



A simple route to synthesize conductive stimuli-responsive polypyrrole nanocomposite hydrogel particles with strong magnetic properties and their performance for removal of hexavalent chromium ions from aqueous solution



Hasan Ahmad^{a,*}, Mohammad Mostafizar Rahman^a, Mohammad Azgar Ali^a,
Hideto Minami^b, Klaus Tauer^c, Mohammad Abdul Gafur^d,
Mohammad Mahbubor Rahman^a

^a Department of Chemistry, Rajshahi University, Rajshahi 6205, Bangladesh

^b Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan

^c Max Planck Institute of Colloid and Interfaces, Am Mühlenberg, 14476 Golm, Germany

^d Pilot Plant and Process Development Centre, BCSIR, Dhaka 1205, Bangladesh

ARTICLE INFO

Article history:

Received 11 January 2016

Received in revised form

3 March 2016

Accepted 21 March 2016

Available online 26 March 2016

Keywords:

Stimuli-responsive

Conductivity

Nanocomposite hydrogel

Magnetic property

Water purification

ABSTRACT

A combination of maghemite polypyrrole (PPy/ γ -Fe₂O₃) and stimuli-responsive properties in the same hydrogel microspheres is expected to enhance their application potential in various fields such as tissue engineering, regenerative medicine, biosensors, biomedical applications and removal of heavy metals from waste water, catalysis etc. In this investigation a simple two step process is used to prepare conductive stimuli-responsive polypyrrole (PPy) composite hydrogel particles with strong magnetic properties. Poly(styrene-methacrylic acid-N-isopropylacrylamide-polyethylene glycol methacrylate) or P(S-NIPAM-MAA-PEGMA) hydrogel seed particles are first prepared by soap-free precipitation copolymerization. The copolymer hydrogel particles exhibited both temperature- and pH-responsive volume phase transition. Conductive P(S-NIPAM-MAA-PEGMA)/PPy/ γ -Fe₂O₃ nanocomposite hydrogel particles are then prepared by seeded chemical oxidative polymerization of pyrrole in the presence of P(S-NIPAM-MAA-PEGMA) hydrogel seed particles using FeCl₃ as an oxidant and *p*-toluene sulfonic acid (*p*-TSA) as a dopant. In the reaction system FeCl₃ functioned as a source of Fe(III) for the formation of γ -Fe₂O₃. This reaction also requires the initial presence of Fe(II) provided by the addition of FeCl₂. The size and size distribution, surface structure, and morphology of the prepared conductive composite hydrogel particles are confirmed by FTIR, electron micrographs, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and UV-visible spectroscopy. The performance of nanocomposite hydrogel particles has been evaluated for the removal of hexavalent chromium (Cr) ions from water.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Recently conducting polymers with nano-sized composites are drawing much interest because of their low density, diversified structure with unique physical and chemical properties [1–3]. Generally conducting polymers are not suitable for many industrial applications due to their low processability and low solubility in common solvents. A usual approach to improve the performance of conducting polymers is to form conductive composite polymers via the combination of conducting polymers with

other organic or inorganic materials having different functionalities. The improved electrical conductivity, processability, magnetic, mechanical, and environmental sensitivity of these conductive composite materials make them useful in field like electromagnetic shielding, biosensors, electrochromism, and corrosion resistance [4–6]. Among the conducting polymers, polypyrrole (PPy) has attracted considerable attention because it offers reasonably high room temperature conductivity, redox properties and has fairly good environmental stability, biocompatibility and the relative ease of its synthesis via simple beaker chemistry [7]. However, it is insoluble and infusible and exhibits relatively low mechanical strength and processability [8,9]. But to overcome these critical limitations, core@shell composite particles with conductive PPy shells coated on inorganic [10–23] or polymeric

* Corresponding author.

E-mail address: samarhass@yahoo.com (H. Ahmad).

cores [24–45] have been the subject of numerous research works from the late 1980s. These PPy-coated particles allow the creation of new polymeric materials have enormous scientific and technological interests following the development of visual biomedical diagnostics [12,38], conductive composites [19,24], conductive paints [46], anticorrosion coatings [34], stationary phase in liquid chromatography [47], conductive pigments [20] and hypervelocity experiments with microprojectiles of PPy mimicking solar dusts [27–31]. Additionally PPy can be prepared in the form of reactive and functional copolymers for the immobilization of metallic nanoparticles and other nano-objects [12,14,48].

The composites based on PPy that contain magnetic nanoparticles generated particular interest because of their unique electromagnetic properties and applications in electro-chromic devices, non-linear optical systems, electrical-magnetic shields, microwave-absorbing materials and electromagnetic interference shielding [49–52]. Several approaches are available in literature to prepare composite materials consisting of magnetic nanoparticles and conducting PPy: (1) electrochemical method to prepare PPy-ferromagnetic composite films [53–55]; (2) one step chemical method to prepare PPy-ferromagnetic composite in the presence of dopant; $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are used as oxidants to react with pyrrole [55–57]; (3) simultaneous gelation and polymerization process to prepare PPy and iron oxide nanocomposites [58]; (4) layer-by-layer self-assembly of conducting polymers and ferrite nanoparticles in aqueous solutions [59]; and (5) *in situ* emulsion polymerization of pyrrole in aqueous solution containing magnetic fluid/powder and dopant to prepare magnetic PPy composite particles [60–66].

The objective of this investigation is to prepare stimuli-responsive conductive PPy magnetic nanocomposite hydrogel particles based on poly(N-isopropylacrylamide) (PNIPAM). Stimuli-responsive polymer hydrogel microspheres are known to have vast application prospect in biomedical, pharmaceutical and industrial applications [67–73]. The incorporation of stimuli-responsive, electrical and magnetic properties in the same materials is expected to increase the biocompatibility and thereby application potential in tissue engineering, regenerative medicine and biosensors. These types of biocompatible magnetic electrical stimuli are also considered to be attractive for several biomedical applications such as to regulate or adjust activities of nerve, cardiac, skeletal muscle and bone cells and to stimulate cell growth, migration, and adhesion as well as to enhance DNA synthesis and protein secretion. Such materials may also provide solutions to many problems in neural biology/medicine [74] and for the time predetermined drug release and delivery. Additionally such magnetic electrical stimuli can also be applied for the efficient absorption of toxic metal ions via anion-exchange reaction with doped PPy segment. Stimuli-responsive property would increase the swelling at temperature below the lower critical solution temperature (LCST) and hence would facilitate the interaction between toxic metals and reactive hydrogel. Simultaneously magnetic property of the hydrogel would promote easy separation of toxic metals loaded hydrogel particles by applying external magnetic field leaving pure water [75]. In general magnetic hydrogel materials can also find application for designing remote controlled drug release [76,77].

In order to prepare multifunctional nanocomposite hydrogel particles with good magnetic and electrical properties a simple, inexpensive and environment friendly process has been suggested. Here stimuli-responsive poly(styrene-NIPAM-methacrylic acid-polyethylene glycol methacrylate) abbreviated as P(S-NIPAM-MAA-PEGMA) hydrogel seed particles are first prepared by precipitation polymerization. Then P(S-NIPAM-MAA-PEGMA)/PPy/ $\gamma\text{-Fe}_2\text{O}_3$ nanocomposite hydrogel particles are prepared by seeded chemical oxidative polymerization of pyrrole in the presence of P(S-NIPAM-

MAA-PEGMA) hydrogel seed particles using FeCl_3 as a oxidant and *p*-toluene sulfonic acid (*p*-TSA) as a dopant.

2. Materials and methods

Styrene and MAA of monomer grade from Fluka, Chemika, Switzerland, were distilled under reduced pressure to remove any inhibitor. NIPAM purchased from Across organics, USA, was recrystallized from a mixture of 90% hexane and 10% acetone and dried under vacuum at low temperature. PEGMA with molecular weight 500 g mol^{-1} for PEG from Aldrich Chem. was used as a reactive stabilizer. Sodium dodecyl sulfate (SDS) from Fluka, Chemika, Switzerland and pyrrole from Sigma-Aldrich, were used without purification. 2,2'-Azobis(2-methylpropanimidamide) dihydrochloride (V-50) from LOBA Chem, India was recrystallized from distilled water and preserved in the refrigerator before use. Ferric Chloride (FeCl_3), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), *p*-toluene sulfonic acid (*p*-TSA), ammonium hydroxide (NH_4OH) and other chemicals were of analytical grade.

Each dispersion was purified by serum replacement after repeated centrifugation prior to the characterization. Temperature dependent variation of hydrodynamic diameter was measured by a dynamic laser scattering particle sizer (NICOMP, model 380, Santa Barbara, California, USA). Transmission electron microscope, TEM (Zeiss EM-912, Omega) was used to see the morphology and particle size distribution. Diluted dispersion was placed on carbon coated copper grid, dried at ambient temperature before observation by TEM at an accelerating voltage of 100 kV. FTIR spectra were recorded in KBr pellets on a Perkin Elmer, FTIR-100 model instrument. The XRD patterns of the powder samples were taken by scanning X-ray diffractometer (Bruker D8 Advance, Germany) using $\text{Cu K}\alpha$ KR radiation at a continuous scan rate of $10^\circ/\text{min}$ with a position sensitive detector aperture at 3° (equivalent to $0.5^\circ/\text{min}$ with a scintillator counter). The surface composition after modification was evaluated by an X-ray photoelectron spectrometer (PHI X-tool, Ulvac-phi inc.) equipped with a monochromatic Al K α radiation (1486.6 eV) at 104 W and 20 kV and an X-ray current of 20 mA. Thermal properties of the dry powdered samples were measured by heating samples under flowing nitrogen atmosphere from 30° to 800°C at a heating rate of $20^\circ\text{C}/\text{min}$ by a thermogravimetry (TG) analyzer (STA 8000, Perkin Elmer, Netherlands). Impedance analyzer (Wayne Kerr, 6500B, UK) and Magnetic Susceptibility Balance (Sherwood Scientific, UK) were used for electrical conductivity and susceptibility measurement.

2.1. Preparation of P(S-NIPAM-MAA-PEGMA) hydrogel seed particles

The P(S-NIPAM-MAA-PEGMA) hydrogel seed particles were produced by soap free precipitation copolymerization of styrene (1.0 g), NIPAM (3.2 g), MAA (0.6 g) and PEGMA (0.2 g) in a three-necked round bottomed flask. Polymerization was initiated using cationic V-50 (0.1 g) as an initiator and the polymerization reaction was continued under a nitrogen atmosphere at 75°C for 24 h. The conversion was gravimetrically nearly 85%. The produced hydrogel particles were washed three times with distilled de-ionized water prior to the analyses.

2.2. Preparation of P(S-NIPAM-MAA-PEGMA)/PPy/ $\gamma\text{-Fe}_2\text{O}_3$ nanocomposite hydrogel particles

P(S-NIPAM-MAA-PEGMA)/PPy/ $\gamma\text{-Fe}_2\text{O}_3$ nanocomposite hydrogel particles were prepared by seeded chemical oxidative polymerization in the presence of P(S-NIPAM-MAA-PEGMA) hydrogel seed particles. Pyrrole (0.1 g) monomer was dissolved in aqueous ammonia solution (10 g, 1.0 M) with ultrasonic stirring to produce

Download English Version:

<https://daneshyari.com/en/article/1797916>

Download Persian Version:

<https://daneshyari.com/article/1797916>

[Daneshyari.com](https://daneshyari.com)