



High-throughput synthesis of cross-linked poly(cyclotriphosphazene-co-bis(aminomethyl)ferrocene) microspheres and their performance as a superparamagnetic, electrochemical, fluorescent and adsorbent material

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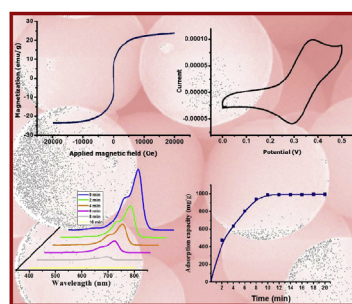
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HIGHLIGHTS

- Ferrocene based phosphazene microspheres have been successfully synthesized.
- The diameters of the cross-linked microspheres vary from 0.3 to 1.3 μm .
- The microspheres act as a potent adsorbent for the removal of methylene blue.
- These multifunctional microspheres can possibly be used in several applications.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 October 2016

Received in revised form 19 December 2016

Accepted 14 January 2017

Available online 17 January 2017

Keywords:

Poly(cyclotriphosphazene-co-bis(aminomethyl)ferrocene)

Microspheres

Superparamagnetism

Electrochemistry

Fluorescence

Adsorption

ABSTRACT

Ferrocenylphosphazenes have been attracting increasing attention for their special properties and potential applications. We describe here a new high-throughput synthesis of cross-linked poly(cyclotriphosphazene-co-bis(aminomethyl)ferrocene) microspheres via the polycondensation of hexachlorocyclotriphosphazene and 1,1'-di(aminomethyl)ferrocene by precipitation polymerization. The mean diameter of the microsphere varies from 0.3 to 1.3 μm , depending on the concentrations of both monomers in a calculated molar ratio. The morphology and structure of microspheres were characterized by FT-IR, SEM, EDX and TEM analyses. TG analysis demonstrated their superior thermal stability owing to the presence of high cross-linked bonding. Magnetic measurements revealed that the microspheres are superparamagnetic with a saturation magnetization of 23.7 emu g^{-1} . The electrochemical properties of the microspheres were also examined by cyclic voltammetry and the results showed a single reversible redox process. Room-temperature photoluminescence spectra of the microspheres exhibited a strong emission peak at 405 nm. The Brunauer–Emmett–Teller (BET) pore-size distribution maximum is about 37.4 nm that leads to efficient adsorption behavior. These microspheres were found to be an excellent high capacity adsorbent for the selective cationic dye (methylene blue) removal from contaminated water. The changes in parameters, such as contact time, temperature and concentration of adsorbate were examined to study their influence on adsorption capacity. The results obtained suggest that the microspheres can effectively adsorb methylene blue with an adsorption capacity increasing from 480 to 2160 mg g^{-1} as the initial concentration was increased from 50 to 400 mg L^{-1} . Owing to the superior properties and novelty of the synthesized hybrid microspheres, they can possibly be used in several applications, e.g., in catalysis, bio-assays, and electric and magnetic devices.

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1. Introduction

The advances being made in the core areas of inorganic polymers are truly remarkable and outstanding by any definition [1,2]. Polyphosphazenes are an important class of inorganic polymers comprising of alternate single-double bonds between phosphorus and nitrogen atoms [2]. The science of polyphosphazenes has emerged as a focal point of much research owing to their inherent backbone stability, structural diversity and ability to form hybrid molecules exhibiting certain desired properties [3–5]. There are two types of polyphosphazene compounds; linear and cyclo-matrix type polymers [6]. The most common linear polyphosphazene is poly(dichlorophosphazene) (PDCP) containing two chlorine atoms per phosphorus atom that is produced by thermal ring-opening polymerization of hexachlorocyclotriphosphazene (HCCP) [7–9]. Cyclo-matrix types of polyphosphazene compounds with high cross-link densities can be synthesized by the reaction of HCCP with difunctional nucleophiles such as amines, alcohols or phenols [10–12]. HCCP plays a crucial role in the development of new polymers due to its excellent tailoring property of the backbone as well as the unprecedented structural diversity obtainable [13–16]. The introduction of metallocene derivatives into the HCCP moiety has been actively studied for many applications [17]. Among metallocene, ferrocene is a unique moiety due to its high thermal/chemical stability, redox nature, and its catalysis, anti-cancer, optical, luminescent, adsorbent, chemo-sensing and separation properties [18–20]. Ferrocene-based polymers predominate the metallocene-based polymers for a variety of reasons including (1) the stability of the ferrocene center itself, (2) the low cost of iron chemicals relative to most of the outer transition and inner transition metal derivatives, and (3) the virtual nontoxicity of iron [21–23]. In materials chemistry, ferrocenyphosphazene compounds have attracted significant attention [24]. With the fast development of science and technology, these materials have found applications in diverse fields, such as magnetism, photo-catalysis, fluorescence, flame retardant coatings and drug delivery systems as well as DNA diagnosis and bio-imaging [25–29]. The nano- and micro- sized cross-linked polyphosphazene materials in the form of spheres, rods, fibers, tubes have been extensively explored due to their specific morphologies, fascinating features and potential applications [30–35].

It has been well established that emulsion, suspension and dispersion polymerization are excellent techniques for preparing polymer microspheres [36,37]. Porous glass-membrane emulsification is a modified suspension polymerization technique that can simply produce the cross-linked polymer microspheres in a single step [38,39]. By addition of a cationic surfactant such as cetyltrimethylammonium bromide at the early stage of emulsion polymerization, mono-disperse micro particles have been prepared by electrostatic coagulation [40]. The dispersion polymerization method also produces stable, micro-sized spherical particles in the presence of a steric stabilizer in organic media [41]. However, the concentration of a cross-linking agent is generally limited based on the amount of the main monomer [42]. Precipitation polymerization is one of the unique methods to prepare cross-linked polyphosphazene particles in a tunable size and shape in the absence of any stabilizing agent such as surfactants or steric stabilizers that are required to obtain spherical particles [33,43,44]. Stover's group has introduced this method to synthesize the fully cross-linked polymer beads in the micrometer scale [45]. Several monomers, including methacrylate, [46] maleic anhydride, [47] and chloromethylstyrene [48], have been copolymerized with divinylbenzene as the cross-linkable monomer by the precipitation polymerization method obtaining microspheres. During the synthetic process, the formation and stable growth of the

resulting particles were achieved by the growth of oligomeric species onto the nuclei and the high degree of cross-linking [31–35,43,44,49,50]. Phosphazene-based microspheres have also been prepared by this method and applied in various applications such as bio-separation, drug targeting, cell isolation, enzyme immobilization, catalysis and wastewater treatment [51–54].

Organic dyes are excellent cost effective agents which encompass a wide area of applicability including construction materials, coatings, paper, leather tanning, plastics, food industries, detergents, textile and agriculture [55,56]. Owing to their extensive use on a large scale by textile and agricultural industries, they are also posing an environmental problem that is a direct threat to humanity on the planet [57]. The main issue the world is facing today is the safe disposal of organic dyes as they contaminate not only surface water but also underground water reservoirs once they are discharged onto any land area. So, industrial waste water treatment is a necessary process before effluents containing these organic dyes are finally discharged from industrial areas [58]. Several treatment methods, including adsorption, absorption, membrane separation, flocculation coagulation and electrochemical and photo-catalysis approaches, have been used for the removal of organic dyes [59,60]. Despite of the continuous attention being paid to the destruction and removal of organic dyes; their complete elimination is still a challenge task owing to the threat of by-products. This means that the development of a highly facile and green method is a pivotal area of research for material scientists. Polymeric nano- and micro-sized materials are being considered as novel agents for the complete removal of the organic dyes [61].

Recently, our group demonstrated the preparation of cross-linked poly(cyclotriphosphazene-co-1,3,5-tri(4-hydroxyphenyl)benzene) hybrid microspheres and results indicated that polyphosphazene possessed special potential in the fabrication of molecular-level inorganic-organic hybrid micro-scale materials [62]. However, ferrocenyphosphazene materials has less been studied. Therefore, the study on the ferrocene based phosphazene hybrid materials appears to be extremely necessary and may offer a new opportunity for their further applications. We report here for the first time the preparation of cross-linked poly(cyclotriphosphazene-co-bis(aminomethyl)ferrocene) (PCPF) microspheres with magnetic and fluorescent properties. We have also investigated the potential of these materials for removal of MB. PCPF microspheres with diameters of about 1–1.3 μm were synthesized by the precipitation polymerization of HCCP with 1,1'-di(aminomethyl)ferrocene (FDA). These PCPF microspheres have excellent fluorescence, high thermal stability, efficient redox properties and also a high adsorption capacity of MB owing to their high cross-linking and uniform morphology. BET measurements showed that the PCPF microspheres have a good surface porosity that leads to efficient adsorption behavior. The sizes of microspheres can easily be tailored easily by changing the concentration of any of the two monomers in a calculated ratio. The properties of these microspheres bode well for their applications in adsorption and catalysis work.

2. Experimental

2.1. Materials

Tetrahydrofuran, petroleum ether, ethanol, acetone, toluene, acetonitrile, triethyl amine (TEA), dichloromethane, methylene blue, tetracyanoethylene and 1,1'-di(aminomethyl)ferrocene were obtained from Beijing Chemical Works, China. TEA was distilled before use. Pure HCCP having a melting point of 114 $^{\circ}\text{C}$ was crystallized from dry petroleum ether (60–90 $^{\circ}\text{C}$) followed by sublimation

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