Modified Chitosan as a Polymeric Nanoreactor for Fabrication of Pure ZnO Nano Particles

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ABSTRACT: ZnO nanoparticles have been prepared successfully by hydrogel decomposition method (HDM). Synthesized ZnO nanoparticles were characterized by X-ray diffraction (XRD), fourier transforms infrared spectroscopy (FTIR), and transition electron microscopy (TEM) techniques. Narrow distribution of sizes with a 20–30 nm diameter and regular distribution of ZnO nanoparticles are attributed to the application of poly(acrylic acid-co-acrylamide) grafted chitosan hydrogel as coating agent. The results show that the polymer thermal decomposition technique is a perfect method for the synthesis of ZnO nanoparticles. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1035–1040, 2010

Key words: hydrogel; ZnO nanoparticles; radical polymerization; thermal decomposition; chitosan

INTRODUCTION

Heavy metal ions constitute a major part of the pollutants in the environment.[1] The use of synthetic resins for chelating toxic metal ions in wastewater is a possible method for preventing environmental pollution. After the metal ion adsorption processes, the resins mainly composed of petroleum-based synthetic polymers, are generally discarded in landfills. Therefore, these processes often result in secondary pollution by contaminating the soil. In addition, these synthetic polymers are usually neither renewable nor biodegradable.[2]

Biopolymers afford eco-friendly and cost-effective materials with diverse properties to be used in a wide spectrum of applications. Hydrogels based upon biopolymers like carrageenan, starch, cellulose, and chitosan are finding extensive use in various fields including wastewater treatment, drug delivery and separation technologies.[1,3–5] Reuse of these hydrogels after waster treatment in synthesis of metal oxide nanoparticles may be a novel idea for preventing environmental pollution.[6]

ZnO nanoparticles have drawn enormous attention due to a wide range of applications such as semi conductor diodes, ultraviolet-protection films, catalysts, sensors, ceramics, solar energy conversion, etc.[7–12] Up to now, many methods have been developed for preparation of magnetite nanoparticles with different morphologies and size distributions such as sol-gel technique, laser heating, mechanochemical process, solvent-thermal process, hydrothermal synthesis, microwave heating synthesis, and homogeneous precipitation.[13–18] In most of these approaches, nanoparticles tend to agglomerate, due to large specific surface area as well as high surface energy. To improve the size distribution and morphology of nanoparticles without any agglomeration during the synthesis, coating the magnetite nanoparticles with a capping agent is necessary. Thermal decomposition of zinc salt is one of the facile methods to fabricate ZnO nanoparticles, in which zinc salt is coated by appropriate coating agent followed by thermal decomposition of coated zinc salt resulting in ZnO nanoparticles. β-cyclodextrin is a coating agent for synthesis of ZnO nanoparticles, but it is expensive and unavailable in most laboratories. Decomposition of organometallic precursors is also an approach to fabricate ZnO nanoparticles.[19] Preparation of organometallic precursors is difficult and needs special conditions. Therefore choosing the coating agent is a critical consideration. Chelating polymer is one of the best choices. Herein, we proposed a facile thermal decomposition route to synthesize ZnO nanoparticles. The strategy in this study is the application of poly(acrylic acid-co-acrylamide) grafted chitosan acting as an inexpensive and available coating agent. Poly(acrylic acid-co-acrylamide) grafted chitosan with hydroxyl, amino, carboxyl and amide functional groups has a certain binding affinity to metal ions, which may control the size and

morphology of ZnO nanoparticles without any agglomeration.

EXPERIMENTAL

Materials and methods

X-ray diffraction (XRD) was preformed with a SiemensD5000 X-ray diffractometer using graphite-monochromatized high-intensity Cu-K$_\alpha$ radiation (λ = 1.5406 Å). Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet (Magna 500). A JEOL JEM-2010 transition electron microscope (TEM) was used for determining the average particle size and morphology of the powders on an accelerating voltage of 100 kV, hydrogel morphology was evaluated by scanning electron microscopy, SEM (Leo, 1455 VP) and an atomic absorption spectrometer (VarianAA-5) was used for the measurements of the metal ion absorption.

Chitosan purchased from Fluka. Acrylic acid (AA, Merck), was used after vacuum distillation. Acrylamide (AAm, Fluka), was used after crystallization in acetone. Potassium persulfate (KPS, Merck) was used without further purification. Methylenebisacrylamide (MBA, Fluka), was used as received. All other chemicals were of analytical grade.

Hydrogel preparation by free-radical polymerization

Hydrogel was synthesized as described by Mahdavinia et al.[20] In brief, chitosan (0.50 g) was dissolved in 30.0 mL of distillated degassed 1 wt % acetic acid solution. The three-neck reactor was placed in a water bath preset at 60°C. Then 0.10 g of KPS as an initiator was added to chitosan solution and was allowed to stir for 10 min at 60°C. After adding KPS, weighted amounts of AA (1.60 g), AAm (1.60 g) and MBA solution (0.050 g in 5 mL H$_2$O) were added simultaneously to the chitosan solution. After addition of monomers, the mixture was continuously stirred (at 200 rpm) for 1 h under argon atmosphere. After 60 min, the reaction product was allowed to cool to ambient temperature and neutralized to pH = 8 by addition of 1 N NaOH solution. Ethanol (500 mL) was added to the gelled product while stirring. After complete dewatering for 24 h, the hardened gel particles were filtered, washed with fresh ethanol and dried at 50°C.

Swelling measurements in zinc chloride solutions

A tea bag (i.e., a 100 mesh nylon screen) containing an accurately weighted powdered hydrogel (0.1 ± 0.0001 g) was immersed entirely in zinc chloride solutions (2000 ppm) and allowed to soak for 48 h at room temperature. The tea bag was hung up for 15 min to remove the excess fluid. The equilibrated swelling (ES) was calculated using the following equation for at least three samples:

$$ES\ (g/g) = (W_s - W_d)/W_d \qquad (1)$$

where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. So, absorbency was calculated as gram of water per gram of hydrogel (g/g).

Metal ion sorption measurement

A zinc chloride solution with a concentration of 2000 ppm was prepared in Erlenmeyer flasks. 0.1 ± 0.0001 g of chelating hydrogel was added to flask. The mixture was shaken for 48 h by a rotary shaker to complete the equilibrium. An exact amount of the supernatant (5.0 mL) was pipette out for metal ion concentration measurements. The initial and final concentrations of the metal ion were determined by atomic absorption spectroscopy.

ZnO nanoparticles preparation by hydrogel decomposition method

Typical synthetic procedure is as follows: ZnCl$_2$ (0.20 g) and chitosan-g-poly(AA-co-AAm) hydrogel (0.40 g) were suspended in 100 mL water. The suspension stirred at room temperature for 48 h. The decantation and freeze drying of the white suspension yielded white powder which heated at 400°C for 4 h. Finally the product washed with water and hexane. Figure 1 illustrates the overall experimental flowchart to prepare ZnO nanoparticles.

RESULTS AND DISCUSSION

Mechanism of hydrogel formation

Crosslinking graft copolymerization of acrylic acid and acrylamide onto chitosan was carried out using KPS as a free radical initiator and MBA as a hydrophilic crosslinker. The proposed mechanism for the grafting and chemically crosslinking reactions are outlined in Scheme 1. The persulfate initiator is decomposed under heating to generate sulfate anion-radicals. The radicals extract hydrogen from the hydroxyl group of polysaccharide substrate to form alkoxy radicals on the substrate. Thus, this persulfate-saccharide redox system results in active centers on the substrate to radically initiate polymerization of AA-co-AAm leading to a graft copolymer. Since a crosslinking agent, e.g., MBA, is present in the system, the copolymer is comprised of a crosslinked structure.
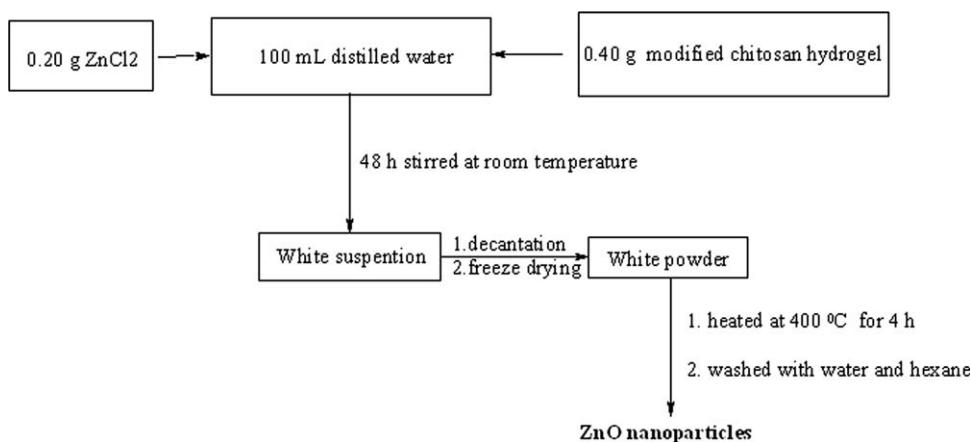
Figure 1 Experimental flowchart to prepare ZnO nanoparticles.

Gel beads morphological studies

The surface morphology of prepared dried modified chitosan beads was studied by SEM (Fig. 2). It is supposed that these surfaces are the regions of water permeation and interaction sites of metal ions with the hydrophilic groups of the modified chitosan.

Hydrogel structural parameters

One of the most important structural parameters characterizing crosslinked polymer is the number average molecular weight between crosslinks ($\overline{M}_c$), which is directly related to the crosslink density. Equilibrium swelling and rubber elasticity theory are two experimental techniques frequently used in the literature for the determination of hydrogel structural parameters.[21]
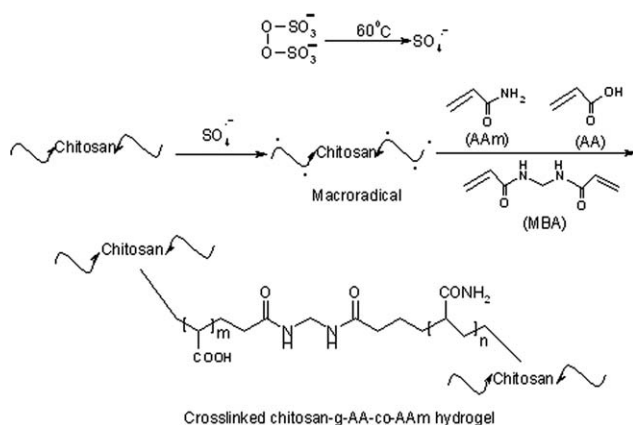
The number of average molecular weights between crosslinks $\overline{M}_c$ was calculated from the swelling data using eq. (2) as discussed by Merril-Peppas.[21]

$$\overline{M}_c = -\frac{\left(\frac{V_l}{\overline{v}}\right)v_{2,r}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{\frac{1}{3}} - \left(\frac{v_{2,s}}{2v_{2,r}}\right)\right]}{\left[ln(1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^2\right]} \quad (2)$$

where $v_{2,s}$ and $v_{2,r}$ was calculated as:

$$v_{2,s} = \left(1 + \frac{\rho(Q_{max} - 1)}{d_1}\right)^{-1} \text{ and}$$

$$v_{2,r} = \left(1 + \frac{\rho(Q_r - 1)}{d_1}\right)^{-1} \quad (3)$$

where Q_r and Q_{max} is the dilution degree after the gel preparing and swelling, respectively, ρ is the polymer density and d_1 is the solvent density, χ is the Flory-Huggins polymer-water interaction parameter, V_l is the molar volume of water, and $\overline{v}$ is the specific volume of the polymer. In hydrogels, thermodynamic interaction is reflected by polymer–solvent interaction parameter (χ), which indicates the

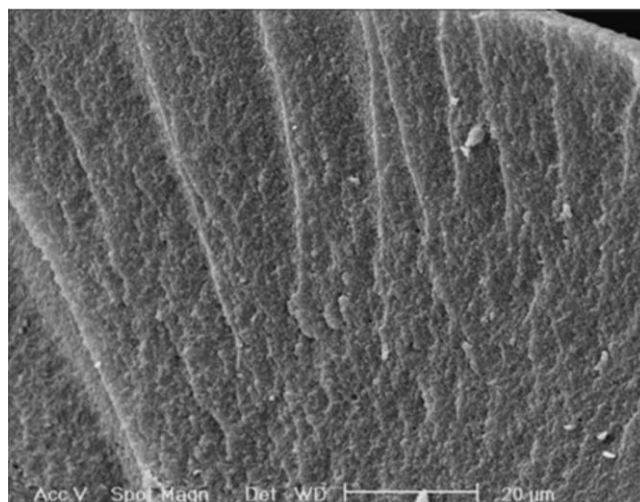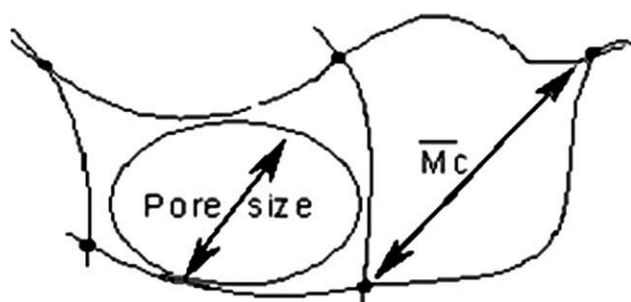Scheme 1 Proposed mechanism for synthesis of chitosan-*g*-AA-*co*-AAm hydrogel.

Figure 2 SEM micrographs of modified chitosan hydrogel beads ×773.

Scheme 2 Representation of the number average molecular weight between crosslinks, (M_c) and the pore size (ξ)

change of interaction energy when polymer and solvent mix together. In polymer–water systems, the higher is the value of χ, the weaker is the interaction between polymer and water, and the stronger is the interaction between hydrophobic groups or between polymer chains. Referred to the literature,[22] the value of χ could be calculated from eq. (4).

$$\chi \cong \frac{1}{2} + \frac{v_{2,s}}{3} \tag{4}$$

The crosslink density v_s was calculated as:

$$v_s = \frac{\rho}{\overline{M}_c} \tag{5}$$

After the network chain length is determined, the correlation length or pore size can be evaluated through eq. (6)[23]:

$$\xi = \alpha \left(\overline{r^2}_0\right)^{1/2} \tag{6}$$

where α is the elongation ratio of the polymer chains related to the swollen polymer volume fraction (v_{2s}), by eq. (7) and $(\overline{r^2}_0)^{1/2}$ is the root mean squared end-to-end distance of the polymer chain in freely jointed state.

$$\alpha = \left(v_{2,s}\right)^{-1/3} \tag{7}$$

TABLE I
Modified Chitosan Structural Parameters in Zinc Solution

Stractural parameter	Modified chitosan
ρ [g/cm^3]	1.44
$v_{2,r}$	0.07636
$v_{2,s}$	0.08579
χ	0.5286
$\overline{M}_c$	65019
v_s	0.000022
N	1680
ξ[Å]	540
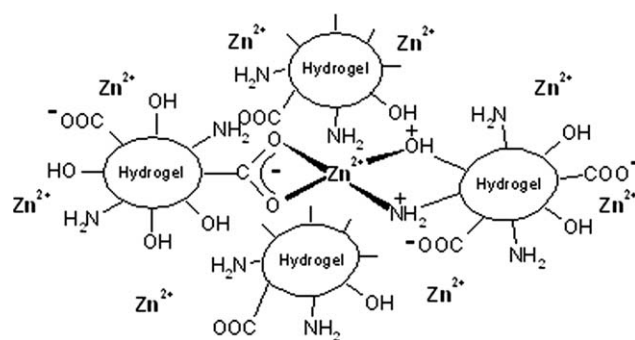
Scheme 3 A possible chelation mechanism of modified chitosan hydrogel with zinc ion.

The unperturbed end-to-end distance of the polymer chain between two adjacent crosslinks can be determinate using the following equation:

$$\left(\overline{r^2}_0\right)^{1/2} = l(C_n N)^{1/2} \tag{8}$$

where C_n is the Flory characteristic ratio of the polymer, gets from related literature, l is the length of the bond along the polymer backbone, and N is the number of links along the polymer chain. This last parameter can be calculated by eq. (9)

$$N = \frac{2\overline{M}_c}{\overline{M}_r} \tag{9}$$

where $\overline{M}_r$ is the molecular weight of the repeating unit.

The correlation length allows classifying the hydrogels as macro-porous, nanoporous and nonporous, depending on the sizes of the pores (Scheme 2). Macroporous hydrogels are those with pore size in the range of >100 nm. Nanoporous hydrogels are characterized by a pore size in the range of 10–100 nm, finally, nonporous hydrogels has a typical correlation length of 10–100 Å.[24,25] The correlation length (pore size) between two subsequent crosslinks (ξ) was obtained 54 nm for chitosan-g-poly(AA-co-AAm) hydrogel proving this hydrogel has nano-pore structure. Table I describes the various network parameters calculated for the modified chitosan hydrogel.

Absorption of zinc ions

Metal binding capacity of chitosan (1.37 mmol/g)[26] is markedly increased by the presence of poly(AA-co-AAm) grafts, which provide additional metal binding sites. Hydroxyl and amino groups of chitosan and carboxylate and amide groups at grafted chains are the sites responsible for metal ion adsorption (Scheme 3). The obtained zinc sorption capacity was 2.7 mmol/g.
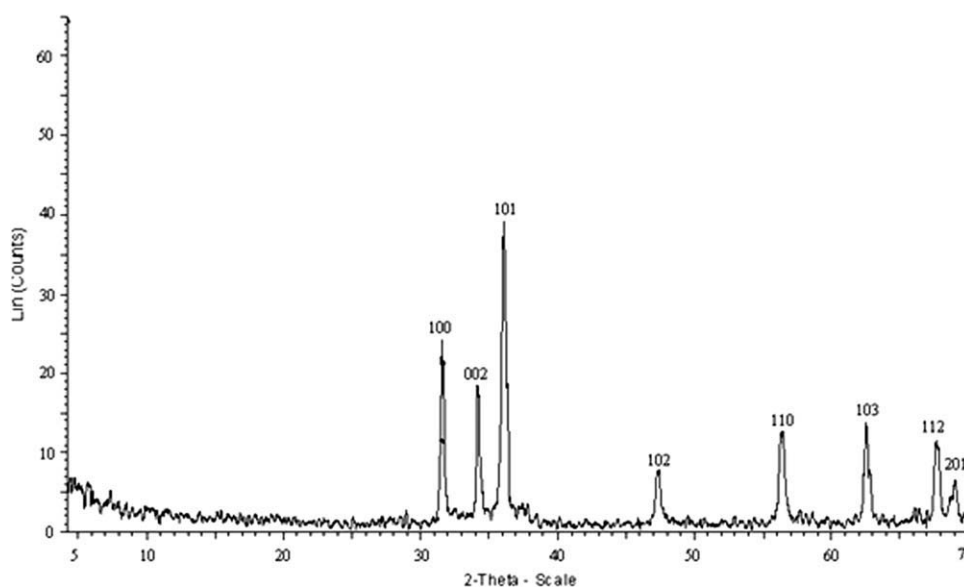
Figure 3 XRD patterns of the ZnO nanoparticles.

X-ray powder diffraction patterns

As shown in XRD pattern of the ZnO nanoparticles (Fig. 3) this method is an effective procedure for synthesis of pure ZnO nanoparticles. Eight characteristic peaks were observed for ZnO nanoparticles (2Θ = 31.6, 34.2, 36.0, 47.4, 31.4, 62.7, 67.7, and 68.9°) marked by their corresponding Miller indices [(100), (002), (101), (102), (110), (103), (112), (201)].[27] The mean particle size was calculated for the ZnO nanoparticles using the Scherrer's equation from the reflections with (100), (002), and (101) indices. The mean size of nanoparticles was calculated to be about 25 nm. This value agreed well with TEM observation of the ZnO nanoparticles. The smaller particles of the ZnO with high purity are the significant advantages of this procedure.

Fourier transforms infrared spectroscopy

The formation of unmodified chitosan, modified chitosan and ZnO nanoparticles were further supported by FTIR spectrum as shown in Figure 4(a–c). Almost all functional groups in a molecule characteristically absorb within a definite range of frequency in this technique.

The FTIR spectrum of the chitosan-g-poly(AA-co-AAm) (Fig. 4 curve b) shows new characteristic absorption bands at 1678 and 1736 cm^{-1} verifying the formation of the graft copolymer. These peaks are attributed to carbonyl stretching of the amide (AAm) and carboxylate groups respectively, also curve c shows characteristic absorption band at 494 cm^{-1} attributed to metal–oxygen (Zn—O) vibrational bands.

Transition electron microscope (TEM) images

Samples of ZnO nanoparticles were milled together with anhydrous alcohol and then dispersed in anhydrous alcohol to form dilute suspension. The dilute suspension was dropped on the carbon-grid and the morphology of the ZnO nanoparticles was observed using TEM. Figure 5 shows the TEM images of ZnO nanoparticles. One can find that the morphology of ZnO crystallites is rather spherical morphology.

Narrow distribution of sizes with a 20–30 nm diameter and the regular distribution of ZnO nanoparticles can be attributed to the using of modified chitosan as coating agent.

A possible chelation mechanism of modified chitosan with zinc ion for the complexation is shown in Scheme 3.

At the nucleation stage, the formation of the ZnO nanoparticles could be induced and confined by the cooperation of modified chitosan with functional groups. At the same time, the oxidation,
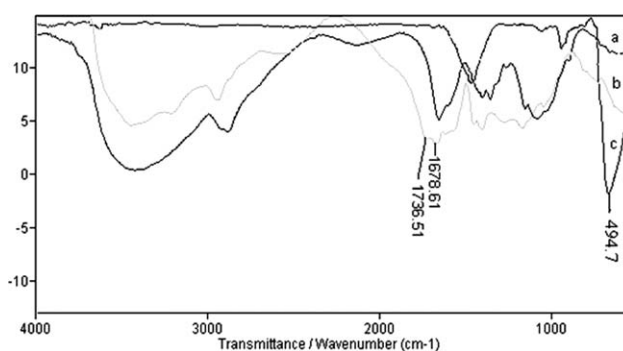

Figure 4 FTIR spectrum of (a) unmodified chitosan, (b) modified chitosan with new functional groups, and (c) ZnO nanoparticles.
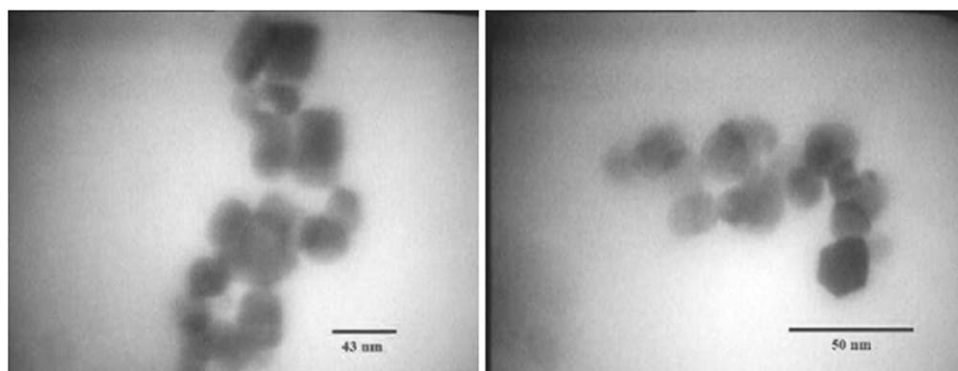
Figure 5 TEM micrographs of the ZnO nanoparticles. (a and b synthesized in presence of modified chitosan).

carbonization and gasification processes of modified chitosan will produce ultrafine carbon black in the system of thermal reactions. Such ultrafine powders with high surface area can allow the produced nanoparticles to remain separated from each other.[19] Thus, the complexation between zinc ion and functional groups on modified chitosan and the following carbonization and gasification processes of modified chitosan are both the important factors responsible for the production of uniform ZnO nanoparticles.

CONCLUSION

Modified chitosan hydrogels were prepared by free-radical polymerization and characterized through swelling studies. The number average molecular weight between crosslinks, crosslinking density, pore size, Flory-Huggins interaction parameter, and the number of links along the polymer chains were calculated.

The feasibility of the synthesis of metal oxide nanoparticles (ZnO, 20–30 nm diameters) by hydrogel nanorectors was studied. The results revealed that the presented hydrogel in this study may serve as a platform for production of metal oxide nanoparticles.

Inexpensiveness of the reactants, green routs for synthesis and high metal sorption capacity are the advantages of polysaccharide as starting material for this method.

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