Microporous and Mesoporous Materials 196 (2014) 335–340

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Conjugated microporous polymer nanotubes and hydrophobic sponges

Wenjie Fan [a], Xuefei Liu [b], Zhen Zhang [b], Qijian Zhang [a], Wei Ma [b], Dazhi Tan [a,b,*], An Li [c,*]

[a] School of Chemical and Environmental Engineering, Liaoning University of Technology, Jinzhou 121001, PR China
[b] Experimental Center of Chemistry, Faculty of Chemical, Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, PR China
[c] College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, PR China

ARTICLE INFO

Article history:
Received 16 November 2013
Received in revised form 26 May 2014
Accepted 27 May 2014
Available online 4 June 2014

Keywords:
Conjugated microporous polymers
Nanotubes
Hydrophobic sponges
Porous materials
Oil–water separation

ABSTRACT

Novel nanotube-like conjugated microporous polymer (CMP) with a large surface area was prepared by one-step chemical synthesis via cross-coupling of 1,4-diethynylbenzene and 2,4,6-tribromophenol. Due to its unique surface hydrophobicity and porous feature, we prepared CMP nanotube-based hydrophobic sponges by filling the CMP nanotubes into melamine sponges to afford a bulk absorbent via the method similar to "ship-in-bottle". The CMP treated sponges exhibit excellent absorption capacity and recyclability for separation of organics from water. Moreover, the absorbates can be re-collected simply by squeezing the treated sponge. This work provides a simple and efficient method to prepare hydrophobic, oleophilic sponge materials, which is of technological significance for potential use, especially for oil-spill cleanups or removal of organic pollutants from water.

1. Introduction

Increasing attention has been paid to the development of materials and technologies for water treatment, due to global scale of severe water pollution caused by industrial organics emission and oil leakage [1–3]. Considering the adsorption ability, several types of porous materials have been discovered, such as activated carbons [4,5], zeolites [6], organic–inorganic hybrids [7], and so forth [8–11]. Although widely used in practical applications, these absorbent materials have shown certain disadvantages: low separation selectivity, low absorption capacity, non-regenerate characteristic, etc. Therefore, there is still an urgent need for the development of novel, efficient and easy-to-recycle absorbent materials for oil–water separation. Recently, several types of porous materials with great surface superhydrophobicity and superoleophilicity have been reported and successfully used for the separation and absorption of organics or oils from water [12–18]. Compared with those traditional absorbent materials, these superwetting porous materials have been reported to exhibit larger absorption capacities, very satisfying recyclability and absorption selectivity. Conjugated microporous polymers (CMPs) are a new class of porous materials of which the physical and chemical parameters can be adjusted by using different molecular components [19–26]. The CMPs have great advantages over those traditional absorbent materials for their excellent selective adsorption performance, due to the superhydrophobic and superoleophilic surface determined by nonpolar functional group (phenylene and ethynylene units) and nanometer- or micrometer-sized porosity in the structure. By altering the monomer ratio [27], the solvents [28] and the structure of monomers [29] during polymerizations, we have prepared several kinds of CMPs with different porous properties and morphologies, and our results show that the characteristics and morphologies of the CMP samples affect the adsorption capacities for organic solvents significantly. However, the powder state of CMP could limit its practical application. On the other hand, the extremely low solubility of CMP nanotubes in water or organic solvents leads to the difficulty when processed or combined with other substrates. To solve the problems, we introduced melamine sponge as CMP's carrier, which is a cheap and commercially available porous and hydrophilic material that can absorb both water and oils or organic solvents. Recently, the loading of CMPs, activated carbon, and graphene nanosheets onto sponges to prepare superhydrophobic sponges for selective absorption of oils and organics from water has been reported by our research group and others [30–32]. In 2011, we reported the first example for preparation of superhydrophobic sponge by coating method [13], and in that case the porous HCMP-1 was loaded into sponge by so called "dust adhesion", and the HCMP-1 particles were easy to be detached from sponge framework during practical operation due to such weak adhesion.

Herein, we report the synthesis of novel nanotube-like CMP (CMP-H) by one-step chemical synthesis via cross-coupling of 1,4-diethynylbenzene and 2,4,6-tribromophenol. By facile filling

---

* Corresponding authors. Address: School of Chemical and Environmental Engineering, Liaoning University of Technology, Jinzhou 121001, PR China. Tel./fax: +86 0416 4198150 (D. Tan). Tel./fax: +86 931 2973560 (A. Li).

E-mail addresses: tandz@dlut.edu.cn (D. Tan), lian2010@lut.cn (A. Li).

http://dx.doi.org/10.1016/j.micromeso.2014.05.038
1387-1811/

the as-prepared CMP nanotubes into sponges, the hydrophilic melamine sponge changes to be hydrophobic and oleophilic, showing good absorption capacity and excellent absorption selectivity for oils and nonpolar organic solvents as well as outstanding recyclability. This work aims to overcome the drawbacks of our previous work [13]. In this study, the CMP-H exhibits a nanotube shape, which makes it difficult to be separated from the melamine sponges and in turn has advantage over our previous work. Therefore, the CMP treated sponges are easier to prepare and handle, and they show better stabilities and recyclabilities than the untreated counterparts. Furthermore, such filling the CMP-H nanotubes into sponges for efficient removal of oils from water has never been reported and quite different from the cases reported before [30–32]. The outstanding properties demonstrated by the CMP-H and CMP-treated sponges makes them promising candidates for potential applications such as oil-spill cleanup and water treatment.

2. Experimental section

2.1. Materials

2,4,6-tribromophenol and 1,4-diethynylbenzene were obtained from TCI, tetrakis (triphenylphosphine) palladium and copper(I) iodide were all purchased from Alfa Aesar. All chemicals used had a purity of 97% or greater and used as received. Et_3N was dried over KOH and p-xylene was distilled mixture with sodium metal.

2.2. Synthesis of CMP-H

1,4-diethynylbenzene (3 mmol), 2,4,6-tribromophenol (2 mmol), tetrakis (triphenylphosphine) palladium (100 mg.) and copper(I) iodide(30 mg) were dissolved in the mixture of p-xylene (5.0 mL) and Et_3N (5.0 mL). The mixture was heated to 80 °C and stirred for 5 h under argon atmosphere. The resulting polymer was filtered and washed with methylene chloroform, acetone, water, dilute hydrochloric acid and methanol for several times, then the polymer was further purified by soxhlet extraction (methanol) for 3 days. The resulting product was dried at 100 °C for 5 h to a constant weight.

2.3. Synthesis of CMP-H nanotube-based sponges

1,4-diethynylbenzene (3 mmol), 2,4,6-tribromophenol (2 mmol), tetrakis (triphenylphosphine) palladium (100 mg)and copper(I) iodide(30 mg) were placed in 500 round-bottom flask which was degassed and nitrogen gas. Et_3N (20 mL), p-xylene (100 mL) and melamine sponges (50 mg with cube) were also added to the flask. The mixtures were stirred at 80 °C for 6 h. The resulting sponges were washed with methylene chloroform, acetone, water and methanol for several times, and further purified by soxhlet extraction (methanol) for 3 days, then dried at 100 °C for 5 h.

2.4. Characterizations

Fourier transform infrared spectroscopy (FTIR) spectra were recorded in the range of 4000–400 cm^{-1} using the KBr pellet technique on Nicolet 6700 spectrum instrument. Solid-state ^{13}C NMR spectra were measured at the molecular level on an Avance Digital 500 MHz spectrometer. High-resolution imaging of the polymer morphology was achieved using a NOVA Nano 450 scanning electron microscope (FE-SEM) and Tecnai G2 F30 transmission electron microscope (TEM, FEI Company, USA). Polymer's surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using the ASAP 2020 volumetric adsorption analyzer. Water contact angle measurements for samples were performed on a contact angle meter (SL200B, Solon Company, China), which was conducted by coating the CMP microgel particles on PDMS films which gives a macroscopically smooth surface for contact angle measurement. Organic solvent adsorption analyses were investigated by weight measurement. The adsorbent tests were all conducted at room temperature. Weighted quantities of the CMP-H networks or the CMP-H treated sponges were immersed in various organic solvents to reach the adsorption equilibrium. After a few minutes, the wet samples were then separated from organic solvents and weight measurements were done quickly to avoid evaporation of absorbed solvents. All tests are triplicated with the mean of the three runs being used for calculations to minimize the errors.

The absorbency of the samples was calculated using the following equation:

$$\text{Absorbency} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}(wt/wt) \times 100\%$$

where W_{dry} and W_{wet} are the weights of the dried samples and the wet samples, respectively.

3. Results and discussion

We synthesized the CMP nanotubes (named as CMP-H) employing 1,4-diethynylbenzene and 2,4,6-tribromophenol in Sonogashira–Hagihara homo-coupling polymerization method. The route to construct CMP-H networks in our work is shown in Scheme 1, with 1,3,5-substitutedphenol connected by struts containing one phenylene moiety and two ethynylene unit. The structures of CMP-H in molecular level were characterized by infrared spectra measurements and ^{13}C solid-state NMR spectrum. As shown in Fig. 1(a), the spectrum shows a stretching band of C–C in benzene ring from1400 cm^{-1} to 1650 cm^{-1} and a peak signal of aromatic C–H bond around 3050 cm^{-1}. The peak around 2208 cm^{-1} corresponds to the C≡C stretching. Meanwhile, we can also observe the characteristic Ar–OH stretching vibration at 1170 cm^{-1}. The ^{13}C solid-state NMR spectrum (126 MHz, $C_2H_5NO_2$, 300 K) of the CMP gives more structural information, as demonstrated in Fig. 1(b). The signals approximately at 82–92, 132, 110–123, 156 ppm are resolved, indicating that there are mainly four kinds of carbons in the networks. The observed appearance of resonance at $\delta = 92$ ppm and $\delta = 82$ ppm can be ascribed to the —C≡C— sites. The resonance at $\delta = 132$ ppm corresponds to sp^2 carbons in the benzene rings (C_{Ar}–H) , and 110 ppm and 123 ppm is assigned to the sp^2 benzene connected with alkynylene. The peak around 156 ppm corresponds to the C_{Ar}–OH stretching.

The porous property of CMP-H was confirmed by nitrogen adsorption analysis at 77.3 K. The adsorption and desorption isotherms are depicted in Fig. 2. The polymer gave rise to Type I nitrogen sorption isotherms with H4 hysteresis loops [33]. The adsorption curve showed a very sharp uptake from 0 to 0.01 bar, indicating the microporous property. We use Langmuir model to calculate the surface area, since the adsorption coefficient <0, and the calculation result shows the surface area $S_{\text{langmuir}} = 340\ m^2/g$. Our results also show the pore volume $V_{\text{tot}} = 0.226\ cm^3/g$ at $P/P_0 = 0.99$ and the micropore volumes $V_{\text{micro}} = 0.067\ cm^3/g$ at $P/P_0 = 0.10$.

Scanning electron microscopy (SEM) for CMP-H samples also provides useful morphological information to explain the observed porosity. The SEM images of CMP-H are shown in Fig. 3(a). As can be seen, the CMP-H networks are amorphous and show no evidence of long range molecular order, as found previously for cross-coupled CMPs [27–29]. The CMP-H are formed of diameters in the range of 100–500 nm and lengths of tens to hundreds of micrometers. The transmission electron microscopy (TEM) images