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Synthesis of Uniform Te@Carbon-Rich Composite Nanocables with Photoluminescence Properties and Carbonaceous Nanofibers by the Hydrothermal Carbonization of Glucose

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A hydrothermal carbonization route has been designed for the syntheses of uniform core–shell Te@carbon-rich composite nanocables with ultrathin and ultralong Te nanowires as the core component and carbonaceous matter with remarkable reactivity as the shell, using ultralong Te nanowires of several nanometers in diameter and glucose as starting materials. The results demonstrated that the presence of uniform Te nanowires can effectively restrain the usual homogeneous nucleation of carbon spheres from the bulk solution and instead promote the heterogeneous deposition of carbonaceous matter on the backbone of Te nanowires for the formation of well-defined Te@carbon-rich composite nanocables. The diameter of the Te@carbon-rich composite nanocables could be controlled by adjusting the hydrothermal carbonization reaction time or the ratio of the tellurium and glucose, and the shell thickness of the core–shell nanocables can be varied from 2 to 25 nm. Simply removing the Te nanowire core can produce well-defined ultralong and functionalized carbonaceous nanofibers. As-prepared Te@carbon-rich composite nanocables display a strong photoluminescence in the blue-violet region. These well-defined nanocables/nanofibers can be well dispersed in water or ethanol solution and are of high reactivity, making it possible to further engineer their surfaces or produce new hybrid materials with potential applications.

1. Introduction

Recently, fabrication of nanomaterials with a controllable size and shape has gained great scientific and technological interest,¹ and composite nanostructures, especially core–shell nanostructures, have received intense attention due to their improved physical and chemical properties for electronics, magnetism, optics, and catalysis.² Since coaxial nanocables were discovered in 1997,³ much effort has been made to design rational methods to synthesize one-dimensional core–shell nanostructures, for instance, by laser ablation,⁴ chemical vapor deposition and epitaxy,⁵ electrophoretic deposition or electrochemical deposition,⁶ carbothermal reduction method,⁷ layer-by-layer coating,⁸ sol–gel methods,^{9,10} and mesoporous silica template method.¹¹

Searching for new synthetic strategies for the synthesis of new core–shell nanostructures such as nanocables has been a hot topic because of their important potential applications in nanoscale electronic devices, cell separation, and medicine delivery. Carbon nanofibers including multi-walled carbon nanotubes have attracted intense attention for important applications as field electron sources, gas-selective adsorbents, catalyst supports, and electrode materials for secondary lithium ion batteries.¹² Carbon nanofibers were usually synthesized by different approaches under very harsh conditions, for instance, chemical vapor deposition (CVD),¹³ laser ablation,^{12a} plasma-enhanced chemical vapor deposition,¹⁴ decomposition of poly(vinyl chloride) (PVC),¹⁵ and magnetic-induced pyrolysis of mesitylene at 700 °C.¹⁶

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Various hollow carbon forms such as shells,¹⁷ filaments (nanotubes),¹⁸ and nanochains¹⁹ can be produced by high-temperature pyrolysis of hydrocarbon compounds on evaporated metal-based catalysts.²⁰

Hydrothermal synthesis of carbon nanofibers with a typical diameter of 50–200 nm has been demonstrated by the autoclave treatment of precursors in the C–H–O system at high temperatures (up to 800 °C) and high pressures (up to 100 MPa) in the presence of a metal powder catalyst.^{21–23} Nevertheless, these methods involved either high energy input, a relatively long period of processing time, or costly experimental equipment.

Monodisperse carbon spheres have been synthesized using glucose or sugar as precursor in absence of any template under low-temperature hydrothermal conditions (≤ 200 °C).^{24,25} Very recently, we have developed a synergistic soft–hard template method for synthesizing flexible noble metal (Ag, Cu)@cross-linked poly(vinyl alcohol) (PVA) coaxial nanocables²⁶ and Te@cross-linked PVA nanocables²⁷ and also a hydrothermal approach for the synthesis of Ag@carbon nanocables²⁸ and PVA-assisted synthesis of Ag@carbon-rich composite submicrocables²⁹ using glucose-based saccharides as carbon sources.

To the best of our knowledge, synthesis of well-defined core–shell Te@carbon nanocables with ultrathin and ultralong Te nanowires as the core component and a carbonaceous shell has not been achieved so far. In addition, a mild solution chemistry route for the production of uniform functionalized carbon nanofibers has not been reported. In this paper, a new kind of Te@carbon-rich composite nanocables with a high aspect ratio has been synthesized from the carbonization and polymerization of glucose under mild hydrothermal conditions in the presence of newly produced tellurium nanowires with a diameter of several nanometers as templates. The detailed reaction and shape-evolution process of core–shell structures were studied. Removal of the core Te nanowires from the cables results in the formation of uniform carbon-rich composite nanofibers.

2. Experimental Section

All reagents are of analytical grade and used without further purification.

Synthesis of Tellurium Nanowires with a Diameter of Several Nanometers. The synthesis was carried out in a Teflon-lined stainless steel autoclave. The synthesis method has been described previously.³⁰ In a typical synthesis, 0.6 g PVP was put into a 34 mL capacity Teflon-lined stainless steel autoclave and was dissolved with 15 mL of double-distilled water under vigorous magnetic stirring to form a homogeneous solution at room temperature. After that, 0.1107 g of sodium tellurite (Na_2TeO_3 , 0.5 mmol) was added into the previous solution and dissolved. Hydrazine hydrate (1 mL, 85% w/w) and 2 mL of an aqueous ammonia solution (25–28% w/w) were added into the mixed solution. The final solution was clear. Double-distilled water was added to up to 80% capacity of the total volume of the Teflon container. The container was sealed and maintained at 180 °C for 4 h in a digital-temperature-controlled oven and then allowed to cool to room-temperature naturally. After that, 40 mL of acetone was added into the final solution, and the product was precipitated. The product was centrifuged and washed several times with double-distilled water and absolute ethanol.

Synthesis of Te/Carbon-rich Composite Nanocables and Carbon-Rich Composite Nanofibers. Half of the produced Te nanowires in the previous experiment were dispersed in 24 mL of double-distilled water with vigorous magnetic stirring to form a dark solution; 1.5 g of glucose was added into the previous solution, and the mixture was stirred for 15 min. The final solution was transferred to a Teflon-lined stainless steel autoclave (30 mL in total volume) and sealed and maintained at 160–200 °C for a controlled reaction time. The final product was centrifuged and washed with double-distilled water and absolute ethanol several times. The product was examined by TEM and found to be core–shell nanostructures. The core of the product can be removed by treatment with 30 mL of an aqueous solution containing 2 mL of hydrochloric acid (36.5 wt %), 5 mL of H_2O_2 (30 wt %), and 20 mL of double-distilled water ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 2:5:20$, v/v) at room temperature for 12 h.

Characterization. The final products were examined by XRD, SEM, TEM, HRTEM, and XPS. X-ray power diffraction (XRD) analyses were carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å), and the operation voltage and current were maintained at 40 kV and 40 mA, respectively. Transmission electron microscope (TEM) images were taken on a Hitachi (Tokyo) H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV and a high-resolution transmission electron microscope (HRTEM) (JEOL-2011) operated at an acceleration voltage of 200 kV. The photoluminescence spectra were recorded on a Fluorolog 3-TAU-P. Raman spectra was excited by radiation of 514.5 nm from a Jobin–Yvon (France) LABRAM-HR confocal laser micro-Raman spectrometer. The element analysis of the product was measured on an Elementar Vario EL-III (Germany).

3. Results and Discussion

3.1. Synthesis of Ultralong Te@Carbon Nanocables and Optical Properties. The first step of our synthesis involved the production of tellurium nanowires with several nanometer diameters and a high aspect ratio,³⁰ which is a crucial step for the production of ultralong Te@carbon nanocables (see the Supporting Information, Figure S1). A general overview

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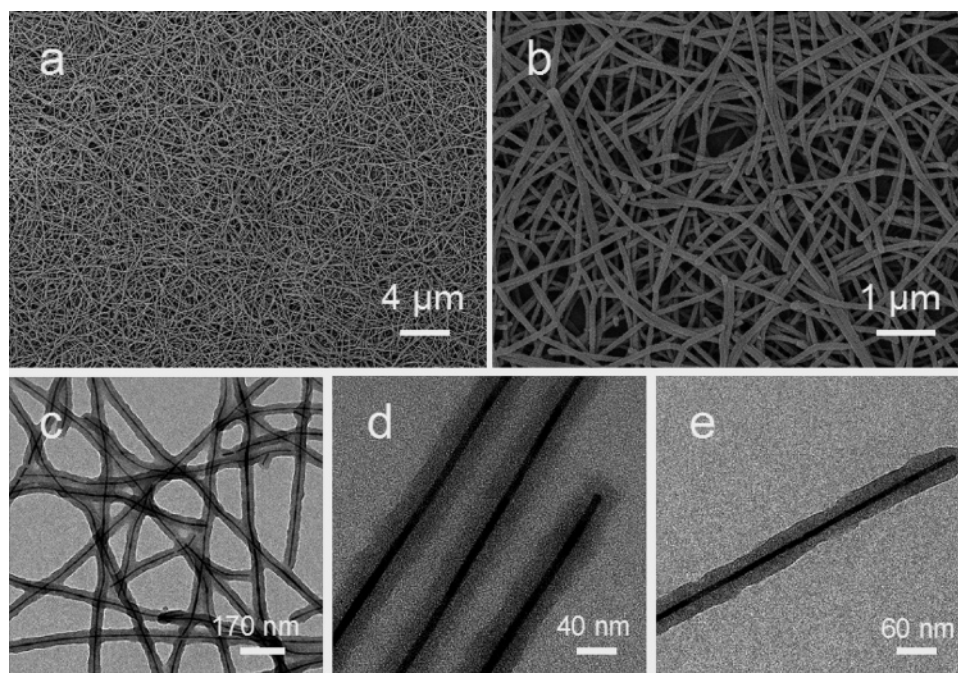


Figure 1. SEM and TEM images of the nanocables obtained from 0.1 mmol tellurium nanowires and 1.5 g of glucose at 160 °C for 12 h. (a) A general view of the nanocables. (b) A magnified SEM image of the cables. (c–e) TEM images of the nanocables.

SEM image (shown in Figure 1a) shows that the product obtained after hydrothermal treatment at 160 °C for 12 h is composed of flexible nanofibers ca. 50 nm in diameter and hundreds of micrometers in length; no carbon spheres were found. In absence of any hard template, the same reaction results in carbon spheres with a diameter of up to 1.5 μm .²⁴ The carbon coating had a uniform thickness (ca. 25 nm) over the entire surface of each tellurium nanowire, including both ends, as shown by the high-magnification TEM images (Figure 1c–e).

The formation of Te@carbon core–shell nanostructures proceeded under hydrothermal conditions at 160–200 °C, which is higher than the normal glycosidation temperature and leads to aromatization and carbonization.³¹ This is a simplified view, as in fact, various chemical reactions of glucose could take place under hydrothermal conditions in a sealed vessel.

The polymerization and carbonization of the glucose dispersed in solution tends to form carbon colloid spheres, which conform to the LaMer mode;³² and the coating of the tellurium nanowires with carbonaceous layers can be attributed to the polymerization and carbonization of the molecules absorbed on the template or in the layer between these absorbed monomers. Precursors dispersed in solution then gradually diffuse near the template and increase the layer thickness, which agrees well with the traditional method that is used to coat the silver nanowires with amorphous silica.³³

The polymerization process is a dehydration and cross-linking process. Reaction time and temperature are the two most important factors that have influence on the polymer-

ization rate and molecular weight of the product of a given reaction system.³⁴ Thus, the diameter of the Te@carbon nanocables could be controlled by adjusting the reaction time or the ratio of the tellurium/glucose. Figure 2 shows that the shell thickness of the core–shell nanocables grows from ca. 2 nm to 10 and 25 nm, when the reaction time increased from 4 to 8 and 12 h, respectively. The curve in Figure 2d presents the relationship between the width of the shell layers and the reaction time, and it is found that the width of the shell layer increased rapidly, especially at the end of reaction, which is typical for the molecular-weight development, as found in polycondensation reactions.³⁴

When the temperature increased to 180 or 200 °C or the concentration of the monomer increased, carbon spheres are found in addition to the nanofibers, which speaks for the homogeneous secondary nucleation of carbon, instead of heterogeneous deposition (shown in Figures 3a,c and 4a). The rate of carbon formation is simply too fast in those cases to keep it structurally defined. At the same time, keeping the conditions, such as reaction time, glucose concentration, and the amount of tellurium nanowires, the same, increasing the temperature from 160 to 180 and 200 °C results in increasing diameters of the nanocables from 60 to 140 nm (Figure 3b,d). If the concentration of monomers (glucose) is doubled and the other conditions are kept unchanged, the diameter of the formed core–shell nanostructures is ca. 70 nm, but as a byproduct, carbon spheres 1–2 μm in diameter are formed (Figure 4).

Nevertheless, the secondary nucleation of carbon nanoparticles was greatly restrained in the presence of the tellurium nanowires used as templates. Figure 5a shows a general overview of the product obtained after hydrothermal

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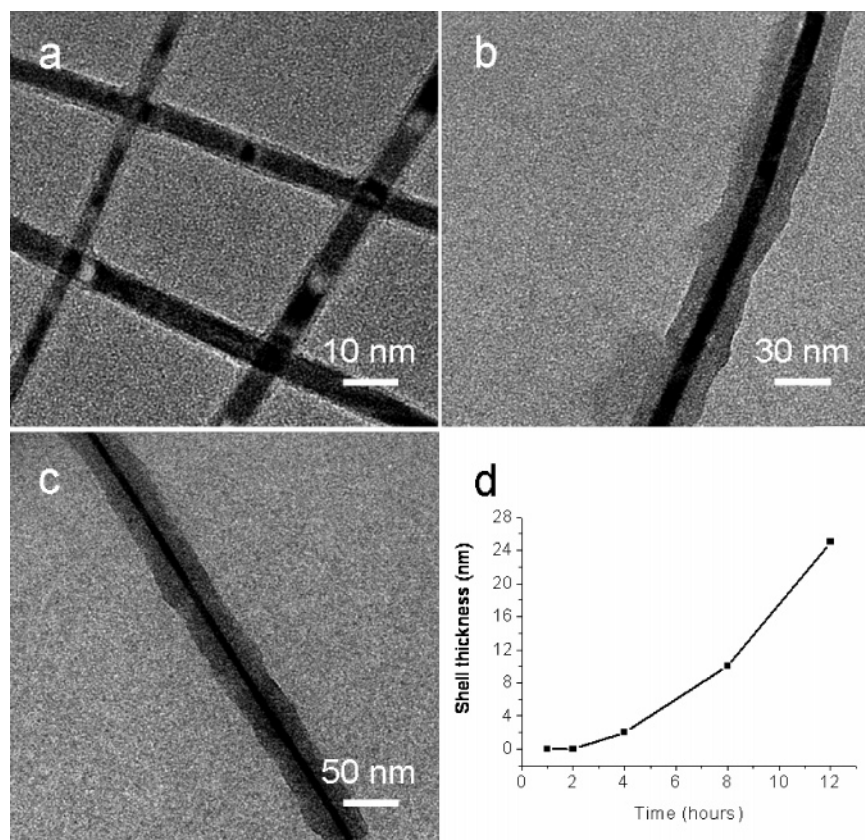


Figure 2. (a–c) Te@carbon nanocables prepared from 0.1 mmol tellurium nanowires and 1.5 g of glucose at 160 °C for varied reaction times: (a) 4, (b) 8, and (c) 12 h. (d) Dependence of the shell thickness vs hydrothermal reaction time.

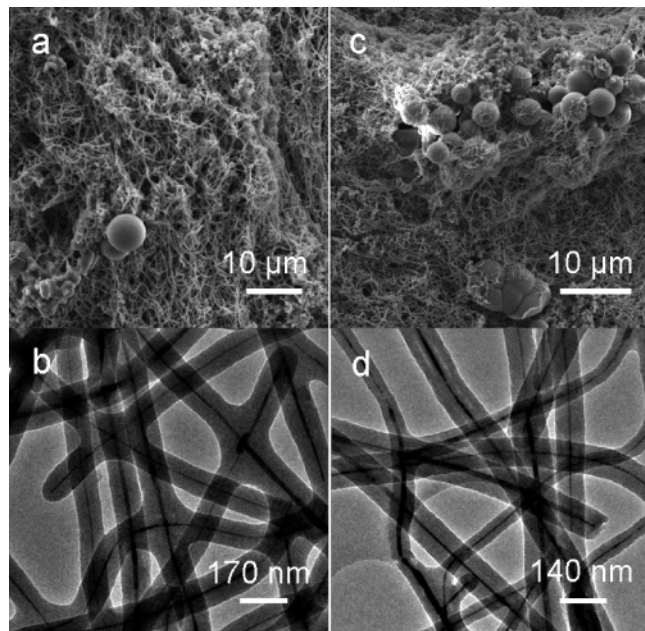


Figure 3. SEM and TEM images of the samples obtained by the reaction of 0.1 mmol tellurium nanowires and 1.5 g of glucose. (a,b) hydrothermal treatment at 180 °C for 12 h; (c,d) hydrothermal treatment at 200 °C for 12 h.

treatment at 200 °C for 7 h. No carbon spheres existed in the product even though the diameter of the core–shell nanostructures reached 120–160 nm and the temperature increased to 200 °C (Figure 5).

The X-ray photoelectron spectra (XPS) of the samples obtained at 160 °C were measured to examine the composi-

tion of the surface, as shown in Figure 6. Peak values at 284.85 and 532.05 eV can be readily assigned to the binding energies of C_{1s} and O_{1s}, respectively. The peak with binding energy at 572.75 eV for Te_{3d5} was not detectable, indicating that all of the tellurium in the product is buried/enwrapped within the carbonaceous shells.

It is interesting to note that the core of the core–shell nanostructures dissolved gradually and formed different tellurium@carbon core–shell nanostructures after further hydrothermal treatment at 200 °C for different reaction times (Figure 7). It is nearly impossible to find a single nanocable with a complete core in the sample obtained after reaction for 12 h (shown in Figure 7c). The core did not disappear completely after a still longer reaction time, which may be due to the residual cores being enwrapped with thicker and thicker carbonaceous layers.

The Raman spectra show the presence of the graphite and amorphous carbon in the samples (see the Supporting Information, Figure S2). Whereas only a peak at 1589 cm^{−1} was clearly seen in the Raman spectra of the Te@carbon nanocables, the higher background of the Te@carbon core–shell nanostructures was observed, which should be attributed to the high photoluminescence properties of the core Te nanowires.³⁰ However, there are two peaks around 1589 and 1361 cm^{−1}, found in selective area Raman spectra of the product after hydrothermal treatment at 200 °C for 6–12 h (see the Supporting Information, Figure S2b,c), which are attributed to the stretching modes of C–C bonds of the G band (in-plane vibrations of graphitic carbon) and D band (disorder-induced band due to double-resonance effect) in

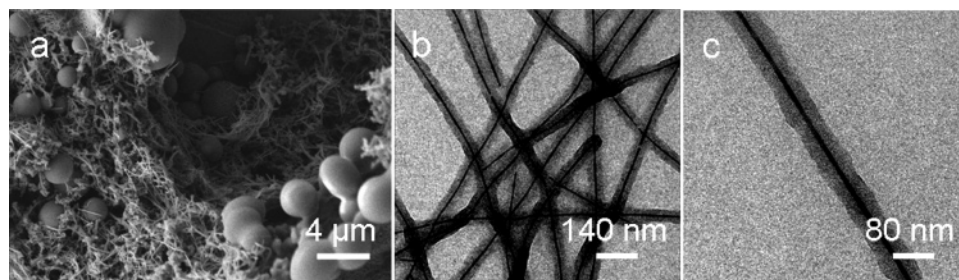


Figure 4. (a) SEM image of the mixture of nanocables and spheres, and (b,c) TEM images of the nanocables shown in (a). The sample was obtained by the hydrothermal reaction of 0.1 mmol tellurium nanowires and 3.0 g of glucose at 160 °C for 12 h.

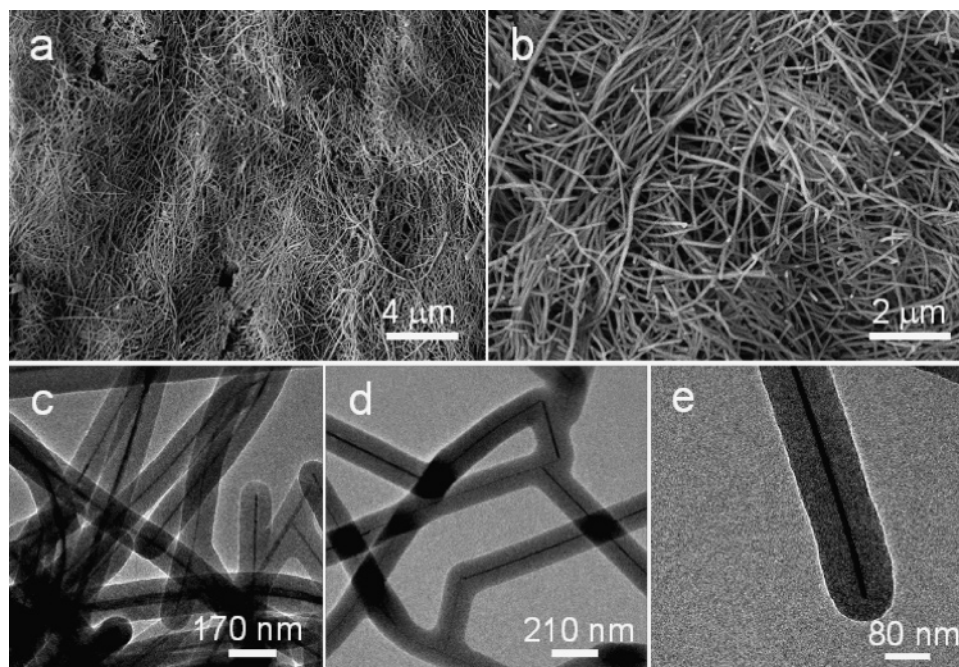


Figure 5. SEM and TEM images of the nanocables obtained from 0.1 mmol tellurium nanowires and 1.5 g of glucose at 200 °C for 7 h. (a) A general view of the nanocables. (b) A magnified SEM image of the cables. (c–e) TEM images of the nanocables.

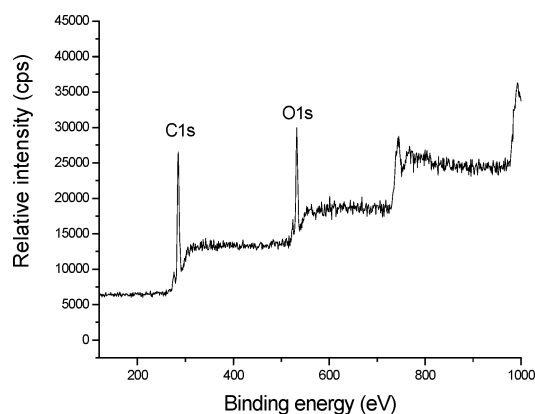


Figure 6. XPS spectrum of the sample obtained by the hydrothermal reaction of 0.1 mmol tellurium nanowires and 1.5 g of glucose at 160 °C for 11 h.

the carbonaceous solid, respectively. In addition, the carbonization degree of the products can be improved after further heat treatment in a dry state. The D and G bands are clearly present after the product is treated at 550 °C in a well-controlled tube furnace with a heating rate of 2 °C/min in an argon atmosphere and kept there for 1 h (see the Supporting Information, Figure S2d) and the morphologies of the product can be still well-kept (see the Supporting Information, Figure S3).

Figure 8 shows the photoluminescence spectrum of the tellurium@carbon core-shell nanostructures recorded with an excitation wavelength of 365 nm. The deconvolution of the strong and broad peak gives three Gaussian components with three peaks at 408, 430, and 451 nm, which are similar to the blue-violet emissions for pure tellurium nanowires.³⁰

3.2. Synthesis of Ultralong Carbon Nanofibers. The core of the product can be removed by treatment with a 30 mL aqueous solution containing 2 mL of hydrochloric acid (36.5 wt %), 5 mL of H₂O₂ (30 wt %), and 20 mL of distilled water (HCl:H₂O₂:H₂O = 2:5:20, v/v) at room temperature for 12 h, resulting in the formation of ultralong carbon nanofibers, as shown in Figure 9. The carbon nanofibers have an average diameter of ca. 50 nm and are tens or hundreds of micrometers in length. Carbon nanofibers with different diameters can be fabricated by controlling the diameter of the Te@carbon-rich composite core-shell nanostructures. In addition, such carbonaceous nanofibers can be further treated under hydrothermal conditions or high temperature to achieve different graphite degrees as required according to the need in practical applications. The element analysis of the product was recorded on an Elementar Vario EL-III (Germany), which revealed that the as-obtained carbon fibers

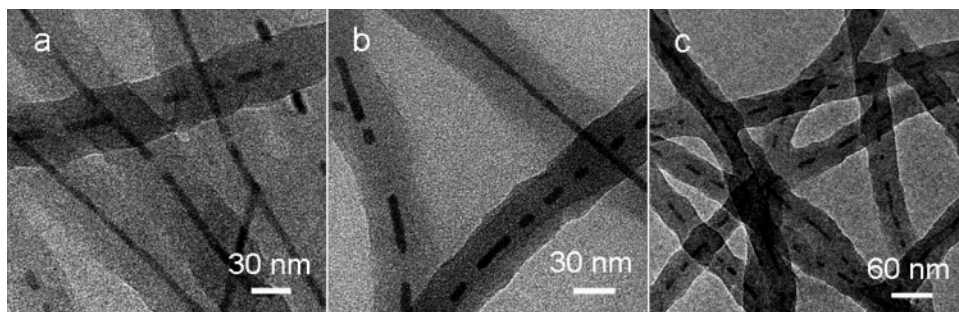


Figure 7. TEM images showing the morphology evolution of the sample obtained at 200 °C for the following times: (a) 4, (b) 8, and (c) 12 h.

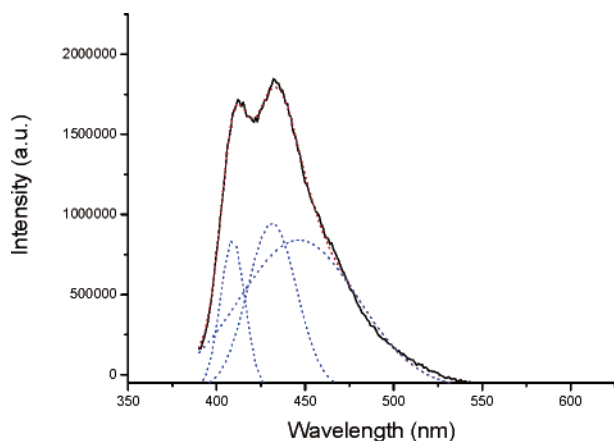


Figure 8. Photoluminescence spectrum (black line) of the tellurium@carbon core-shell nanostructures obtained at 160 °C for 12 h, recorded with an excitation wavelength of 365 nm. The deconvolution of the strong and broad peak gives three Gaussian components with three peaks at 409, 431, and 446 nm.

contain 70.0 wt % C and 6.4 wt % H; it also revealed that the Te element is not detectable and indicates that the core of the product can be removed by this method.

The FTIR spectra have been used to detect the functional groups of these samples, as shown in Figure 10. The peaks around 1000–1300 cm^{-1} indicate that the C–OH stretching and OH bending vibrations decreased gradually as the reaction temperature increased from 160 to 200 °C, compared to those in the pure glucose (Figure 10b–d). The peak value around 1650 cm^{-1} is attributed to the C=O vibration, which becomes stronger after hydrothermal treatment. The surface of these carbon samples is obviously highly functionalized, but the identification of the specific groups needs further studies by a high-resolution XPS technique. As-prepared uniform carbon nanofibers with functional groups show high reactivity and reductive behavior for further loading noble metal nanoparticles (data not shown).

As these Te@carbon-rich composite nanocables and carbonaceous nanofibers can be easily accessed on a large scale, they may provide good candidates for wide application in nanodevices, field electron sources, gas-selective adsorbents, catalyst supports and electrode materials for secondary lithium ion batteries, and heterogeneous catalysis even after further treatment according to the practical need. Further studies are ongoing and will be reported in due course.

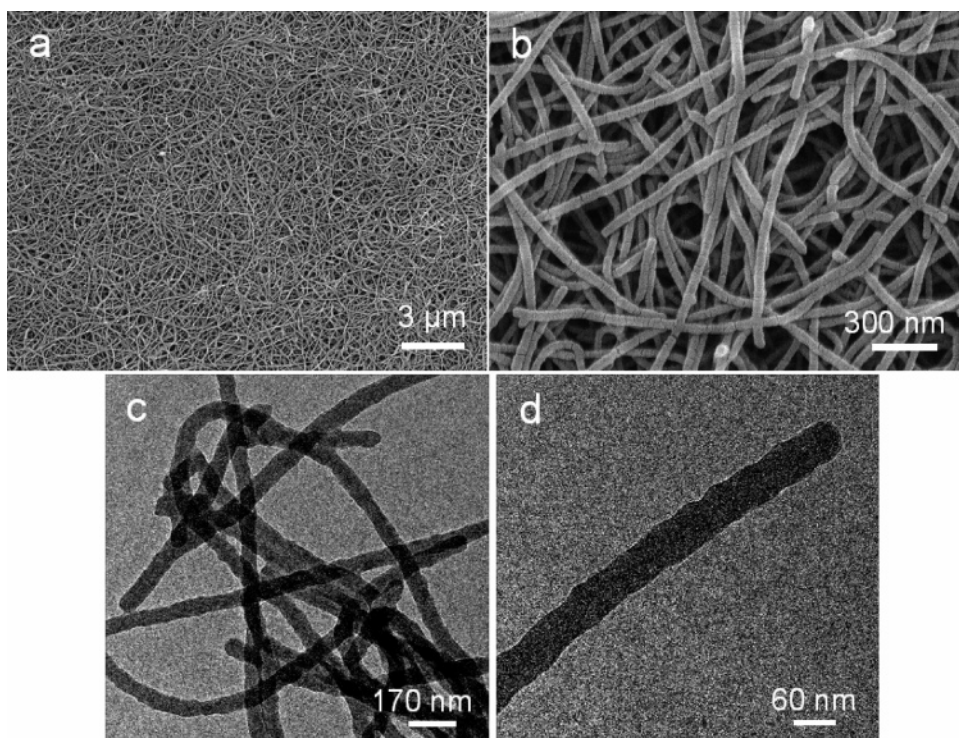


Figure 9. SEM and TEM images of the carbon nanofibers obtained by removal of the core of the product (shown in Figure 4c) by treatment with a 30 mL aqueous solution containing 2 mL of hydrochloric acid (36.5 wt %), 5 mL of H_2O_2 (30 wt %), and 20 mL of distilled water ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 2:5:20$, v/v) at room temperature for 12 h. (a) A general view of the nanofibers and (b) an enlarged SEM image. (c,d) TEM images of the nanofibers.

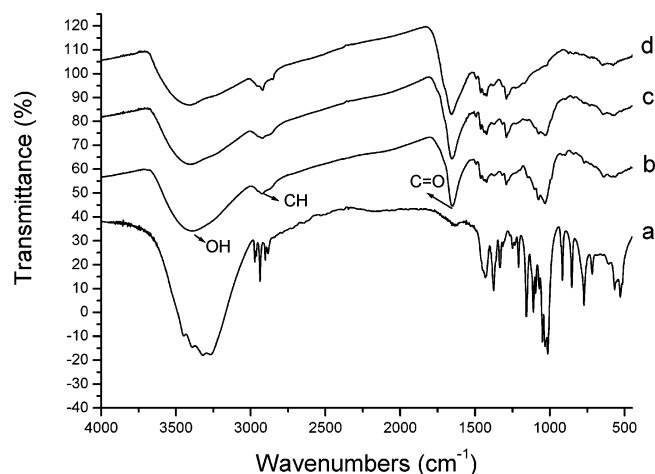


Figure 10. FTIR of (a) pure glucose; (b–d) different samples obtained after hydrothermal treatment: (b) 160 °C for 12 h; (c) 180 °C for 12 h; and (d) 200 °C for 12 h.

4. Conclusions

In summary, we have reported a mild chemistry route for large-scale syntheses of uniform photoluminescent Te@carbon-rich composite nanocables with ultrathin and ultralong Te nanowires as the core and a carbonaceous matter as shell by the hydrothermal carbonization of glucose using ultralong Te nanowires of several nanometers in diameter and glucose as starting materials. Removal of Te cores from such nanocables can produce uniform and functionalized carbonaceous nanofibers. The Te@carbon-rich composite nanocables give strong blue-violet emission, which could have applications in nanodevices. The presence of uniform Te

nanowires under the hydrothermal carbonization of glucose can effectively restrain the usual homogeneous nucleation of carbon spheres from the bulk solution and instead promote the heterogeneous deposition of carbonaceous matter on the backbone of Te nanowires for the formation of well-defined Te@carbon-rich composite nanocables. Controlling the hydrothermal carbonization reaction time or the ratio of the tellurium and glucose and the shell thickness of the core-shell nanocables make it possible to vary the diameter of the nanocables as well as the shell thickness. In addition, removal of the Te nanowire core can produce uniform ultralong and functionalized carbonaceous nanofibers. These nanocables/nanofibers have a polar, oxygen-containing layer and can be well dispersed in water or ethanol solution, which is of great importance from the viewpoint of applications.

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Supporting Information Available: TEM image of the tellurium nanowire, Raman spectra of the samples, and SEM image of the as-prepared Te@carbon nanocables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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