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Synthesis and characterization of full interpenetrating structure mesoporous polycarbonate-silica spheres and p-phenylenediamine adsorption

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ABSTRACT

As a common used and hardly emulsified amorphous thermoplastic, the bisphenol-A polycarbonates were used as the polymer candidate to form a novel monodispersed sub-micrometer mesoporous polymer–silica spheres with full interpenetrating structure. The synthesis procedure was based on a modified sol–gel approach in which the polycarbonate was plasticized in advanced by the surfactant of polymer emulsion. The mesoporous spheres possess a perfect uniform particle size and the polymer–silica spheres are held together by permanent entanglement in three dimensions. The defined crystallization of the polycarbonate was occurred when it was entrapped in the silica laminated matrix due to the plasticizing effect of the surfactant, and directly affected the thermal stability of the mesoporous spheres. The specific surface areas and pore diameters of mesoporous sphere were affected by the mass content and crystallization behavior of the polycarbonate. The p-phenylenediamine was used as adsorbate to investigate the cationic organics adsorption ability of the mesoporous spheres. The results shown that the polycarbonate-silica possess a well adsorption capacity for p-phenylenediamine by virtue of two kinds of hydrogen bond, and the maximum adsorption capacity was nearly 7.5 times larger than that of the hollow mesoporous silica.

1. Introduction

Since the discovery of the new family of mesoporous silica M41S in 1992 [1], this kind of novel materials has received considerable attention both in academic and in industry. As a very important class of the mesoporous materials, the polymer–silica system intrigues the great interest in recent years for their tunable pore sizes, high specific surface areas, versatile possibilities of surface functionalization as well as diversity in chemical composition, monolithic morphology and inner structure [2–6]. The morphology of polymer–silica mesoporous materials has been controlled to produce composite fibers [7,8], membranes [9,10], rodlike particles [11], films [12], spheres [13–16] and hard spherical particles [17–19] to satisfy diverse practical applications. Among these various forms, spheres gained many interests for their widespread potential applications in many fields, such as catalysis [20], pollutant adsorption [21] and drug delivery [22,23]. Some researchers have synthesized polymer–silica spheres with diverse inner structures, such as the core–shell structure in which the polymer acts as the core and silica serves as the shell [24,25], and interpenetrating structure in which the polymer–silica 3D (three-dimensional) networks are held together by permanent entanglements [26]. Compared with the core–shell structure, the polymer–silica spheres with the interpenetrating structure had some excellent unique features, such as nanosized precise distribution of organic and inorganic substances thanks to the well intercalation between the polymer and silica matrix.

However, although these polymer–silica spheres with various inner structures have been synthesized in recent years, but the most utilized of them are core–shell structure and the polymer is commonly used as the core template for further producing the hollow silica spheres instead of exerting their own characteristics [27–29]. There were few reports shown that the interpenetrating structure polymer–silica spheres were applied in any fields, especially the mesoporous ones which may not even have been synthesized. Therefore, the synthesis and utilization of the interpenetrating structure mesoporous polymer–silica spheres is a very creative and meaningful work.

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Commonly, the straightforward strategy to synthesize the polymer–silica mesoporous spheres is in situ polymerization or post-grafting approach [30,31]. However, although these two approaches are facial and general, but they usually could not obtain a perfect interpenetrating structure. An effective way to control the inner structure of the polymer–silica spheres is the sol–gel method in which the polymer emulsion acts as the template. David Avnir et al. have synthesized some diverse polymer–silica spheres with interpenetrating structure by this approach [32–35]. The synthesis procedure is based on hydrolysis and poly-condensation of the inorganic silica precursor in the presence of the organic polymer within droplets of an emulsion, in brief, the forming silica within the droplets entraps the dissolved polymer. The sol–gel approach for the organic polymers utilized an O/W emulsion as the template, where the oil phase was composed of the tetraethoxysilane (TEOS), precursor for the silica matrix, along with the polymer and a co-solvent, and where the water phase was an alkaline water–alcohol solution to which a proper polymer surfactant was added. By using this method, well sub-micrometer polymer–silica spheres with interpenetrating structure could be obtained.

However, this approach may only be suitable for the easily dissolved and emulsified polymers but not for the other opposite ones, such as polypropylene, polylactic acid and polycarbonate. Furthermore, the synthesis procedure is under alkaline condition, so it may not be appropriate for the polymers which are easy to be hydrolyzed under alkaline condition. More importantly, the polymer–silica spheres synthesized through this approach are non-mesoporous and the specific surface areas are quite small, even less than 10 m^2/g according to the results of David Avnir et al.. Accordingly, for solving these drawbacks, a new approach should be performed to synthesize the interpenetrating structure mesoporous polymer–silica spheres with a relatively large specific surface area in which the polymer is hardly dissolved and emulsified.

Bisphenol-A polycarbonates, produced by the reaction of bisphenol-A and phosgene, received their name because they are polymers containing carbonate groups (—O—(C=O)—O—). As a clear and amorphous thermoplastic, owing to its chain rigidity retards the chain diffusion, the PC undergoes thermal-induced crystallization very slowly and could not be emulsified easily. Therefore, the synthesis of the PC-silica mesoporous spheres with interpenetrating structure would not be done by the David Avnir's method. There are a great number of hydrophilic polar groups on the macromolecular chairs of PC, leading an extremely strong hydrogen bond interaction with the cationic organic compounds. As a similar interaction example, An et al. [21] synthesized PMAA-silica in which the methacrylic acid (MAA) was grafted onto the surface of silica gel to adsorb aniline. The results presented that the PMAA/silica possesses a strong adsorption ability for aniline depending on the interaction of hydrogen bond between the carboxyl groups of PMAA and aniline. According to this result, it is reasonable to presume that if composited with the silica to form mesoporous materials with large specific surface areas, the nano-sized bisphenol-A polycarbonates could also be used as a potential aniline or p-phenylenediamine cationic organics adsorbent by virtue of the similar strong hydrogen bond effect.

The p-phenylenediamine is one of the simplest aromatic diamine, and there are two cationic polar groups connected on the para-position of the benzene ring, so the p-phenylenediamine could form a strong hydrogen bond and/or electrostatic interaction with the other anionic organics. The p-phenylenediamine is commonly used as an intermediate in various fields [36–38], but the accumulation harmful effect has been emerged gradually, especially the p-phenylenediamine-contained wastewater. Therefore, the elimination of the p-phenylenediamine is so important to public health and environmental quality.

In this paper, novel mesoporous PC-silica spheres with full interpenetrating structure were synthesized by a modified sol–gel approach which inspired by the achievements of David Avnir et al. The p-phenylenediamine adsorption performances were also investigated to estimate the possibility of the PC-silica served as an adsorbent for cationic organics. The full interpenetrating structure of the PC-silica mesoporous spheres was obtained by using the Pluronic P123 as the surfactant which was added into the oil phase to plasticize the PC and formed a stable polymer emulsion template. There was no stable polymer emulsion could be gained if the P123 was put into the water phase due to the plasticizing effect of the P123 was absent. Therefore, it is reasonable to infer that the polymer–silica mesoporous spheres with interpenetrating structure could be obtained via making a choice of putting the surfactant into the water or oil phase, according to the difficulty of the polymer was emulsified. For investigating the adsorption capacity of the PC-silica, the p-phenylenediamine was served as the adsorbate under the alkaline condition.

2. Experimental characterization

2.1. Materials

Pluronic P123 ($EO_{20}PO_{70}EO_{20}$; M_{av} = 5800), bisphenol A polycarbonate (Mw = 64 kg/mol, density = 1.20 g/cm^3), tetraethyl orthosilicate (TEOS), p-phenylenediamine, cyclohexanone and hydrochloric acid (HCl) were all purchased from Aldrich Chemical Co. and used as received without any purification.

2.2. Synthesis of mesoporous PC-SiO_2

In order to investigate the influence of the PC content on the structure of PC-silica, a series of samples with different PC contents was prepared by the modified sol–gel method. The samples were named S1, S2 and S3, respectively when 0.05 g, 0.1 g and 0.3 g PC were added into the synthesis system. The synthesis procedure is depicted in Fig. 1. In a typical procedure, 0.1 g PC, and 1 g P123 were placed in 5 g cyclohexanone and stirred at 60 °C for 2 h to make a transparent hydrophobic solution and then decreased the temperature to 35 °C. After 40 g ultrapure water and 4 g HCl were added at 35 °C, a stable emulsion was formed immediately, then pour 2 g TEOS into the emulsion quickly and stirred for another 24 h. After the reaction, the resulting dispersion was centrifuged at 10,000 rpm for 20 min. The precipitate was washed with ultrapure water twice and dried at 60 °C for 24 h, then washed with ethanol to remove the P123 completely by using the soxhlet extractor. The same procedure was carried out to prepare the hollow silica when the PC was absent and the precipitate was calcined at 650 °C for 3 h.

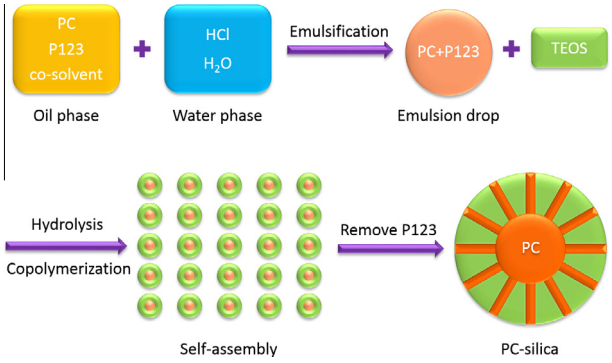

Fig. 1. Synthesis procedure schematic diagram of PC-silica.