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Thermo-responsive hydrogels containing mesoporous silica toward controlled and sustainable releases

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ABSTRACT

Here we prepare thermo-responsive hydrogel containing mesoporous silica (KIT-6) with high surface area. Our hybrid hydrogel is prepared by gelation of NIPAM monomer with mesoporous silica particles in presence of cross linker. Owing to the doped mesoporous silica, a large amount of guest molecules are adsorbed easily. With increase of temperature, the hybrid hydrogel shrinks to retard the release of guest molecules.

1. Introduction

Mesoporous silica (MPS) materials have demonstrated very interesting properties in the development of drug delivery system (DDS), because of high adsorption capacity of guest molecules and their release [1–4]. Also, MPS has shown to be highly biocompatible and its self-degradation in aqueous solution solves the problems related to the removal of the material after use [5]. MPS itself, however, cannot show the intelligent properties such as controlled release as a function of external stimuli, which is highly demanding in DDS. On the other hand, use of several stimuli-responsive polymers (*e.g.*, polymeric micelles) can optimize adsorption and delivery of drugs [6–9]. In spite of their fast response with change in external factors, their poor mechanical properties limit their applications, since most of the polymers consist of organic backbone.

The combination of stimuli responsive properties of polymer and mechanical and thermal stability of MPS can help to develop smart MPS-based delivery systems in which encapsulation and release of guest molecules can be controlled by a variety of external stimuli [10–12]. Some efforts have been made to realize hybrid systems using MPS materials for controlled release. pH-responsive hybrid carrier system is constructed by electrostatic interaction between polycations and anionic SBA-15. The ionizable carboxylic acid can act as a reversible gate to release drug in a controlled way [13]. pH-induced conformational change of protein molecules forms pH-responsive nanovalve to lock and unlock the pore entrances of MCM-41 [14].

Poly(N-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer, which shows a reversible coil-to-globule transition at elevated temperature (known as lower critical solution temperature (LCST)) in aqueous solution [15]. Raising the temperature above its LCST, water bound to the polymer chain is released and soluble polymer coils start to form insoluble globular particles. The LCST of PNIPAM is at around 32–34 °C which is very close to human body temperature. Therefore, PNIPAM-based hybrid gel has been widely studied in biomedical applications [16–18]. Hybridization of MPS particles with functional polymer not only enables functionalization with various molecules but also provides the opportunity to tune the loading and release of guest molecules [19]. Liu et al. synthesized a magnetic MPS nanoparticle coating with PNIPAM polymer. The phase transition temperature of hybrid spheres can be finely tuned by adjusting the amount of hydrophilic comonomer [20]. Interpenetrating network of PNIPAM is formed within the pores by organic and inorganic gelation. The property

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of hybrid gel is optimized by controlling the molar ratios of silica source and NIPAM [21]. Radical microemulsion polymerization is used to graft PNIPAM on the Fe_3O_4@SiO_2 core–shell nanoparticles [22]. Lopez et al. impregnated the polymer into the pores of MCM-41 [23]. The kinetics of molecular diffusion was observed when the polymer chain changes from open coil to globule conformation as a function of temperature.

Our goal in this study is a smart hybridization of PNIPAM hydrogels with MPS particles to realize sustainable release. Mesoporous structures are easily accessible for the adsorption of guest molecules. Mechanical strength, encapsulation and controlled release of guest molecules as a function of temperature are investigated.

2. Experimental

2.1. Preparation of PNIPAM hydrogels with MPS particles

MPS (KIT-6) was prepared, according to our previous study [24]. Pluronic P123 block copolymer (6.00 g) was dissolved in water (217 mL) and HCl (37.0 wt%) solution (10.0 mL). After the complete dissolution of block copolymer, *n*-butanol (7.39 mL) was further added to the mixture and stirred at 35 °C for 1 h. Butanol is believed to act as a co-surfactant which co-micellizes with the block copolymer. Tetraethyl orthosilicate (TEOS) (12.9 g) was dropped into the homogenous clear solution and additional stirring was carried out at 35 °C for 24 h. Finally, the obtained particles were washed with ethanol/HCl solution and then calcined at 550 °C in air to remove the polymer. For preparation of typical hybrid hydrogel, 0.73 g of NIPAM monomer and 0.01 g of N,N'-methylenebisacrylamide (NMBA) were added into aqueous dispersion of KIT-6 (0.2 g, 0.5 g, or 1.5 g in 1.5 g of water). The resulting solution was stirred for 1 h. The mixture was kept into ice bath with N_2 bubbling for 30 min. Ammonium persulphate and N,N,N',N'-tetramethylethylenediamine (TEMED) was added and kept at 20 °C for 12 h for gelation. The gel was removed from reaction vessel and kept in distilled water for 7 days to wash away the reaction residues. The obtained hybrid gels containing MPS particles are noted as PNIPAM-MPS(*x*) where *x* indicates the doped amounts of MPS in gram.

2.2. Characterization of MPS particles

Transmission electron microscope (TEM, JEOL JEM-2100F) was used to observe the mesostructure of MPS particles. Belsorp 28 apparatus (Bel Japan, Inc.) was used to measure nitrogen-adsorption isotherms and the pore-size distribution. Low-angle XRD patterns were recorded by using a NANO VIEWER (Rigaku, Japan).

3. Results and discussion

N_2 adsorption desorption isotherm of MPS shows typical IV type with specific surface area (717 $m^2\ g^{-1}$) (Fig. 1**a**). XRD peaks in low-angle region shows excellent structural ordering with *Ia*-3*d* symmetry (Fig. 1**b**). Highly interconnected mesopores of MPS (KIT-6) was observed by TEM (Fig. 1**c**). The main achievement of this study is that gelation of PNIPAM on/into the MPS does not perturb the mesoporosity. The XRD pattern of the hybrid gel (Fig. 1**b**) is nearly the same as the original one, indicating no mesostructural shrinkage or destruction was occurred. The *d*-spacing of the hybrid

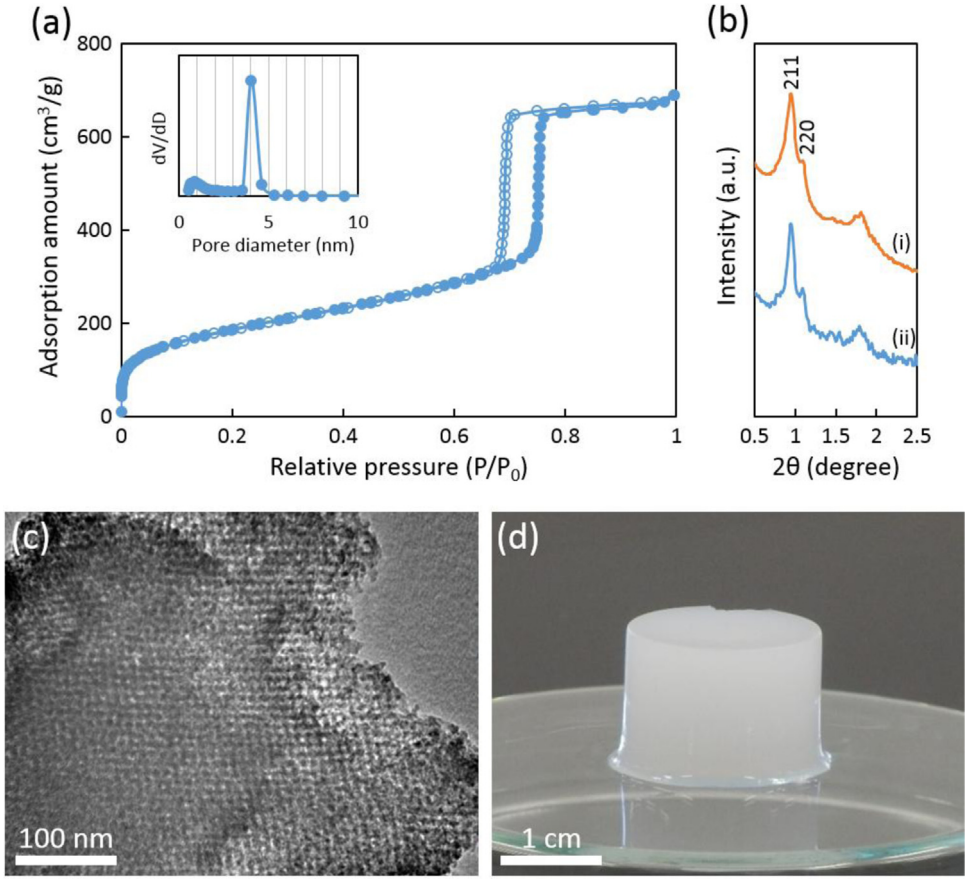

Fig. 1. (a) Nitrogen adsorption-desorption isotherm and pore size distribution of the used MPS (KIT-6). (b) low-angle XRD patterns of (i) the MPS (KIT-6) and (ii) the PNIPAM-MPS (0.5). (c) TEM image of MPS (KIT-6). (d) Photograph of the obtained PNIPAM-MPS (0.5).