



Original article

Ionic liquid functionalized polymer composite nanotubes toward dye decomposition



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ABSTRACT

Poly(ionic liquid) functionalized composite nanotubes are achieved by ATRP grafting ionic liquid monomers for example $\text{ViEtIm}^+\text{Br}^-$ from the poly(DVB-co-VBC) nanotubes surface. $\text{PW}_{12}\text{O}_{40}^{3-}$ anion is introduced through anion exchange. The $\text{PW}_{12}\text{O}_{40}^{3-}$ based composite nanotubes can synchronously absorb and decompose water soluble dyes for example methyl orange (MO). The cooperative interplay is promising in highly efficient decomposition of dyes.

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1. Introduction

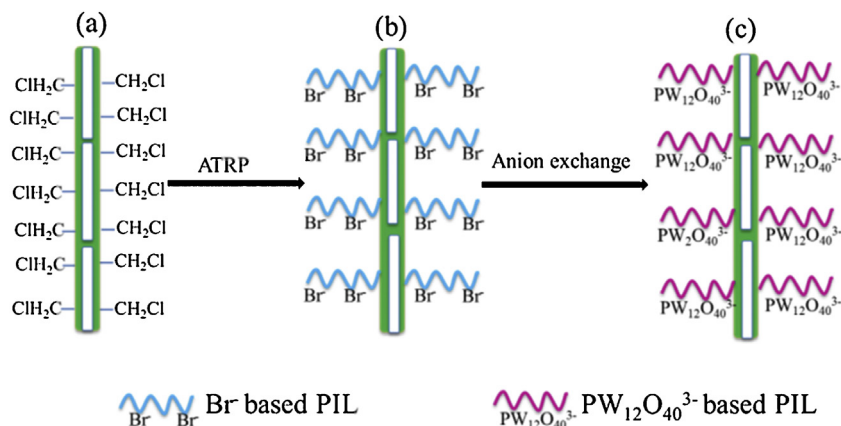
Ionic liquids (ILs) have gained increasing concerns due to low melting point, good chemical stability and easiness to be functionalized such as catalysis [1]. In recent few years, polymer ionic liquids (PILs) as novel polyelectrolytes are becoming more attractive [2]. It is worthy to note that PILs can derive a huge family of functional materials after substitution of the corresponding anions or cations [3]. For instance, the imidazole based ionic liquids can experience a reversible affinity transition in between hydrophobic–hydrophilic by simply exchanging anions [4]. Wettability of the IL or PIL coating is thus simply tunable from hydrophilic to hydrophobic when the anion BF_4^- is substituted with PF_6^- group [5]. Besides controlling wettability, PILs will possess excellent redox-catalytic activity after the corresponding functional anions such as polyoxometalates (POMs) are introduced [6]. The catalytic PILs are promising in decomposition of water pollutants [7]. Among the pollutants, those water soluble azo-based dyestuffs are commonly used but toxic to environment. It is important to develop methods to effectively decompose the dyestuffs. Oxidation process [8] is more efficient than other

methods including physical adsorption process [9] and biological method [10]. Polyoxometalates (POMs) are a series of molecular metal-oxygen clusters with varied structures [11]. Especially, those polyoxometalates with a Keggin structure such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ have shown excellent redox-catalytic activity in the decomposition of azo dyes [6]. It is expected that POMs based IL or PIL will be capable to catalytic degradation of dyes. It becomes a key concern to support the catalysts for easy recycling after the decomposition process. We have recently reported on synthesis of bamboo-like crosslinked polymer nanotubes *via* a rapid cationic polymerization [12]. Compared with previously reported methods such as self-assembly, template synthesis and electrospinning [13], the method is highly effective to synthesize the nanotubes in large scale.

Herein, we report on the synthesis of $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL functionalized polymer nanotubes (Scheme 1) and decomposition of the azo-based dyestuffs. Poly(divinylbenzene-co-vinylbenzyl chloride) (DVB-co-VBC) nanotubes are synthesized. The poly(VBC) block can further initiate ATRP to graft IL monomer of $\text{ViEtIm}^+\text{Br}^-$ onto the polymer nanotubes. After a simple anion substitution of Br^- with $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL functionalized poly(DVB-co-VBC) nanotubes are synthesized. The composite nanotubes are dispersed in aqueous solution well, which can catalyze decomposition of water soluble dyes. Compared with IL molecules and their polymeric PILs, the PIL modified nanotubes can be easily collected from water for separation and regeneration.

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Scheme 1. Schematic synthesis of the $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL composite nanotubes. Poly(DVB-co-VBC) nanotubes are fabricated by cationic polymerization of DVB and VBC monomers (a). Br^- based PIL composite nanotubes are synthesized by ATRP grafting of $[(\text{ViEtIm})^+\text{Br}^-]$ from the poly(DVB-co-VBC) nanotubes surface (b). $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL composite nanotubes are synthesized by anion exchange of Br^- with $\text{PW}_{12}\text{O}_{40}^{3-}$ (c).

2. Experimental

2.1. Materials

Divinyl benzene (DVB), vinylbenzyl chloride (VBC) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMEDTA) were purchased from Sigma-Aldrich. Boron trifluoride diethyl etherate ($\text{BF}_3\text{O}(\text{Et})_2$, CP), ethanol (AR), *n*-hexane (AR) were supplied by Beijing Chemical Works. The example dye methyl orange (MO) was purchased from Sinopharm Chemical Reagent Beijing. The ionic liquid monomer of 1-vinyl-3-ethylimidazolium bromide $[(\text{ViEtIm})^+\text{Br}^-]$ was synthesized [5].

2.2. Synthesis of the poly(DVB-co-VBC) nanotubes

At room temperature, e.g. 25°C , 150 mg of BFEE was immediately added into 150 mL of heptane under ultrasonication. A given amount of DVB and VBC mixture (3/2, v/v) was added to start the polymerization under ultrasonication. In order to monitor growth of the polymer nanotubes at different stages, 10.0 g of ethanol was added to terminate the polymerization. The samples were filtered and washed with ethanol to remove residual initiator and monomer.

Synthesis of the Br^- based PIL composite nanotubes: 20.0 mg of poly(DVB-co-VBC) nanotubes, 12.0 μL of PMEDTA, 1.0 g of $[(\text{ViEtIm})^+\text{Br}^-]$ were mixed in 6.0 mL of methanol. The mixture was degassed by freeze thawing. After 6.0 mg of CuBr was added, the green mixture was sealed under vacuum. After the ATRP reaction was performed at 70°C for 12 h, the product was washed with methanol and centrifugated. The Br^- based PIL composite nanotubes were obtained.

2.3. Synthesis of the $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL composite nanotubes

After 20.0 mg of the Br^- based PIL composite nanotubes was dispersed in 20.0 mL of water, 60.0 mg of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was added. The system stood under stirring at room temperature for 1 h to allow the anion exchange. The $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL composite nanotubes were obtained after centrifugation and wash with water.

2.4. Catalytic decomposition of MO

5.0 mg of $\text{PW}_{12}\text{O}_{40}^{3-}$ based PIL composite nanotubes was dispersed in 2.0 mL of methyl orange (MO) aqueous solution

(20.0 mg L^{-1}). After 10.0 μL of H_2O_2 (30 wt%) was added under stirring at room temperature, the MO solution was centrifugated from the reaction system at a given interval. The characteristic absorption band at 463 nm of MO is used to evaluate removal degree calculated by $(C_0 - C)/C_0$, while C_0 is the original MO concentration, C is the MO concentration after the decomposition time.

2.5. Characterization

Morphology of the samples was characterized *via* scanning electron microscopy (SEM) characterization (HITACHI S-4800 operating at 15 kV) and transmission electron microscopy (TEM) characterization (JEOL 100CX operating at 100 kV). The samples for SEM observation were prepared by vacuum sputtering with Pt after being ambient dried. FT-IR spectroscopy was performed after scanning the samples for 32 times using a Bruker EQUINOX 55 spectrometer with the sample/KBr pressed pellets. UV-vis spectroscopy was performed using UV spectrophotometer (TU1901).

3. Results and discussion

As previously reported [12], PDVB bamboo-like nanotubes are easily fabricated within minutes by cationic polymerization using immiscible initiator nanodroplets of BFEE at room temperature. In our current concern, vinylbenzyl chloride (VBC) is used to copolymerize with DVB forming the corresponding poly(DVB-co-VBC) nanotubes (Fig. 1a). The polymerization is completed within 5 min. Bamboo-like segmental cavity is clearly discerned with a periodic diaphragm about 500 nm. The nanotubes are ~ 150 nm in diameter, whose surface is smooth (Fig. 1b). Presence of VBC is confirmed by FT-IR spectrum (Fig. 1c). The characteristic peaks at 671 cm^{-1} and 1264 cm^{-1} are assigned to $-\text{CH}_2-\text{Cl}$ of DVB in the polymer nanotubes. EDX result reveals the presence of Cl element (Fig. 1d). The benzyl chloride group onto the poly(DVB-co-VBC) nanotubes can be used as an agent to initiate ATRP grafting of other polymers from the nanotube surface. An IL monomer of 1-vinyl-3-ethylimidazolium bromide ($(\text{ViEtIm})^+\text{Br}^-$) is selected for the polymerization. Presence of the imidazolecation is confirmed by the bands at $1700\text{--}1750\text{ cm}^{-1}$ in FT-IR spectrum (Fig. 1e). The characteristic peaks at 1465 cm^{-1} is assigned to C-N. EDX result indicates the presence of N and Br elements at the PIL composite nanotubes (Fig. 1f).

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