Synthesis, Characterization, and Properties of Multi-walled Tubular Silicon Nitride Nanotube

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A broad range of potential applications in numerous industries for silicon nitride (Si_3N_4) has received extensive attention owing to its intriguing properties such as hardness, high-temperature strength, light weight, large elastic modulus, thermal shock resistance, and electrical resistance.[1-3] There are numerous methods for generation of silicon nitride such as sol-gel,[4] plasma-assisted hot filament chemical vapor deposition,[5] solid-state reduction-nitridation,[6] nitridation of high-Si-content Fe-Si alloy particles by ammonia (here Fe is a catalyst for NH_3 dissociation),[7] thermal-heating chemical-vapor deposition,[8] and catalytic reaction of silicon substrate.[9] Si_3N_4 nanotube was synthesized before by heating tetra-ethoxysilane with N_2 gas at 165 ºC.[8]

We attempted to synthesize idealized silicon nitride nanotube (SiNNT) in an effort to realize potential materials for hydrogen storage by using the similar synthetic method employed previously for the synthesis of carbon nitride nanotube (CNNT).[10] We prepared SiNNT in a stainless steel autoclave by the reaction of silicon chloride and sodium azide in benzene at 220 ºC in nitrogen ambient for 15 h. The molar ratio of sodium chloride and sodium azide was 1.0:4.0.

We characterized the as-synthesized SiNNT by means of TEM, XPS, XRD, and porosimetry. Figure 1 presents a TEM image of the SiNNT synthesized for 15 h. The nano-

materials turn out to be a hollowed and multi-walled nano-tube having a long uniform tubular scaffold. The inner diameters of the nanotubes were measured to be 31.9 ± 7.1 nm. The wall thicknesses were measured to be 11.0 ± 0.3 nm. The nanotubes appear to be end-closed. As presented in Figure 2, we clearly observe the N(1s), Si(2s), and Si(2p) photoelectron emission peaks. The corrected XPS spectral data based on Figures 2(b), 2(c), and the sensitivities of the photoelectron ejections indicate that the as-prepared SiNNT has a stoichiometry of Si:N = 1.000:1.018, the value of which deviates slightly from the theoretical stoichiometry 1.000: 1.3333 for Si_3N_4. In the present study, we better represent the nanomaterials as Si_xN_y ($x = 1.0$, $y \approx 1.0$) nanotubes.

The XRD spectrum as shown in Figure 3 is well matched to the reported SiN crystals.[1,4,9] We measured the BET surface area of the nitride nanotube, from which we also
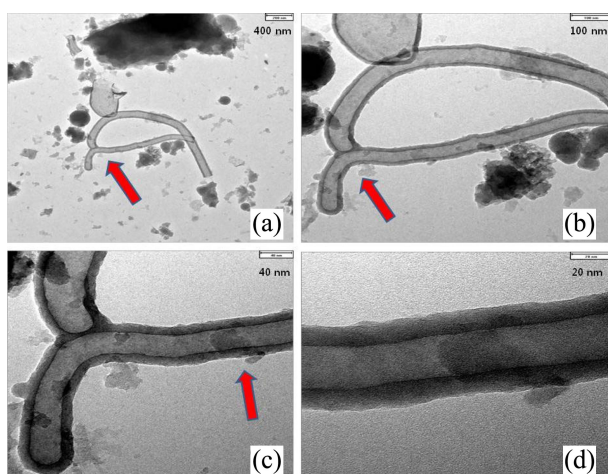

Figure 1. Typical TEM images of the as-synthesized SiNNT. (a) The total TEM image. (b) The magnified image of the region specified in Figure 1(a). (c) The magnified image of the region specified in Figure 1(b). (d) The magnified image of the region specified in Figure 1(c).
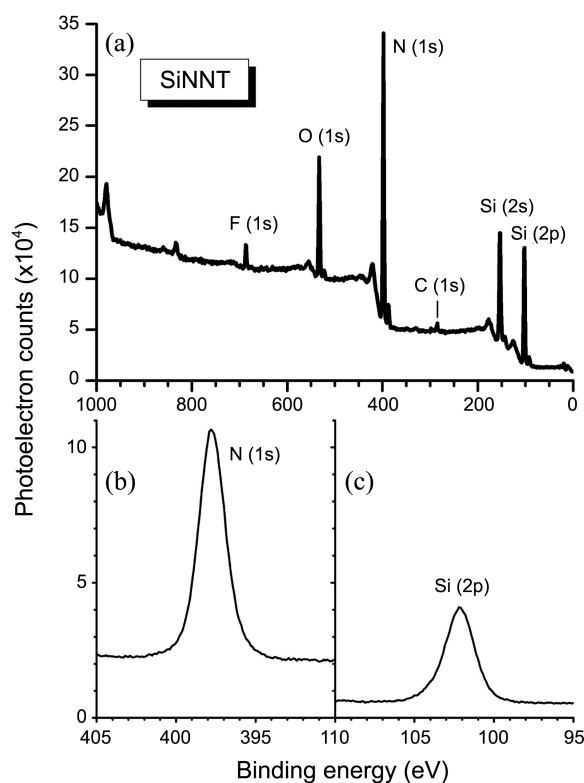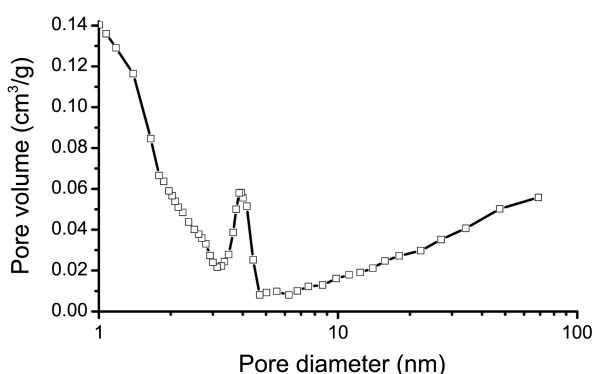

Figure 2. XPS spectra of the as-synthesized SiNNT. (a) The total photoelectron spectrum. (b) The N(1s) photoelectron spectrum. (c) The Si(2p) photoelectron spectrum.
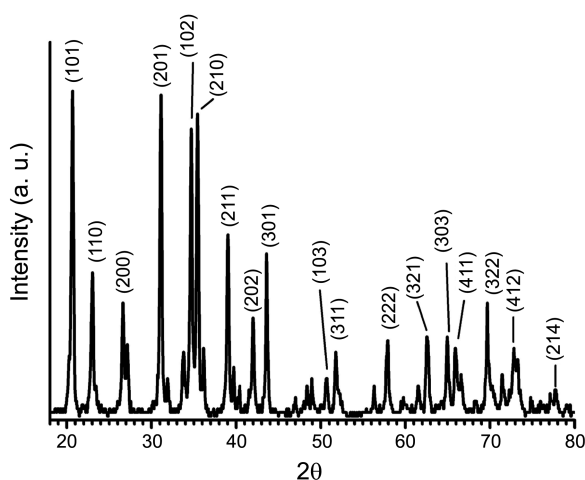
Figure 3. XRD spectrum of the as-synthesized SiNNT. The Miller indices indicated above are from refs. 1, 4, and 9.
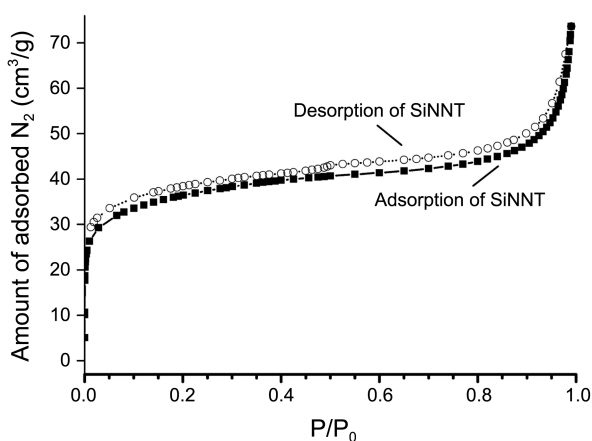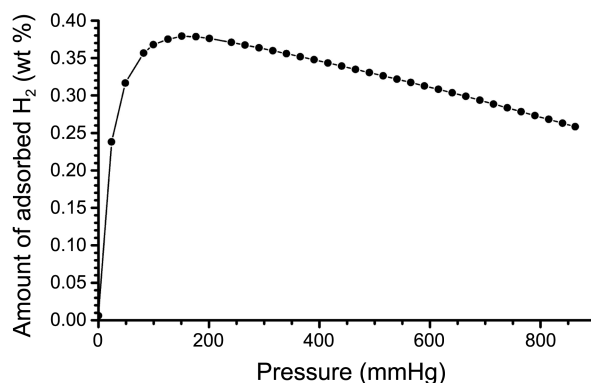

Figure 4. Nitrogen adsorption and desorption isotherms on the as-synthesized SiNNT at 77 K.

Figure 5. Pore size distribution curve of the as-synthesized SiNNT obtained by the Barrett-Joyner-Halenda (BJH) method.

calculated the pore diameter and volume. Figure 4 reveals nitrogen adsorption and desorption isotherms on the as-synthesized SiNNTs measured at 77 K. The N_2 isotherms of the as synthesized SlNNTs are presumed to have a type merged with type IV, on the basis of the IUPAC classification.[11] The as-prepared SiNNTs are found to have relatively a large surface area and have a variety of pores

Figure 6. Amount of H_2 adsorbed on the as-prepared SiNNT at 77 K.

such as micro and mesopores. In Figure 5, we present the calculated pore size distribution curves of the as-synthesized SiNNT obtained by the Barrett-Joyner-Halenda (BJH) method.[12] Figure 5 shows that there exist three type pore sizes giving the local maximum pore volumes. Note that the pore sizes ranges from micro to macro sizes based on the IUPAC classification.[11]

We checked the hydrogen storage of the as-synthesized SiNNT. Figure 6 shows the amount of hydrogen molecules adsorbed in the SiNNT. The weight % of the hydrogen adsorbed in the SiNNT increases with increasing the hydrogen pressure, and then decreases monotonically with increasing the hydrogen pressure, yielding a maximum wt % 0.38 at 150 mmHg. We confirmed that the as-prepared SiNNT can store a relatively small amount of hydrogen molecules.

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