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Synthesis of conductive macroporous composite polymeric materials using porogen-free method

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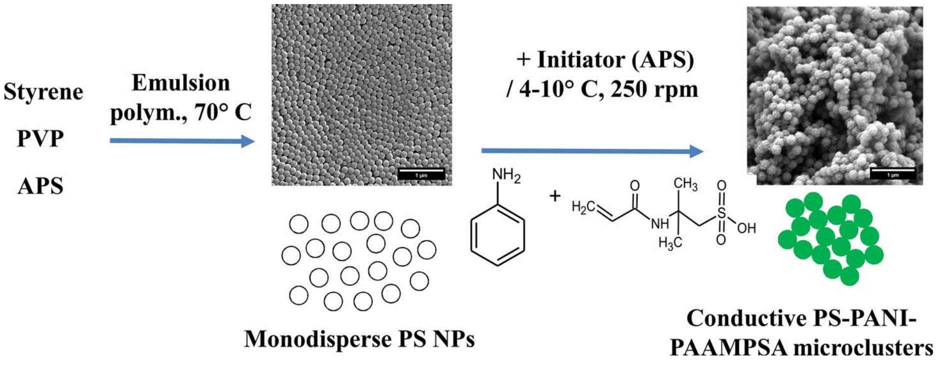
GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis of stable conductive macroporous materials by chemical oxidative polymerization of aniline-(2-acrylamido-2-methylpropanesulfonic acid) in the presence of polystyrene nanoparticles (PS-NPs). The presented method allows, without using any pore generating agent, to prepare conductive highly porous materials with tunable properties. In particular, by changing the composition, i.e. ratio between poly(aniline-(2-acrylamido-2- methylpropanesulfonic acid)) (PANI-PAAMPSA) and PS-NPs, we were able to modulate structure moieties of PANI-PAAMPSA on the surface of PS-NPs as well as the size and internal structure of the formed microclusters. The materials exhibited high porosities up to 80% and surface areas up to 18 m^2/g depending on the ratio between PS and PANI-PAAMPSA. In addition, by differential scanning calorimetry (DSC), it was observed that the PANI-PAAMPSA coating serves as a thermal barrier for PS-NPs. Such a high thermal stability of the prepared microclusters, up to 350 °C, was confirmed by the thermal gravimetric analysis (TGA). Despite the presence of non-conductive PS-NPs, the synthesized composite materials exhibited specific conductivities in the order of 10^{-3} S cm^{-1}, comparable to aniline-based conductive polymers studied in the literature.

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1. Introduction

Over the last decade, there has been increased interest in the development of new functional materials using intrinsically conducting polymers (ICPs) [1,2]. This reflects the growing demands in technologies such as electrorheological fluids [3], organic lightweight batteries, conductive packaging [4], smart sensors and switches [5], energy storage materials [6] etc. ICPs are an interesting class of materials that combine the electrical, optical and magnetic properties typical of metals with the mechanical properties, chemical stability and processability typical of conventional polymers [7–11]. Because they offer additional properties such as lightweight, ease of preparation and low cost as compared to metallic conductors, these polymers are being considered as substitutes for inorganic semiconductors [12]. Recent studies have combined ICPs with polymers, inorganic materials, or even metals to form composites in the form of individual coated particles [1,2]. This approach combines the good characteristics of two or more constituent materials usually yielding functionalities superior to those of the individual materials [13]. Additionally, due to the fact that the content of the core and outer coating can be manipulated independently [14,15], they offer the flexibility to tune the properties of the final materials.

The common approach to the preparation of coated particles from conductive polymers involves first the preparation of colloidal particles from a non-conducting inorganic or vinyl polymer [11] that provides the material with good mechanical or structural properties. Subsequently, a coating of the preferred conductive polymer is deposited onto the surface of the colloidal particle. This results in materials with entirely new properties or an improvement in a particular – mechanical, thermal, or optical property [16,17]. Several researchers have synthesized conductive polymer-coated particles for use as particulate fillers in anisotropic conductive films [7] or electrorheological applications [3]. The deposition of conductive polymers on sacrificial core materials has also been used to prepare hollow particles after removal of the core [18–20]. These materials have applications including photonic crystals, insulation materials, materials for controlled delivery and separations.

Despite the efforts made in the controlled deposition of conductive polymers onto the surfaces of colloidal particles for applications in solution or films, it has been very challenging assembling such coated nanoparticles into ordered 3-D structures [21]. For certain applications, particularly catalysis, chromatography and chemical sensing, the individual coated particles are not suitable. This is because they possess only small or no diffusive pores that lead to mass transport problems. Additionally, many materials display certain functionalities only when they get assembled into specific 3-D structures or morphologies [22]. Many researchers have focused on devising ways of assembling nanoparticle building blocks into 3-D porous structures with larger pores and large surface areas [23–26]. To our knowledge, there has not been any study based on a simple approach to obtain such hierarchically structured materials from conductive polymers with controlled pore properties. Additionally, the systematic investigation of the porous properties of these 3-D materials has not yet been reported elsewhere.

In this paper, applying a combination of the concepts of supramolecular and colloidal chemistry, we describe the fabrication of 3-D conductive macroporous materials using porogen-free method based on chemical oxidative polymerization of aniline-(2-acrylamido-2-methylpropanesulfonic acid) in the presence of polystyrene nanoparticles (PS-NPs), used as building blocks. PS is selected as the model core polymer due to its high glass transition temperature (T_g), which gives rigid and non-deformable particles that make the composites mechanically stronger than they would be by using PANI without a support [3,19,27,28]. Polyaniline (PANI) remains one of the most investigated conjugated polymers, not only because of its high electrical conductivity but also its multiple electronic states, electrical tuneability, nontoxicity, low manufacturing costs and relative environmental stability [12,29–34]. Incorporation of (2-acrylamido-2-methylpropanesulfonic acid) (AAMPSA) during the synthesis of PANI confers several advantages on the materials. This includes the maintenance of pH around 2 during the aniline polymerization, which is crucial for the synthesis of the conductive form of PANI [35,36]. Additionally, due to the conjugated bond system, PANI is rigid and mechanically brittle thus the incorporation of polymer acids such as PAAMPSA or poly (amic acid) with lower glass transition, improves the flexibility of the final material [37]. Use of polymeric acid in PANI synthesis, would also preserve the electrical conductivity of the materials, since it has been reported that small-molecule acid dopants e.g. hydrochloric acid could leach out of the materials leading to a loss in conductivity over time [38].

The novelty of our work lies on several aspects. We prepared 3-D materials having large porosity and not individually coated particles. Additionally, unlike other approaches to macroporous materials, which involve multiple complicated steps, our approach involves only two simple steps that result in the formation of microclusters. It is also important to note that the coating of the PS-NPs with polyaniline-poly-(2-acrylamido-2-methylpropanesulfonic acid) PANI-PAAMPSA and their formation into the porous structures occur in a single reaction medium without using any pore generating agent. Due to its chemical composition and 3D porous structure, the produced material can find applications in catalysis.

2. Experimental section

2.1. Materials

Styrene (Sty, > 99%), ammonium peroxydisulfate (APS, 98%), poly (vinyl pyrrolidone) (PVP, Mw = 40000 g/mol), aniline (ANI, ACS reagent, > 99.5%), 2-acrylamido-2-methyl-1-propanesulfonic acid (AAMPSA, 99%) were all purchased from Sigma Aldrich and used as received. All aqueous solutions were prepared with deionized water.

2.2. Synthesis of monodisperse polystyrene nanoparticles (PS-NPs)

With the intention to make clusters of conductive polymer-coated nanoparticles, the PS-NPs were first prepared by a radical emulsion polymerization of styrene using APS as initiator and PVP as stabilizer in a radical emulsion polymerization system. The ratio between monomer, initiator and surfactant was adopted from the work of Davodi et al. [34] and was equal to 6 g: 0.06 g: 0.5 g, respectively. The detailed steps are as follows: The aqueous phase was prepared by dissolving PVP (0.5 g) in deionized water (90 mL) followed by the addition of styrene (6 g). The mixture was stirred in an ice bath using ultraturrax (IKA® T25 digital) at 15000 rpm for 30 min. The resulting emulsion was transferred into a three-neck round bottom flask, equipped with a reflux condenser and degassed by applying sequential vacuum/nitrogen cycles while mixing with a magnetic stirrer at 350 rpm for about 15–20 min. The reaction mixture was then heated to 70 °C, while the temperature in the reactor was monitored with a standard thermometer inserted directly into the solution through a septum. When the temperature of the solution reached 70 °C, aqueous initiator solution (0.06 g APS in 4 mL of DI water) was injected. The polymerization was carried out for 8 h and the resulting latex was allowed to cool down and stored for further experiments.

2.3. Synthesis of PANI-PAAMPSA-PS NPs composite microclusters

For preparation of the microclusters, aniline-(2-acrylamido-2-methylpropanesulfonic acid) (ANI-AAMPSA) was polymerized by chemical oxidative route in the presence of the PS-NPs. The PS-NPs concentration was kept constant at 1 wt.% while varying the amount of ANI-AAMPSA according to the composition in Table 1. (The samples were named PS – PANI-PAAMPSA 1–4 depending on the ratio between the PS-NPs and PANI-PAAMPSA).

The procedure is as follows: ANI-AAMPSA solution was prepared