

Ionic liquid mediated synthesis of silica/polystyrene core-shell composite nanospheres by radical dispersion polymerization

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ABSTRACT

This report describes the novel preparation of silica/polystyrene (SiO₂/PS) core-shell composite nanospheres by *in situ* radical dispersion polymerization in an ionic liquid (IL). Silica nanoparticles were first surface modified by the silane coupling agent methacryloxypropyltrimethoxysilane (MPTMS), which is capable of copolymerizing with styrene and provided a reactive C=C bond. Transmission electron microscopy (TEM) revealed core-shell morphology with smooth surfaces. X-ray photoelectron spectroscopy (XPS) analysis demonstrated that almost all of the SiO₂ nanoparticles were encapsulated by the polymer. The composite particles were also analyzed by FT-IR spectroscopy and thermogravimetric analysis (TGA). In principle, this simple and environmentally-friendly synthetic procedure can be employed to prepare other inorganic oxide-containing polymer composites.

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1. Introduction

Recently, the synthesis of polymer/inorganic filler composite particles has received much attention because polymer-encapsulated nanoparticles can be used in very interesting current and potential applications [1–3]. Different colloidal inorganic materials have been used to construct polymer-based hybrid colloidal particles [4–9]. Among them, SiO₂ is the most studied model system due to its high surface energy and activity. Composite submicron particles made of organic polymers and oxides such as SiO₂ utilized in myriad applications: catalysis, chromatography, controlled release, optics, as materials additives (fillers), and for application in many other fields. Owing to the many uses of SiO₂, different methods for the synthesis of polymer-SiO₂ nanocomposite particles have been reported [10]. Though a wide variety of methodologies have been employed, the traditional method of producing core-shell nanocomposite particles is emulsion polymerization [10]. Dispersion polymerization has also been reported to be a viable method for preparing core-shell nanocomposites [10].

Dispersion polymerization is a simple and fast (i.e., single step) technique used to prepare monodisperse polymer particles of a range of sizes (1–20 μm) with very high yields [11–16]. Dispersion polymerization may be defined as a type of precipitation polymerization; the polymerization reaction is performed in the presence of a suitable polymeric stabilizer, that is, soluble in the reaction

medium. The selected continuous is a solvent for the monomer to be polymerized and a non-solvent for the resultant polymer [17,18]. A steric stabilizer is used to produce a colloiddally-stable dispersion, without which the polymerization would generate macroscopic polymer particles of uncontrolled size [19]. The dispersion polymerization process takes place in a homogeneous medium of monomers, free-radical initiator, and polymeric stabilizer dissolved in a suitable solvent. At elevated temperature the initiator decomposes and generates free radicals, which initiate chain growth by the addition of monomers. The growing chain remains in solution until a critical chain length is reached; then the polymer precipitates in a process known as nucleation. These unstable, nanosized particles aggregate into larger particles, stabilizing themselves against further aggregation by adsorbing the stabilizer from the medium. These particles grow by capturing small nuclei and oligomeric radicals from the continuous phase, and polymerizing the absorbed monomer inside the particles. This continues until all of the oligomeric radicals and nuclei generated in the reaction medium are consumed [20]. Bourgeat-Lami and Lang [21,22] reported the synthesis of SiO₂/PS composite particles by non-aqueous dispersion polymerization of styrene in alcoholic media in the presence of surface-functionalized SiO₂ particles using 3-(trimethoxysilyl) propylmethacrylate as the coupling agent. In related work, Sondi et al. [23] described stable dispersions of SiO₂ that were coated with tert-butyl acrylate polymer by *in situ* polymerization of monomer in 2-propanol. Various polymer/metal oxide nanocomposites including SiO₂ composites have been synthesized via many different protocols with different requirements

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[24–28]. However, the process for synthesizing nanocomposites requires large quantities of volatile organic solvents, and the disposal of waste is a major economic and environmental concern. Consequently, a shift to environmentally-friendly solvent such as supercritical carbon dioxide (scCO₂) is under way [29–32].

In the last decade, interest in the use of ionic liquids (ILs) has increased, as these salts that melt at ambient temperature, for electrochemical and separation processes and may also serve as a medium for chemical and biochemical syntheses [33–35]. ILs are considered to be environmentally-friendly solvents as they are nonvolatile, nonflammable, recyclable and dissolve many organic and inorganic compounds. In the field of polymer chemistry, application of ILs as solvents for polymerization processes is gradually receiving increased attention [36]. Preparation of inorganic nano-

structures [37], conducting polymer nanoparticles [38] and conducting polymer–inorganic filler nanocomposites [39] in ILs have also been reported. Recently, Minami et al. prepared spherical polystyrene particles [40] and polystyrene/poly(methyl methacrylate) [41] composite particles in an IL. Further, it may be possible to prepare novel types of composite particles in ILs due to the high thermal stability and polarity of the ILs, which strongly affect polymer morphology. However, to the best of our knowledge, the preparation of core–shell composite nanospheres in an IL has not been previously reported. In this article, we describe SiO₂/PS core–shell composite nanospheres via *in situ* radical dispersion polymerization in an IL, N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide ([DEME][TFSI]). This radical polymerization route allowed for environmentally-friendly

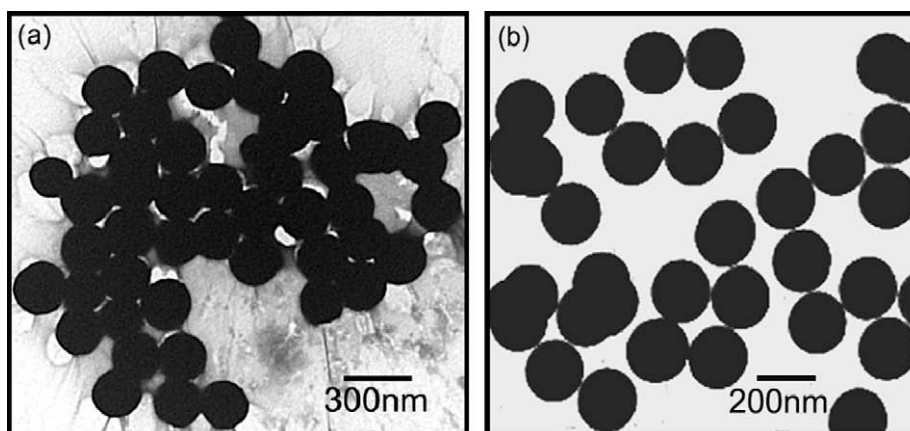
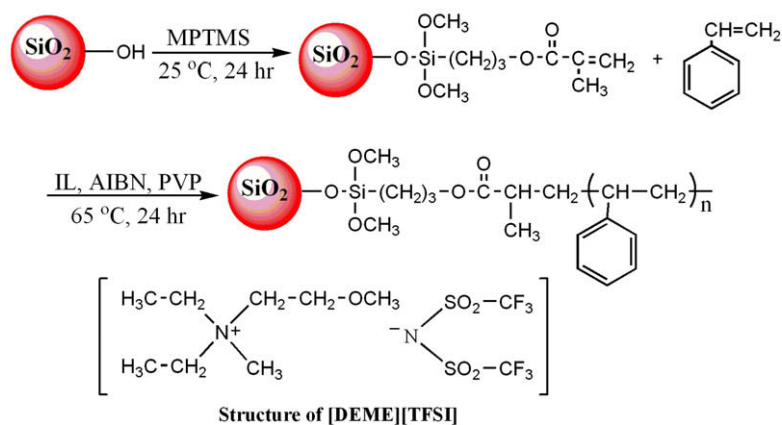
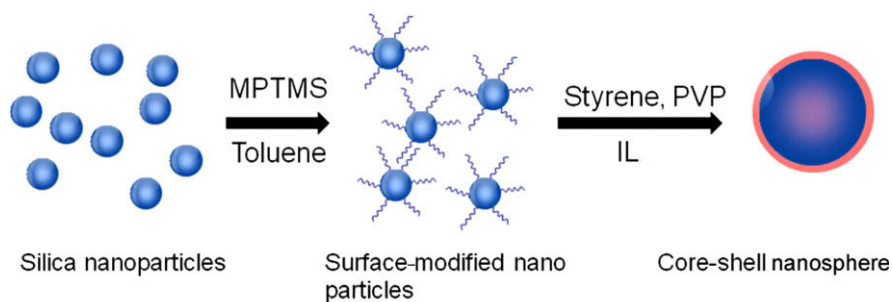


Fig. 1. TEM images of: (a) as prepared SiO₂ and (b) MPTMS-modified SiO₂.



Scheme 1. Schematic representation of the preparation of SiO₂/PS composite nanospheres.

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