Large scale synthesis of uniform silver@carbon rich composite (carbon and cross-linked PVA) sub-microcables by a facile green chemistry carbonization approach†

Lin-Bao Luo, Shu-Hong Yu,* Hai-Sheng Qian and Jun-Yan Gong

A facile green chemistry carbonization method has been discovered for the synthesis of uniform silver@carbon rich composite (carbon and cross-linked polyvinyl alcohol) core-shell sub-microcables in large quantities, where the carbon sources such as glucose-based saccharides have played important roles in the formation of these novel sub-microcables.

Core/shell nanostructured materials have been of great interest among scientists, since their intrinsic properties can be easily tuned by changing the diameter, chemical composition of both core and shell.[1] Nanocables with comparatively long nanowires encapsuled in various nanotubes have been widely investigated recently.[2,3] To date, many methods have been reported to produce nanocables with distinctive functions. Nanocables containing Si cores have been fabricated by employing a laser ablation method.[4] Iijima *et al* have developed a similar method to synthesize three-layered nanocables consisting of silicon carbide cores, amorphous silica intermediate layers, and sheaths of boron nitride and carbon (BNC).[5] SiC/SiO$_2$ nanocables have been produced through the carbothermal reduction of silica xerogels with carbon nanoparticles.[6] Besides these high-temperature routes, an electrochemical deposition method has also been reported to fabricate nanocables inside metal nanotubes.[7] CdSe/poly(vinyl acetate) hybrid nanocables have been obtained by growing the semiconductor nanowires inside polymer tubules through a solution-based strategy at comparatively low temperature.[8]

Nanocables with metal silver as core have begun to attract intensive attention recently due to the fact that the metal silver is an ideal material for current as well as temperature conduction and nanocables of that kind may find wide application in fabricating nanoscale electronic, and sensing devices.[9] Up to now, several methods have been developed to obtain a variety of nanocables with silver nanowires encapsuled inside. For instance, silver nanowires can be coated with silica through the slow hydrolysis of tetraethylorthosilicate (TEOS) to form well-controlled Ag/amorphous silica nanocables.[10] Ag/polypyrrole nanocables were synthesized by a redox reaction between silver nitrite and pyrrole monomer in aqueous solution at room temperature with addition of poly(vinyl pyrrolidone) (PVP) as coordinating agent.[11] Additionally, Ag/PVP nanocables were also obtained by using a seed-mediated and photochemical approach in the presence of PVP.[12] More recently, we have successively reported the preparation of silver/carbon nanocables *via* a facile mild hydrothermal co-reduction process(HCCR) and flexible silver/cross-linked PVA (polyvinyl alcohol) nanocables through a synergistic soft–hard template process.[13,14] Normally, the polymerization and carbonization of glucose dispersed in solution tends to form carbon colloid spheres,[15,16] which conform to the LaMer mode.[17] In the presence of silver ions, hydrothermal carbonization of starch or glucose results in the formation of a fraction of Ag@carbon nanocables accompanying the formation of massive carbon spheres.[13] However, so far it is very difficult to produce pure silver/carbon composite sub-microcables in high yield.

In this Communication, we report a simple one-pot synthesis route to produce uniform sub-microcables with a carbon rich composite (carbon and cross-linked PVA) as shell and silver nanowires as core.‡ Different saccharides have been examined as carbon sources and only glucose-based saccharides are favorable for the formation of sub-microcables by the present hydrothermal carbonization approach.

The XRD patterns (ESI, Fig. S1†) of the cables from glucose-based saccharides (glucose, maltose, starch, β-cyclodextrin) show that there are two distinct phases. One phase can be readily indexed as cubic *fcc* silver crystal structure (JCPDS Card No. 04-0783 $a = 4.08$ Å). Considering the carbonization of carbohydrates used during the reaction procedure, the broadening diffraction peak located at about 20° can be indexed to carbon. When fructose or sucrose were chosen for hydrothermal carbonization, the peaks of silver phase were remarkably weakened. The addition of PVA in the carbonization of starch under the similar conditions as we reported previously[13] results in the formation of uniform fibers with a diameter of 1 μm and length up to 200 μm, as shown in scanning electron microscopy (SEM) images (Fig. 1). Some

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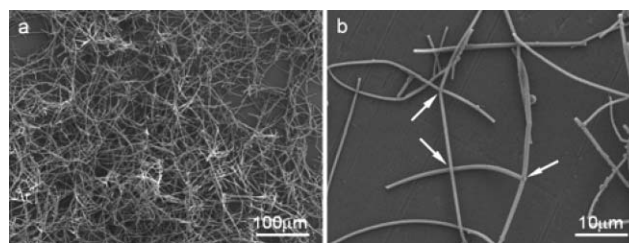
Fig. 1 SEM images of silver@carbon rich composite sub-microcables from 0.5 g starch and 5 ml PVA solution at 180 °C for 4 days. (a) An overview image, (b) the typical cables with junctions.
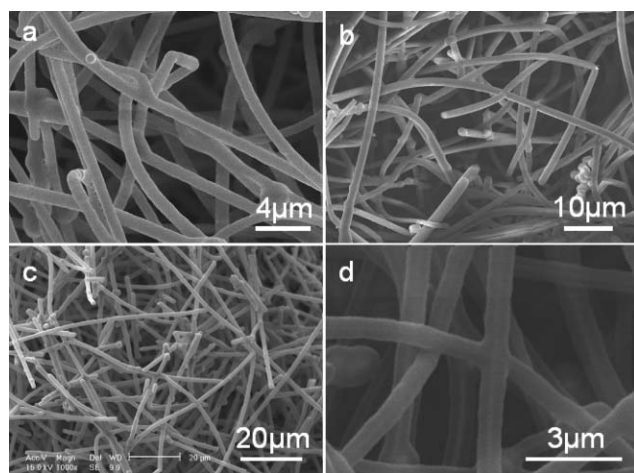
Fig. 2 SEM overview images of silver@carbon rich composite sub-microcables from different saccharides. (a) 0.3 g glucose, (b) 0.3 g β-cyclodextrin, (c) 0.5 g starch, (d) 0.3 g maltose at 180 °C for 4 days.

Fig. 4 SEM and TEM images of the samples by use of sucrose and fructose as carbon source, respectively. (a),(c) sucrose, (b),(d) fructose.

junctions were also formed (Fig. 1b). Similarly, the fibers can also be synthesized by use of other glucose-based saccharides (glucose, maltose, starch, β-cyclodextrin) (Fig. 2). The transparency of the shell can even be observed and gives a hint of the core–shell structure (Fig. 2d).

Energy dispersion spectra (EDS) show the presence of an Ag element in the core of the cables (ESI Fig. S2†). The molar ratio of C/O for the cables is about 3.67, which is higher than 2.43 found for the pure silver@cross-linked PVA cables (ESI Fig. S2†). Transmission electron microscopy (TEM) images (Fig. 3) showed that the fibers are well-defined core–shell cables with well-defined smooth core and shell. Each of the cables synthesized using glucose, β-cyclodextrin, starch and maltose as carbon sources has a core of diameter 150 nm, and a shell of thickness 0.8–1.2 μm. The aspect ratio of most of the composite cables is about 30–50, which is higher than that of silver@carbon cables synthesized previously.[13] However, it is interesting to note that the samples from sucrose and fructose were quite different from those samples synthesized by glucose-based saccharides. SEM images (Fig. 4a, b) and TEM images (Fig. 4c, d) reveal that the product from sucrose is primarily composed of both sub-microcables with thin shell and massive carbon microspheres, while the harvest from fructose is found to predominantly consist of carbon microspheres and few isolated silver nanowires.

The FT-IR analysis showed that the samples contained functional groups (ESI Fig. S3†). All samples had their absorption peaks in nearly sim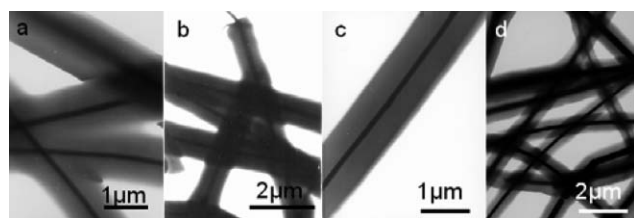ilar locations, although they were from different saccharides (both glucose-based and fructose-based). In the case of sub-microcables, the presence of the bands at 1705 and 1627 cm^{-1}, which are usually attributed to C=O and C=C vibrations, respectively, confirms the aromatization of saccharides during hydrothermal treatment.[15] The wider bands from 1050 to 1100 cm^{-1} clearly show the presence of C–O–C of cross-linked PVA.[14] On the basis of above analysis of the sub-microcables, it is difficult to distinguish carbon embedded in the shell of cables from the cross-linked PVA, however, the composite can be divided into two parts: one is the graphite core (mainly C=C) and the other one is assumed to be $C_xH_yO_z$, rich in functional groups (such as C=O=, –OH), the precise composition of which is hard to determine.[18] UV-laser Raman spectroscopy substantiates the existence of graphite. A broad peak at 1590 cm^{-1}, usually attributed to stretching vibration of typical graphitic carbon,[19] can be clearly observed (ESI FigS4†). The weak shoulder located at 1377 cm^{-1} indicates the in-plane vibrations of carbon atoms with dangling bonds of disordered graphite or glassy carbon. The high background resulted from strong fluorescence and could be due to carbonaceous materials in the samples (ESI Fig. S4†).

According to the above analysis, it is supposed that, during the hydrothermal carbonization, glucose favors the formation of cable-like structures *via* an effective but ill-defined way. We attribute the unique function of these four glucose-based saccharides to the fact that they can all be easily converted into glucose, catalysed by hydrogen ions or metal ions. Interestingly, in the same process, fructose is not favored for the formation of silver@carbon rich composite sub-microcables. The coexistence of both cables and carbon microspheres when using sucrose as a precursor is understandable considering the following hydrolysis reaction:

$$C_{12}H_{22}O_{12} + H_2O = C_6H_{12}O_6 \text{ (glucose)} + C_6H_{12}O_6 \text{ (fructose)}$$

Generally, it is very difficult to study the exact reaction mechanism in a sealed autoclave, and glucose-based saccharides can be transformed into various complex forms when treated under hydrothermal condition.[20] A possible formation mechanism for carbon rich cables during the carbonization reaction is illustrated in Fig. 5. Shortly after the solution is transferred into

Fig. 3 TEM images of silver@carbon rich composite sub-microcables synthesized by use of different carbon sources. (a) glucose, (b) β-cyclodextrin, (c) starch, (d) maltose.
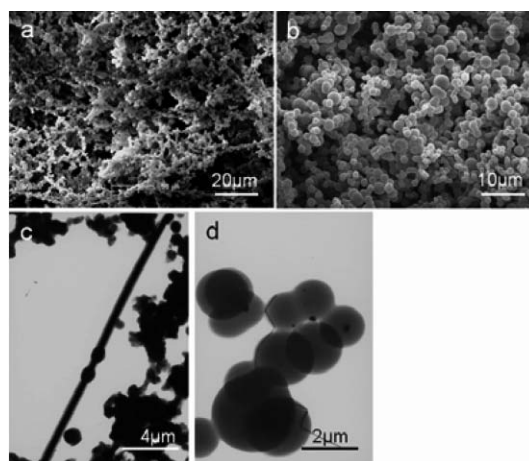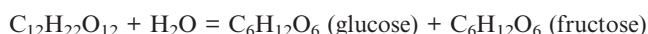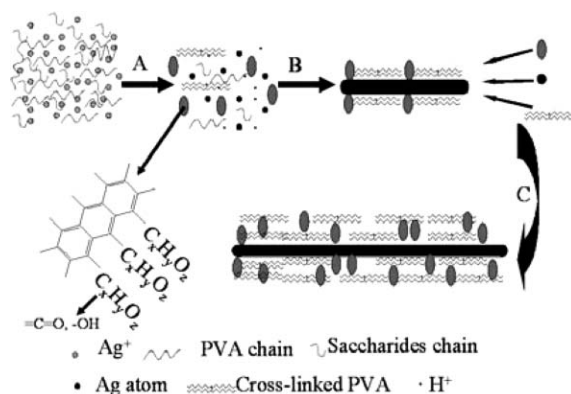
Fig. 5 Schematic illustration of nanocables formation mechanism during the hydrothermal process. (A) a process in which silver was reduced and polymerization, hydrolysis and carbonization of saccharides take place, (B) oriented growth of the sub-microtubes by coating the silver nanowires with a mixture of carbon and cross-linked PVA. (C) continuing growth of the cables.

the autoclave, the silver ions are slowly reduced into silver atoms, and at the same time the cross-linking reaction of PVA chains will generate huge numbers of H^+, in whose presence, glucose molecules first form the aromatic compounds, and then partly carbonize to transform into carbonaceous materials including graphitic carbon.

In the whole reaction process, PVA plays two vital roles. Firstly, PVA acts as a capping reagent that can guide the oriented growth of microcables through a synergistic soft–hard template process as we reported previously.[14] Secondly, as we have discussed previously, mass hydrogen ions will be released in the solution during the slow reduction of PVA by silver nitrite,[14] which will effectively catalyze polymerization and carbonization of these carbohydrates. Increasing the amount of saccharides (from 0.3 g to 1 g) in this reaction system leads to mass amorphous carbon microspheres with smooth surfaces (ESI Figs. S5–7†).

In conclusion, well-defined silver@carbon rich composite (carbon and cross-linked PVA) sub-microcables can be produced by a one-step hydrothermal reaction of a mixture of silver nitrite, PVA solution and a glucose-based saccharide. All six saccharides chosen for experiment can be easily carbonized, but only the glucose-based saccharides are favorable for the production of silver@carbon rich composite sub-microcables. The smart combination of the syngerstic effects both from the PVA and the glucose during the carbonization and formation of silver nanowires is essential to effectively restrain the formation of carbon spheres which are nucleated from the bulk solutions homogeneously by the previous approaches. This opens a new avenue toward large scale production of well-defined silver@carbon rich composite sub-microcables. In addition, this approach is being further extended for the production of other noble metal/carbon rich composite sub-microcables. As-prepared composite sub-microcables containing carbonaceous matter in their shells are obviously straighter than the entangled silver/cross-linked PVA nanocables. In addition, the sub-microcables reported here have a larger aspect ratio than that of silver@carbon nanocables obtained before.[13] It is expected that these sub-microcables with high aspect ratio could find potential applications in microdevices and catalysis area *etc*.

Notes and references

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