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A chemical route from PTFE to amorphous carbon nanospheres in supercritical water

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Amorphous carbon nanospheres with diameters of 140–200 nm have been synthesized by treating poly(tetrafluoroethylene) in supercritical water at 550 °C using $Ca(OH)_2$ as defluorination reagent.

Poly(tetrafluoroethylene) (PTFE) is widely used as a plastic material for its excellent heat and chemical resistance, low friction coefficient, and little water absorption *etc.*, partly due to the strong C–F bond (481 kJ mol^{-1}).[1] However, the waste PTFE materials may become persistent solid pollutants which are difficult to degrade in the environment.[2,3] Traditionally, the waste PTFE can be decomposed *via* thermal treatment at over 500 °C.[4,5] Up to now, many new defluorination methods have been applied to deal with PTFE.[6–10] For example, Hlavaty and Kavan have reported that PTFE could react with alkali metals in organic solvents and generate highly reactive polyynes and metal fluorides.[6] Huczko and his co-workers have developed a self-sustaining reaction for the defluorination of PTFE using various metals or their alloys.[8] However, these reactions either employ organic solvents, or cannot avoid the serious corrosion of fluorine at high temperatures. In addition, PTFE powder can be defluorinated into SrF_2 and CO by a mechanochemical solid-reaction method using strontium oxide.[11] To reduce the burden on the environment, green methods are required to deal with PTFE.[12]

Supercritical water treatment is a promising method for the decomposition of various halogenous organic compounds,[13,14] because water has many environmental and technological advantages in the state above its critical point (T_c: 374 °C, P_c: 22.1 Mpa).[12,15] Recently, Sato and co-workers have reported that polyvinyl chloride (PVC) could be decomposed into various organic compounds by supercritical water treatment.[16] Herein, we report a novel chemical transformation of PTFE in supercritical water at 550 °C using $Ca(OH)_2$. In this process, PTFE can be completely transformed into carbon nanospheres, which have potential applications as reinforcement materials for rubber,[17] supports for catalysts,[18] and anodes in second lithium ion batteries.[19] Besides, the elemental fluorine could be strongly absorbed by $Ca(OH)_2$ to form fluorite, CaF_2.

Typically, thermal treatment in supercritical water was carried out in a stainless steel autoclave with 12 mL capacity. 0.5 g commercial bulk PTFE (Shanghai Shanghua PTFE Material Co., Ltd), 0.74 g $Ca(OH)_2$ (Shanghai Chem. Reagent Corp.) and 10 mL distilled water were mixed in the autoclave. Then the autoclave was sealed, and maintained at 550 °C for 12 h in an oven. After being cooled to room temperature, the products were collected and washed with dilute hydrochloric acid. The sample exhibited two striking colors (black and white), which indicated that it consisted of two different substances. Due to the difference of densities, they were separated by the flotation method, and then filtered off, washed with pure alcohol respectively. Finally, the black and the white samples were collected and dried in vacuum at 60 °C for 4 h.

The products are determined by XRD on a Philips X'Pert PRO SUPER X-ray powder diffractometer using Cu Kα radiation (λ = 1.541874 Å). From the XRD pattern of the white product (Fig. 1a), all the sharp reflection peaks can be indexed to cubic CaF_2 with lattice parameter a = 5.46 Å (JCPDS 35-0816). In the XRD pattern of the black sample (Fig. 1b), only a broad diffraction peak can be observed at 20–30°, indicating that low crystalline or amorphous carbon is produced.

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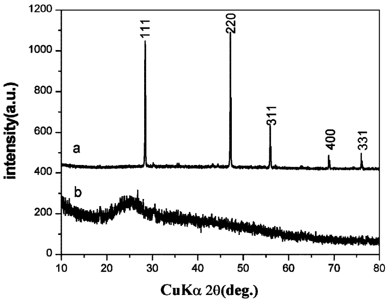

Fig. 1 XRD of CaF_2 (a) and amorphous carbon (b) prepared in supercritical water at 550 °C.

The carbon nanospheres are observed on a JEOL JSM-6700F field-emission scanning electron microscope (FESEM) and a JEOL 2010 high resolution transmission electron microscope (HRTEM) with an accelerating voltage of 200 kV. In a typical FESEM image (Fig. 2a), we can find a large number of carbon spheres with diameters of 140–200 nm. TEM images (Fig. 2b) also reveal a

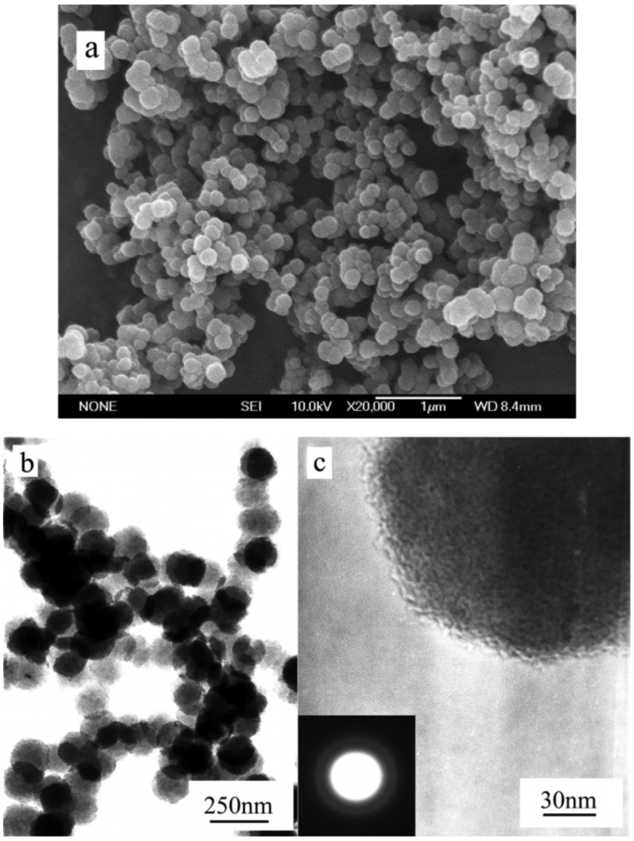

Fig. 2 (a) is the FESEM image, (b) and (c) are TEM images of amorphous carbon nanospheres prepared in supercritical water at 550 °C.

number of carbon nanospheres with sizes of 100–210 nm. And some striped nanostructures could be observed on the surface of an individual carbon sphere (Fig. 2c). The selected area electron diffraction of these carbon nanospheres shows dispersed rings, indicating that the carbon spheres have low crystalline micrographite structures, which could also be revealed by Raman scattering (in the next paragraph). Nitrogen sorption isothermal measurement is conducted on a Coulter Omnisorp 100CX specific surface analyzer. From the sorption data, the BET surface area of the carbon nanospheres is about 20.0 $m^2 g^{-1}$.

The crystallinity of the prepared carbon is investigated by Raman spectrometry on a LABRAM-HR Confocal Laser MicroRaman Spectrometer using an Ar^+ laser with 514.5 nm radiation at room temperature. In Fig. 3(a), the peak at 1585–1600 cm^{-1} (G-band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional graphite layer.[20] Compared with the G-band at 1580 cm^{-1} for the graphitic carbons,[21] the G-band of the products shifts towards a higher wavenumber due to the less orderly arrangement of the carbon atoms. The D-band at 1331–1339 cm^{-1} (in Fig. 3(a)) is associated with vibrations of carbon atoms with dangling bonds at the plane termination of disordered graphite or glassy carbon. With the treating temperature increasing, the intensity of the D-band (I_D) decreases and the intensity of the G-band (I_G) increases. According to the relationship $L_a = 4.4(I_D/I_G)^{-1}$ (in nm),[20] the small microcrystalline planar size is 1.4–2.0 nm for the produced carbon nanospheres.

IR spectra of the samples produced at 400 and 550 °C are shown in Fig. 3(b) and (c). All the absorption peaks (Fig. 3(b): 1225, 1153, 639, 554 and 503 cm^{-1}) are assigned to the vibrations of carbon–fluorine bonds ($–CF_2–$) in PTFE.[22] The absorption peaks at 1640 and 3450 cm^{-1} could be ascribed to the δ and ν vibrations of water molecules, respectively. IR spectra of the sample prepared at 550 °C (Fig. 3(c)) show that no absorption peaks can be indexed to $–CF_2–$ or fragments such as C_2F_4 (1342, 913, 407 cm^{-1}), C_4F_8 (960 cm^{-1})[22] or other organic functional groups. This indicates that the degradation of PTFE in the supercritical water could be complete at 550 °C.

Based on the results of the IR spectra (Fig. 3(c)), the defluorination of PTFE can hardly take place at 400 °C, indicating that the reaction temperature plays an important role in the decomposition. To our knowledge, PTFE could degrade to monomers (96%) at 510 °C with a half life of ~30 min (eqn. (1))[4] in an isolated atmosphere. Therefore, it is probable that PTFE can decompose to monomers in our reaction system at 550 °C. A possible reaction process is proposed as follows. Firstly, the main chain scission of PTFE takes place as the temperature increases. Subsequently, at 500–600 °C, the produced monomer C_2F_4 is converted into CaF_2, carbon clusters and CO_2 in the supercritical alkali $Ca(OH)_2$ fluid (eqn. (2)), following a disproportionation reaction pathway. Eventually, the carbon clusters grow into amorphous carbon nanospheres. The whole reaction could be formulated as eqn. (3).

$$–(CF_2)–_n \rightarrow n/2\ CF_2{=}CF_2 \qquad (1)$$

$$CF_2{=}CF_2 + 2\ Ca(OH)_2 \rightarrow 2\ CaF_2 + C + CO_2 + 2\ H_2O \qquad (2)$$

$$2\ –(CF_2)–_n + 2n\ Ca(OH)_2 \rightarrow 2n\ CaF_2 + n\ C + n\ CO_2 + 2n\ H_2O \qquad (3)$$

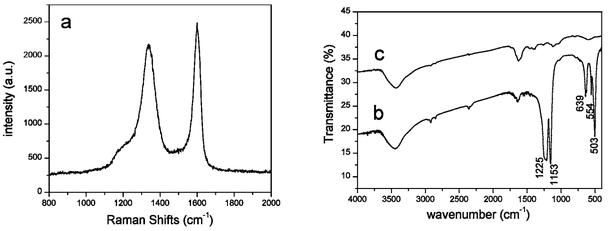

Fig. 3 Raman shifts of amorphous carbon nanospheres (a); IR spectra of the samples prepared at 400 °C (b) and 550 °C (c).

In addition, without any water added in the autoclave, the direct solid reaction between PTFE and $Ca(OH)_2$ was incomplete. At 550 °C, the water in the autoclave can be regarded as being in the supercritical state, which can eliminate the limit of transport between different reactants, and then promote the convertion from PTFE to amorphous carbon.

In summary, in the supercritical water system at 550 °C, bulk PTFE materials have been successfully converted into amorphous carbon nanospheres and the by-product of CaF_2, which can be recycled and have potential applications in industry. The possible reaction mechanism is also discussed. Supercritical water may play a key role in the degradation of persistent PTFE wastes. This method provides an efficient way to deal with waste PTFE materials. In addition, there is promise in applying this method to deal with and recycle other stable halogenous polymers.

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