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Solid protonic acids and luminescent carbon dots derived from waste expanded polystyrene

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ABSTRACT

We reported a simple route to prepare strong solid protonic acids (SPAs) from waste expanded polystyrene using a small amount of sulfuric acids while stirring at 130 °C for 3 h followed by heating at 220 or 260 °C, respectively, for 2 h. Such SPAs were amorphous carbon materials. It was found that they were efficient and recyclable catalysts for acid-catalyzed esterification reaction. Meanwhile, luminescent carbon dots were found on the surface of the obtained SPAs at 220 °C. The photoluminescence emission peak position shifted from 415 to 542 nm as the excitation wavelengths progressively increased from 310 to 470 nm. The quantum yield was 13.2% at 310 nm excitation wavelengths.

1. Introduction

Nowadays, a large amount of expanded polystyrene (EPS) for packaging is discarded. It is therefore desirable to develop an effective method to use the waste materials. Lately, because of the environmental issues, people's attention has focused on waste expanded polystyrene (WEPS), led to the development of a variety of chemical recycling technologies, such as pyrolysis [1], sulfonation [2,3], etc. On the other hand, the solid protonic acids (SPAs) have attracted considerable attention because of their potential application in various acid catalyzed reactions to replace homogeneous catalysts such as sulfuric acid and *p*-toluenesulfonic acid to simplify the process of separation and purity of the products [4]. Hara [5] first reported a carbon material from naphthalene as a strong SPA in 2004. Afterwards, Toda [6] reported carbon-based solid acids from glucose or sucrose. Further, some other carbon-based solid acids have also been prepared from different raw materials, such as furfuraldehyde [7], glycerol [8], cellulose [9], starch [10], bagasse [11] and so on. However, their experimental conditions were relatively harsh, usually required high temperature and/or large amounts of sulfuric acid. Therefore, seeking a simple, low cost preparation method to obtain SPAs with high catalytic activity and long cycle life has become the core issue of the research of carbon-based solid acids. Herein, a simple method for the preparation of SPAs from WEPS has been explored. When treated WEPS using a small amount of sulfuric acid, the WEPS was sufficiently sulfonated, followed by heating for cross-linking and partial carbonization, SPAs were obtained. It was found that the SPAs are recyclable and efficient catalysts for acid-catalyzed esterification reaction. Moreover, in the course of the purification of the SPAs, we collected luminescent carbon dots (CDs) with strong fluorescence.

2. Experiment

Preparation of WEPS-based SPA: All of chemicals were purchased from Tianjin Kermel chemical reagent Co. Ltd., China. An amount of 5 g of WEPS (from packaging materials) was dissolved in 30 ml of cyclohexane while stirring. Then, 14 g of concentrated sulfuric acid was dropped into the mixture at 130 °C (in silicone oil bath) for 3 h. Afterwards, cyclohexane was recovered by distillation (95% of rate of recovery). The mixture was further heated at 260 °C for 2 h; a black solid acidic powder was obtained. The product was cooled to ambient temperature and washed with hot water under agitation until the filtrate showed a neutral pH value. The product was dried in an oven at 80 °C for 12 h and obtained 7 g of WEPS-based SPA, designated as SPA-260. Furthermore, the SPA obtained from 6 g of sulfuric acid and dehydration temperature at 220 °C was also prepared for comparison and designated as SPA-220-w.

Use of SPAs for the production of luminescent CDs: Extracted the SPA-220-w with alcohol for 6 h by Soxhlet extractor, luminescent carbon dots (designated as WEPSCDs1) from the solution was collected. The remaining solid acids were designated as SPA-220.

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The SPA-220 as a catalyst for the esterification of acetic acid with glycerol: A mixture of 5 g of glycerol (0.054 mol), 18.65 ml of acetic acid (0.324 mol) and 1 g of the SPA-220 as catalyst was stirred and heated for reflux and removal of the water at the top of the column via fractionating distillation during 2.5 h. The distributions of the products were investigated by gas chromatography coupled with mass spectrometry (6890N GC/5973MS, Agilent Technologies).

The SPA-260 as a catalyst for the esterification of citric acid with n-butanol: The esterification reactions of citric acid with *n*-butanol were performed in a liquid phase in batch condition: mix 10.5 g of citric acid (0.05 mol), 17.8 ml of *n*-butanol (0.20 mol) and 0.6 g of the SPA-260 at 150 °C for 4 h. Under the same conditions, the catalytic performances of NKC-9 (A strong acid cation exchange resin, see Table S1 in Supplementary material) with equivalent acid density were investigated for comparison.

3. Results and discussion

Fig. 1 showed the scanning electron microscopy (SEM) images of SPA-260 and SPA-220, which were block materials with a grain size of 10–200 μm. The X-ray diffraction patterns (XRD) of SPA-260 and SPA-220 (Fig. 2a) exhibited two broad and weak diffraction peaks ($2\theta = 10$–$30°$, 35–50°) attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion, similar to that of the carbon-based solid acids reported previously [5].

Titration analysis revealed that the acid density of the SPA-260 and SPA-220 was 2.49 and 4.48 mmol/g, respectively. The characteristic absorption bands of –OH groups at 3412 cm^{-1}, of –COOH groups at 1709, of –SO_3H groups at 1031 and 1161 cm^{-1} were observed in the FT-IR spectra (Fig. 2b) for the SPAs revealing that the local structure of the SPAs were composed of –OH, –COOH and –SO_3H groups.

Both SPAs were characterized by X-ray photoelectron spectroscopy (XPS) techniques. In the case of the SPA-260, two strong peaks at 284.78 and 532.1 eV were attributed to C_{1s} and O_{1s}, and a weak peak at 168.37 eV was attributed to S_{2p}. Their atomic ratios were respectively 82.8, 13.01 and 4.2% ($CO_{0.158}S_{0.051}$), indicating that the bonded sulfonated groups existed. The further analysis of high resolution XPS for C_{1s} was fitted into four individual component peaks [12]: 284.18, 285.38, 286.96 and 289.21 eV. Their atomic ratios were 72.58, 19.67, 1.94 and 5.80%, suggesting that the SPA-260 contained a small amount of –COOH and –OH groups, and –SO_3H groups was mainly acidic groups. Similarly, for the SPA-220, peaks of C_{1s}, O_{1s} and S_{2p} occurred at 284.46, 531.77 and 168.36 eV, and the corresponding atomic ratios were 77.21, 16.78 and 6.01% ($CO_{0.217}S_{0.078}$) respectively. Analysis of high resolution XPS for C_{1s} of the SPA-220 also indicated that –SO_3H groups were mainly acidic groups.

Thermal gravimetric analysis (TG-DTG, under flowing N_2, see Fig. S1 in Supplementary material) indicated that the thermal stability of the SPA-260 was higher. Their thermal weight change could be divided into three stages. For the SPA-260, the first stage of mass loss (6.58%) was in range of 66.4–160 °C, which was mainly due to the loss of absorption water on the surfaces and combined water with sulfonic acid groups. Then, it arrived at a thermal stable platform of 160–301.6 °C, which had not obviously mass loss. Between 301.6–394.2 °C, the second mass loss was 14.48%, which revealed that sulfonic acid groups abscised in the form of SO_2 gas and water. Lastly, in the range of 394.2–999.3 °C, mass loss was 23.46%, which showed that the cross-linked structure with –SO_2-groups was damaged (about to 460 °C) and further carbonized (remaining 55.47%) via lost carbon dioxide. By

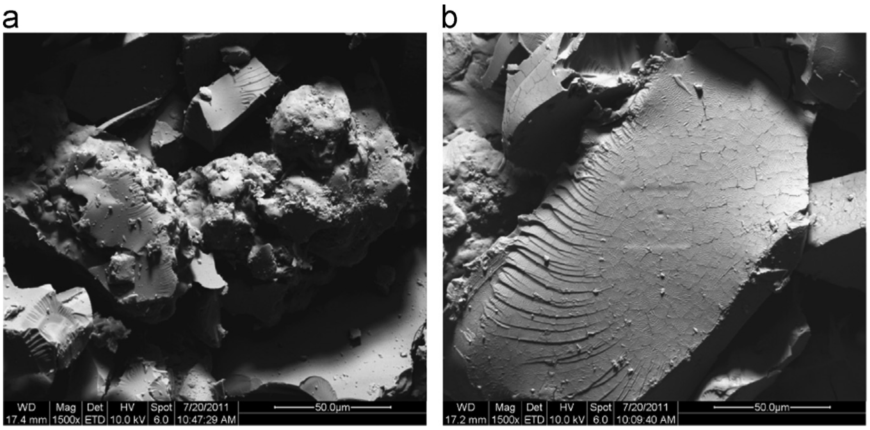

Fig. 1. SEM of the SPA-260 (a) and SPA-220 (b).

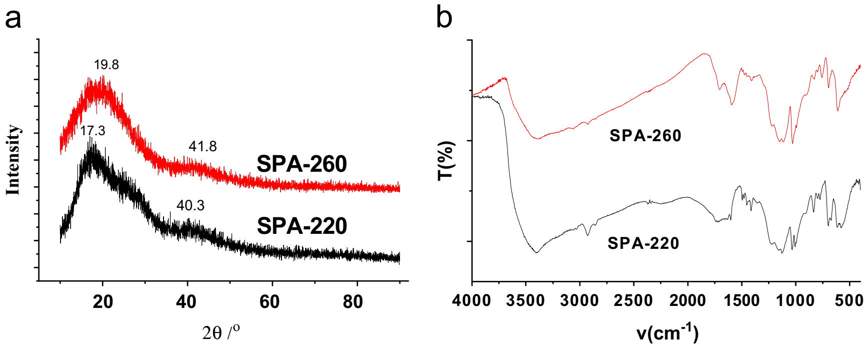

Fig. 2. The XRD (a) and FT-IR spectra (b) of the SPA-260 and SPA-220.