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High hydrogen storage capacity of heteroatom-containing porous carbon nanospheres produced from cross-linked polyphosphazene nanospheres

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ABSTRACT

Heteroatom-containing porous carbon nanospheres were fabricated by forming polyphosphazene nanospheres and carbonizing them with NaOH as activating agent. They were then examined as a material for hydrogen storage. N_2 sorption and H_2 sorption measurements showed that the carbon nanospheres possess a BET surface area of 1140 $m^2\ g^{-1}$, a total pore volume of 0.90 $m^3\ g^{-1}$, an ultramicropore volume of 0.30 $m^3\ g^{-1}$, a bimodal pore size distribution (3–5 nm and 0.6–0.8 nm diameter pores), and a gravimetric hydrogen uptake of 2.7 wt.% at 77 k and 1 atm.

1. Introduction

Hydrogen storage is an essential prerequisite in the development of hydrogen-fueled vehicles. As an attractive candidate for hydrogen storage, porous carbon materials have attracted considerable attention due to their good adsorptive capacity, low density, low cost, and high surface area. Generally, high surface area and pore volume are essential for enhancing the hydrogen storage capacity [1,2]. Also, narrow pore size distributions for carbon materials in which the pore sizes are mainly smaller than 1 nm are expected [3,4]. In addition, the heteroatoms (such as N, P, S, and B) in carbon materials can play the role of activator, resulting in the doped carbon materials exhibiting remarkable potential in hydrogen storage [5]. Hence, finding novel nanostructured carbon materials and tailoring their pore structures and textures for hydrogen storage are of great significance.

Poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) (PZS) is a typical cross-linked polymer that forms carbon materials during carbonization [6]. Nanostructured PZS can easily be synthesized in bulk quantities under ambient conditions through polycondensation of comonomers hexachlorocyclotriphosphazene (HCCP) and 4,4′-sulfonyldiphenol (BPS) [6,7]. NaOH or KOH is a good activating agent, which helps to the development of porosity in carbon frameworks, leading to a higher specific surface area and pore volume [8,9]. In this study, we selected PZS nanospheres as carbon precursor and NaOH as activating agent for preparing porous carbon nanospheres with high hydrogen storage capacity.

2. Experimental section

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) (Aldrich) was recrystallized from dry hexane followed by sublimation twice before use. 4,4′-Sulfonyldiphenol (BPS), triethylamine (TEA), sodium hydroxide (NaOH), acetonitrile, and ethanol were commercially obtained and used as received.

2.2. Preparation of PZS nanospheres

PZS nanospheres were synthesized according to our previous report [7]. Briefly, 4 mL TEA was added to a solution of 0.8 g HCCP and 1.78 g BPS in 210 mL acetonitrile under ultrasonic irradiation (150 W, 40 Hz) at room temperature. After ultrasonic irradiation for 10 min, the solution was centrifugated and then the precipitates were washed three times with ethanol and de-ionized water respectively. The resulting products were dried under vacuum to yield PZS nanospheres.

2.3. Preparation of the heteroatom-containing porous carbon nanospheres

Briefly, 0.6 g NaOH was first dissolved in 4 mL de-ionized water to afford NaOH solution. 0.6 g PZS nanospheres and the above solution were mixed at room temperature and stirred for 2 h. After the impregnation process, the samples were dried at 110 °C. Then, the carbonization process was performed by heating the PZS nanospheres

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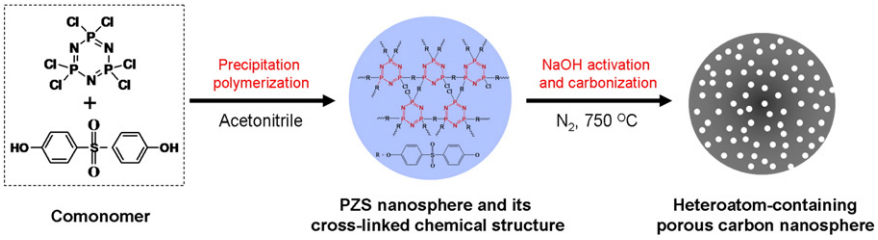

Fig. 1. Preparation of the heteroatom-containing porous carbon nanospheres.

impregnated by NaOH with a heating rate of 5 °C min^{-1} to 750 °C and holding at this temperature for 2 h under a nitrogen atmosphere.

Fig. 1 illustrates the overall preparation procedures of the porous carbon nanospheres.

2.4. Characterization

The microstructures of the PZS nanospheres and the carbonized samples were characterized by scanning electron microscopy (SEM)

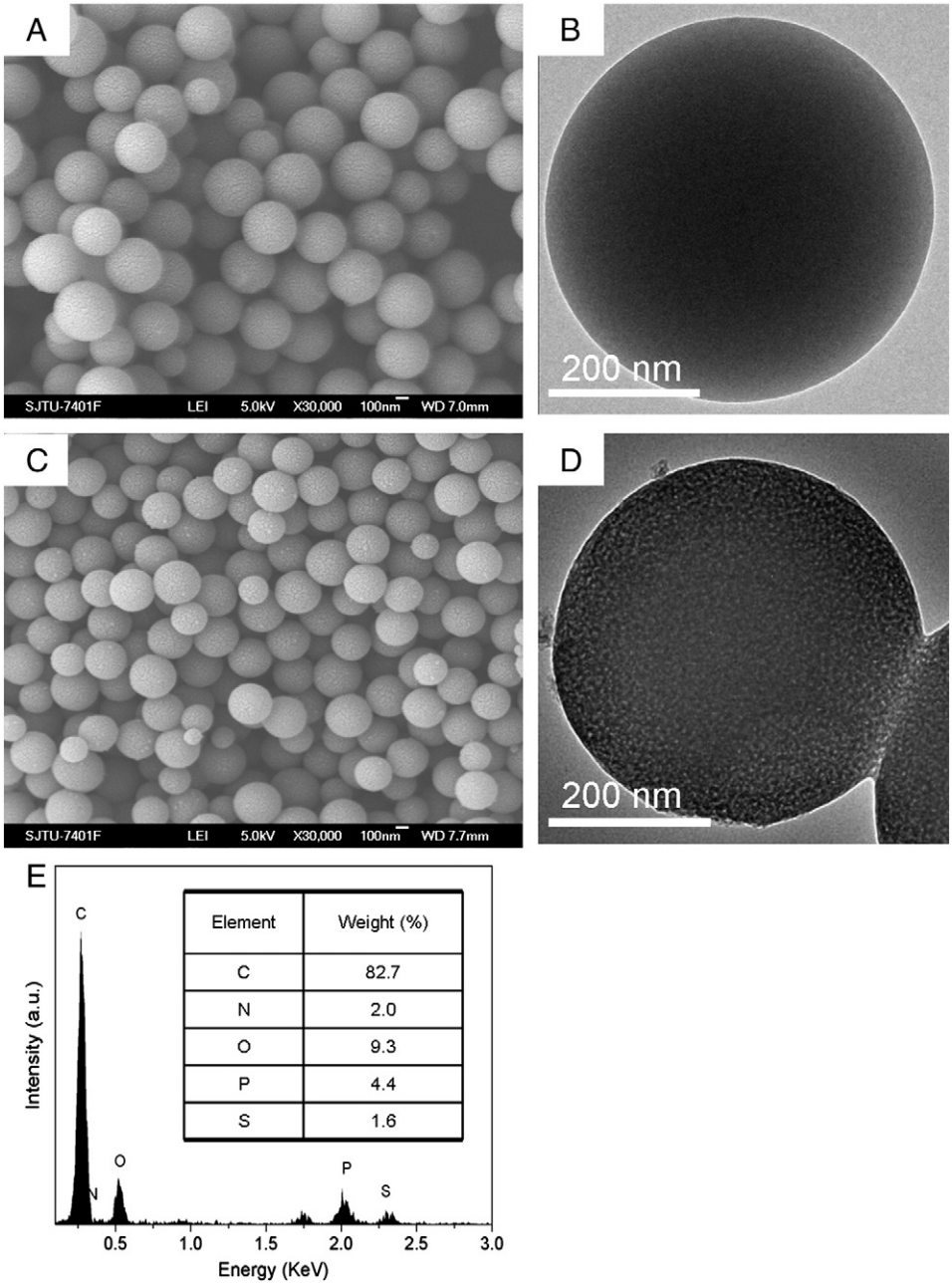

Fig. 2. (A, B) Representative SEM and TEM images of the PZS nanospheres. (C, D) SEM and TEM images of the porous carbon nanospheres. (E) The EDX pattern of the porous carbon nanospheres.