vibration. It implied that the QTPA was successfully chemical covalent bonded on the surface of Fe$_3$O$_4$ nanoparticles through chloroacetyl chloride linker.
Fig. 3 showed XPS spectra of QTPA functionalized Fe₃O₄ nanoparticles. As illustrated in Fig. 3A, the O 1s core-level spectrum of Fe₃O₄-QTPA can be curve-fitted into three peak components with binding energies at about 532.3, 531.5 and 529.4 eV, attributed to the Si-O, C=O and Fe-O species, respectively. N 1s core-level spectrum (Fig. 3B) presented three peak components having binding energies at about 401, 399.5 and 398.1 eV, assigned to the N-C=O, N-H and N-C species, respectively. The results confirmed the formation of quinoline derivates on the surface of Fe₃O₄.

Fig. 3. O 1s core-level (A) and N 1s core-level (B) spectra of Fe₃O₄-QTPA nanoparticles

The efficiency of Fe₃O₄-QTPA nanosensor for Cu²⁺ removal was demonstrated in Fig. 4. In this case, accurate removal responses were observed from 63.5 ppm to as low as 27 ppm and 6.35 ppm to 0.53 ppm for the initial concentration of Cu²⁺ 1 mmol/L and 0.1 mmol/L, respectively. It implied that the amount of the functionalized Fe₃O₄ as chemosensor would play an important role in the efficiency of Cu²⁺ removal at room temperature. The coming investigation will be carried out to further examine the sensitivity and selective removal of Cu²⁺ in the presence of the other interfering cations.

4. Conclusions

In conclusion, the chemosensor synthesized and functionalized onto the surface of magnetic...
nanoparticles exhibited significant binding ability to Cu\(^{2+}\). After magnetic separation, the maximal removal efficiency of magnetic nanosensor was 91.7 % when the initial concentration of Cu\(^{2+}\) was 0.1 mmol/L. The sensor design and results presented here would offer a new approach to construct high sensitive and selective chemo-/biosensors. It may also be utilized to fabricate a nanosensor to directly sense or remove specific targets in intracellular environment.

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References

[1] P.C.Bull, G.R.Thomas, J.M.Rommens, J.R.Forbes, D.Wilson Cox, “The Wilson disease gene is a putative copper transporting P–type ATPase similar to the Menkes gene”, Nat. Genet., vol. 5, 1993, pp. 327-337, doi: 10.1038/ng1293-327
[2] K.J.Barnham, C.L.Masters, A.I.Bush, “Neurodegenerative diseases and oxidative stress”, Nat. Rev. Drug Discovery, vol. 3, 2004, pp. 205-214, doi: 10.1038/nrd1330.
[3] D.R.Brown, H.Kozlowski, “Biological inorganic and bioinorganic chemistry of neurodegeneration based on prion and Alzheimer diseases”, Dalton Trans., 2004, 1907-1917, doi: 10.1039/B401985G.
[4] J.S.Valentine, P.J.Hart, “Misfolded CuZnSOD and amyotrophic lateral sclerosis”, PNAS, vol. 100, 2003, pp. 3617-3622, doi: 10.1073/pnas.0730423100.
[5] B.P.Zietz, H.H.Dieter, M.Lakomek, H.Schneider, B.Kebler-Gaedtke, H.Dunkelberg, “Epidemiological investigation on chronic copper toxicity to children exposed via the public drinking water supply”, Sci.Total Environ., vol. 302, 2003, pp. 127-144, doi: 10.1016/S0048-9697(02)00399-6
[6] A.Reynal, J.Etxebarria, N.Nieto, S.Serres, E.Palomares, A.Vidal-Ferran, “A Bipyridine-based “Naked-Eye” fluorimetric Cu\(^{2+}\) chemosensor”, Eur.J.Inorg.Chem. vol. 2010, 2010, pp. 1360-1365, doi: 10.1002/ejic.200900887.
[7] W.Ngeontae, W.Aeungmaitrepirom, T.Tuntulani, A.Imyim, “Highly selective preconcentration of Cu(II) from seawater and water samples using amidoamidoxime silica”, Talanta, vol. 78, 2009, pp. 1004-1010, doi: 10.1016/j.talanta.2009.01.017
[8] J.Yin, X.Guan, D.Wang, S.Liu, “Metal-chelating and dansyl-labeled poly(N-isopropylacrylamide) microgels as fluorescent Cu\(^{2+}\) sensors with thermo-enhanced detection sensitivity”, Langmuir, vol. 25, 2009, pp. 11367-11374, doi: 10.1021/la901377h.
[9] J.W.Liu, Y.Lu, “A DNAzyme catalytic beacon sensor for paramagnetic Cu\(^{2+}\) ions in aqueous solution with high sensitivity and selectivity”, J.Am.Chem.Soc. vol. 129, 2007, pp. 9838-9839, doi: 10.1021/ja0717358
[10] Y.Zhou, S.Wang, K.Zhang, X.Jiang, “Visual detection of copper(II) by azide- and alkyn-functionalized gold nanoparticles using click chemistry”, Angew.Chem.Int.Ed. vol. 47, 2008, pp. 7454-7456, doi: 10.1002/anie.200802317.
[11] L.Mu, W.Chi, J.C.Chang, S.T.Lee, “Silicon nanowires-based fluorescence sensor for Cu(II)”, Nano Letters, vol. 8, 2008, pp. 104-109, doi: 10.1021/nl072164k.
[12] M.A.A.Kal, I.M.M.Kenawy, R.R.Lasheen, “Organically modified silica gel and flame atomic absorption spectrometry: employment for separation and preconcentration of nine trace heavy metals for their determination in natural aqueous systems”,Microchem.J. vol. 78, 2004, pp. 143-156, doi: 10.1016/j.microc.2004.03.019.
[13] A.G.S.Prado, A.H.Tosta, C.Airoldi, “Adsorption, separation, and thermochemical data on the herbicide picloram anchored on silica gel and its cation interaction behavior”, J.Colloid Interf. Sci. vol. 269, 2004, pp. 259-264, doi: 10.1016/S0021-9797(03)00685-4.
[14] P.K.Jal, S.Patel, B.K.Mishra, “Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions”, Talanta, vol. 62, 2004, pp. 1005-1028, doi: 10.1016/j.talanta.2003.10.028.

[15] F.C.F.Barros, F.W.Sousa, R.M.Cavalcante, T.V.Carvalho, F.S.Dias, D.C.Queiroz, L.C.G.Vasconcellos, R.F.Nascimento, “Removal of copper, nickel and zinc ions from aqueous solution by chitosan-8-hydroxyquinoline beads”, Clean, vol. 36, 2008, pp. 292-298, doi: 10.1002/cen.200700004.

[16] Yang Zhou, Shixing Wang, Bingjun Ding, Zhimao Yang, “Modification of magnetite nanoparticles via surface-initiated atom transfer radical polymerization (ATRP)”, Chem.Eng.J. vol. 138, 2008, pp. 578-585, doi: 10.1016/j.cej.2007.07.030.