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Synthesis of macroporous polymer through heterogeneous polymerization by redox initiator and application as scaffold for Pd nanoparticles

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HIGHLIGHTS

- Heterogeneous polymerization initiated by redox pair under mild conditions is performed.
- Synthesis of macroporous amphiphilic copolymer is achieved.
- Macroporous copolymers are demonstrated to be suitable scaffold for Pd nanoparticles.
- Up to 8.5 wt.% Pd is immobilized on the macroporous copolymer.

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ABSTRACT

Heterogeneous polymerization of the binary hydrophilic/hydrophobic monomers initiated by the redox pair to synthesize macroporous amphiphilic copolymers is reported. This strategy employs the initiator of the hydrophilic/hydrophobic redox pair of $K_2S_2O_8$/1-octylamine or the hydrophilic/hydrophilic redox pairs of $K_2S_2O_8$/diethylamine and $K_2S_2O_8$/Na_2SO_3 to initiate the polymerization on the O/W emulsion interface at mild temperature. Following this strategy, both the macroporous poly(methyl methacrylate-*co*-methacrylic acid) with the pore size ranging from 80 to 400 nm and the macroporous poly(styrene-*co*-methacrylic acid) with the pore size at about 180–190 nm are synthesized. The synthesized macroporous amphiphilic copolymers are demonstrated to be suitable scaffold for Pd nanoparticles. The immobilization of Pd nanoparticles with the Pd content up to 8.5 wt.% and with the Pd nanoparticle size ranging from 4.6 to 7.1 nm is achieved. The proposed strategy is believed to be a valid method to synthesize porous amphiphilic copolymer.

1. Introduction

Recently, porous materials are of great scientific interests due to their applications in many areas including separation, drug delivery, tissue engineering, supports for exchange of ionic compounds and catalyst scaffold [1–3]. Up to now, the methods for synthesis of porous polymers including hollow micro/nanoparticles are generally divided into two categories: (1) template polymerization [4–9] and (2) template-free or soft-template polymerization through the emulsion system such as the oil-in-water (O/W) emulsion, the oil-in-water-in-oil (O/W/O) emulsion, the water-in-oil-in-water (W/O/W) emulsion [10–17] and the high internal phase emulsion [18–27]. The template method, which employs either the non-cross-linked polymeric particles or the linear polymers as the pore-forming agent, has the advantage of controllable tuning in the pore size [4–9]. However, the template synthesis of porous polymers generally involves multiple and complex procedures. For examples, the general method to fabricate hollow microspheres by template polymerization includes the synthesis of a suitable particle template, the polymerization of the shell-forming monomer on the surface of the particle template to form coated microspheres, and then the template removal by solvent etching [4–9]. The O/W emulsion, O/W/O emulsion and W/O/W emulsion polymerization methods are proved to be convenient and economical for the preparation of porous polymeric micro/nanoparticles [10–17]. Owing to the amphiphilic character and the unique molecular geometry, the emulsifier molecules can aggregate into the bilayer-structured vesicles [28]. When suitable monomer is inherently emerged within the emulsions, polymerization of these emulsions leads to the formation of porous polymers [12–15]. Besides the O/W, O/W/O and W/O/W emulsions, the high internal phase emulsion with a continuous organic phase is also used to produce polymer foams with an open porous polymeric network [18–27]. Compared with the template polymerization, the emulsion polymerization to produce porous polymer has the obvious advantage that the use of template is needless. However, careful

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