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Facile synthesis of monodisperse hollow carbon nanospheres using sucrose by carbonization route ☆

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ABSTRACT

Hollow carbon nanospheres (HCNSs) supported on monodisperse iron oxide nanoparticles (IONPs) were synthesized by a carbonization route using sucrose as the carbon precursor. The resulting product of the obtained HCNSs possessed a narrow size distribution of 15 nm and an interlayer distance of 0.35 nm. The intensity of the D to G value was less than 1, which confirms the obtained HCNSs with graphitization. This study is expected to pave the way for the application of HCNSs in nanoelectronics.

1. Introduction

In recent years, fullerenes, carbon nanotubes, graphene, and related carbon nanostructure have been synthesized and examined extensively [1–5]. Among the various forms of carbon nanostructures, hollow carbon nanospheres (HCNSs) are a new class of attractive materials because of their fascinating properties. These types of carbon materials have been proposed for use in a range of applications including catalyst support, hydrogen storage materials, nanoelectrodes, supercapacitors, drug delivery, dye encapsulation, contaminated waste removal, the protection of enzymes and proteins, and so on [6–9]. The metal particle plays an important role during the growth of graphitic carbon nanostructures, such as HCNSs, and many reports have shown a direct correlation between the size of the metal nanoparticles and the eventual inner diameter of the tube or sphere [10]. The HCNSs have been synthesized by various methods, such as self-assembly, carbonization and wet chemical, etc [11,12]. The smaller HCNSs have higher activates owing to their high aspect ratio and large surface area. Many studies have examined the synthesis of HCNSs with excellent properties. Wang and co-workers reported the synthesis of HCNSs with a diameter of 20 nm using mannose as the carbon source in a non-coordinating solvent [13]. Hu et al. [14] reported the synthesis of hollow carbon spheres with a size of 50–100 nm using hexachlorobenzene and sodium via a self-assembly approach. Feng et al. [15] synthesized nitrogen-doped HCNS with a size of 220 nm, Liu et al. reported the B-doped HCNS with a size of 170 nm, [16] and other research groups have also reported this [17–22]. On the other hand, it is still a challenge to find an appropriate route to obtain HCNSs with excellent graphitization and a smaller size with monodispersity of the sphere.

In the present work, IONPs and sucrose were used as a catalytic template and carbon precursor, respectively for the preparation of HCNSs with graphitization by simple carbonization at 450 °C. The temperature used for carbonization was much lower than the reported elsewhere [14,15,17,19]. The HCNSs were synthesized with a mean size of 15 nm. The best of the author's knowledge, this is the first report of the synthesis of HCNSs with a smaller size by simple carbonization route.

2. Materials and methods

Iron (III) acetylacetonate, benzyl alcohol, sucrose, argon gas, hydrogen gas, and hydrochloric acid were purchased from Sigma

☆Electronic Supplementary Information (ESI) available: HRTEM images, FT-IR spectrum and TGA curve of HCNSs.

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Aldrich and used as received. Deionized (DI) water was used throughout this work.

The monodisperse IONPs were synthesized by the following procedure described in earlier reports without any major modifications [23]. 3.0 g of iron (III) acetylacetonate was added to 60 mL of benzyl alcohol inside a glovebox. The reaction mixture was taken into a 100 mL of Teflon lined autoclave. The autoclave was heated to 180 °C for 48 h in a hot air oven. The final mixture was centrifuged and washed with ethanol followed by dichloromethane. The obtained solid was dried at 70 °C for 5 h in a hot air oven.

The synthesis of HCNSs was carried out using sucrose and IONPs as the carbon precursor and catalytic template through carbonization with help of horizontal tubular furnace, respectively. A simple tubular furnace setup with gas flow control units were used to produce the HCNSs for the experiments, which are shown in Fig. 1 [24]. In a typical synthesis, sucrose and IONPs with a 1:10 ratio was mixed thoroughly by a dry grinding process. About 100 mg of the mixture was placed in a quartz boat inside the middle of quartz tube. The sample was purged with a mixture of argon gas and hydrogen gas at a flow rate of 95 and 5 SCCM, respectively, from 100 to 450 °C with a heating rate of 5 °C/min. The reaction was maintained at 450 °C for 2 h and then cooled to room temperature under an argon atmosphere. The as-synthesized carbon sample was mixed with hydrochloric acid and sonicated for 20 min at ambient temperature to remove the IONPs. The mixture was then filtered and washed with DI water until the aqueous layer became neutral. The residue was dried at 100 °C for 5 h in a hot air oven.

The XRD pattern was obtained on a PANalytical X'Pert diffractometer using Cu Kα radiation (K=1.54 Å). The FT-IR spectrum was recorded on a Perkin Elmer spectrum 2. HRTEM images with elemental mapping were obtained using a TITAN G2 ChemiSTEM Cs Probe electron microscope operated at 200 kV. The Raman spectra were recorded with a Raman spectrometer Almega X/Thermo using laser excitation line at 532 nm.

3. Results and discussion

3.1. Characterization of synthesized IONPs

The synthesized IONPs possess excellent monodispersity with a near-spherical shape, as shown in Fig. 2(a)–(c). The HRTEM image clearly shows the lattice fringes of IONPs, which confirm that the prepared material has high structural order [25]. The mean size was 9 nm (inset of Fig. 2(a) is the size distribution graph of IONPs) and the interlayer distance was 0.25 nm. Fig. 2(d) shows the FFT image of the IONPs, which confirms the crystallinity and facet of the sample. Fig. 2(e) shows the XRD pattern of IONPs and the pattern is a cubic crystal system that matches well with the JCPDS No. 88-0315. The main intense peak in the XRD pattern is broadened, indicating that the crystalline portion of the IONPs is small [26]. The XRD pattern suggests that the synthesized nanomaterial is crystalline. The mean size of the nanoparticles was calculated from the XRD pattern according to the linewidth of the (311) plane refraction peak using the Scherrer equation (1):

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where, L is the mean size of the nanoparticles, K is a dimensionless shape factor (0.9), λ is the wavelength of incident X-rays (λ=1.54 Å), β is the full width at half maximum of the diffraction peak, and θ is the position of the (311) peak. The average size of the IONPs was found to be 9 nm, which match the HRTEM images. The d-spacing value of IONPs was calculated using Bragg law (Eq. (2)) based on the position of the (311) reflection peak.

$$n\lambda = 2d\sin\theta \,(\text{or})\, d = \frac{n\lambda}{2\sin\theta} \quad (2)$$

where, n is a positive integer (1), λ is the wavelength of incident X-ray (λ=1.54 Å) and θ is the position of the (311) peak. The calculated d-spacing value was 0.252 nm, which matched the HRTEM image.

Fig. 2(f) shows the FT-IR spectrum of the IONPs. The spectrum showed a very small absorption band at 3300–3400 and 1620 cm^{-1} due to the O–H stretching and bending vibrations of the physically adsorbed H_2O and surface –OH groups, respectively. The strong absorption band at 570 cm^{-1} and weak band at 440 cm^{-1} corresponds to the vibrations, Fe–O bond in IONPs. These results suggested that the synthesized IONPs are pure and are in agreement with the literature [27].

3.2. Characterization of synthesized HCNSs

Fig. 3 shows HRTEM images with EDS and elemental mapping of as-synthesized HCNSs. The $IONP_S$ occluded carbon nanospheres are clear from Fig. 3(b) and the graphitic carbon nanospheres and IONP are marked in HRTEM images. EDS and elemental mapping identified the elemental composition of as-synthesized HCNSs, and the results are presented in Fig. 3(d) and Fig. 3(e–g). These results indicate that the elemental signals of C and Fe are present in as-synthesized material. Additionally, Cu signals were also observed in the images due to the TEM sample holders were made from copper grids. Fig. 4(a)–(d) shows HRTEM images of the resulted HCNSs with a narrow size distribution [28,29]. The inner diameter of the HCNSs directly correlates with the size of the IONPs. The IONPs eliminated carbon nanospheres named as HCNSs

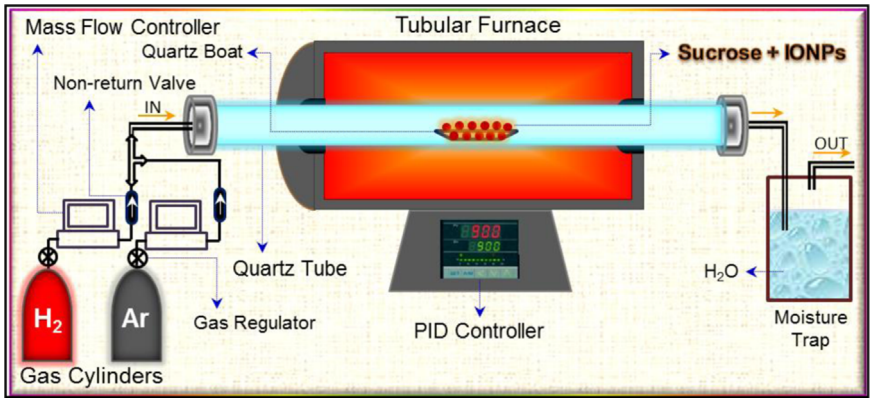

Fig. 1. Schematic diagram of the horizontal tubular furnace employed for the synthesis of HCNSs.