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Synthesis of carbon nanotubes with totally hollow channels and/or with totally copper filled nanowires

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ABSTRACT Carbon nanotubes (CNTs) with totally hollow channels and/or totally filled copper nanowires have been fabricated by methane decomposition using copper microgrid as a catalyst at 1173 K. The formation mechanism of CNTs with totally hollow channels is carbon precipitation at carbon-metal interface via the preferable surface diffusion mode of carbon. The selectivity of these CNTs can be improved by increasing the purity of copper catalysts and adding hydrogen in the feed gas. To form long and continuous copper nanowires up to 8–10 μm the filling of copper in the CNT channel requires the liquid or quasi-liquid state capillary adsorption of nanosized copper at 1173 K under the thermal driving force. The filling volume ratio of copper to total nano-channel of the CNTs is firstly increased to about 50%. The copper inside the CNTs is of single crystalline form and face centered cubic (fcc) structure. The method is useful for further controlled synthesis of CNTs with totally hollow channels and/or totally copper filled nanowires.

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1 Introduction

Filling carbon nanotubes (CNTs) with other materials [1–15] is an effective way to prepare nanostructural materials with extraordinary properties in electronic [5, 8] and thermal conductivity [6], magnetic [9], and mechanical strength [7], etc. Typically, CNTs filled with Cu or Ag species are useful for the fabrication of ultra-low resistance nanoscale electronic devices [8]. It can, therefore, be expected that the formation of long and continuous coaxial carbon-copper nanowires with a high filling ratio of copper is favorable for further application. However, the filling of CNTs is a relatively complex process, which is not only dependent on the electronic state of the filled materials [3], but also on the morphology of CNTs directly. Apparently, CNTs with open ends and totally hollow channels are the ideal host for filling with other materials at high ratio. However, except for the single-walled CNTs, we have been unable to achieve multi-walled CNTs with the desired structure to date. CNTs deposited over nickel, iron and cobalt catalysts – more or less – always have the inside carbon layers perpendicular to the tube axis, dividing their channel into many isolated chambers (i.e., the bamboo CNTs) [16–18], making them unfavorable for filling in high ratio. So far, the filling volume ratio of other materials in CNT channel is always lower than 20%–30% [1–16, 21, 22]. To address this problem, we report a method to prepare the CNTs with totally hollow channels and to in situ fill copper into the nanotubes. Specifically, the filling ratio of copper can be up to 50% of the totally hollow channels of the CNTs. These copper species can form continuous single crystalline copper nanowires (8–10 μm), by tailoring the copper catalyst and the composition of feed gas. These results are favorable for the large scale synthesis of carbon-copper coaxial nanowires and are useful for the further fabrication of nanoscale electronic device.

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2 Experimental

The catalyst was the nanometer copper species on the microgrid, normally as the sample carrier for the high-resolution transmission electronic microscopy (HRTEM) observation. Firstly, such a microgrid was directly put into in a horizontal quartz tube reactor, with an inner diameter of 25 mm. Secondly, the mixture of H_2, CH_4 and Ar, with the flow rates of 100, 100 and 400 ml/min, respectively, was fed into the reactor and decomposed to synthesize CNTs at 1173 K at atmospheric pressure. The products were directly deposited on the microgrid. After 30 min, the power was switched off and the reactor was cooled to the ambient condition. The carbon product on the microgrid was directly characterized by HRTEM (JEOL JEM2010, excited at 200 kV), equipped with the selected area electron diffraction (SAED) and the X-ray energy dispersive spectrometer (EDS).

To understand the formation mechanism of such copper-filled CNTs, we compared the morphology of CNTs using the pure Cu catalyst and the Fe–Cu catalyst. The latter catalyst was prepared by dropping some $Fe(NO_3)_3$ solution (0.1 mol/L) on the copper microgrid, following the in situ drying and calcination in the reactor. The CNTs were prepared by following the above-mentioned procedure. The composition of the metal particles for the CNT growth was characterized by EDS, covering an area of about 1 μm^2. The individual metal nanoparticle, absent of other nanotubes or impurities in the detected range of EDS, was selected to assure measure-

ment accuracy. The Cr or P species in EDS diagram was from the HRTEM instrument and/or the microgrid, respectively. From the comparison of CNTs produced on different catalysts with different activities, the morphology dependence of as-grown CNTs on the nature of the catalyst can be understood.

The effect of feed gas composition with or without hydrogen, on the morphology of CNTs, was also investigated following the above procedure. The filling volume ratio of copper to the total channel volume of all nanotube products was roughly estimated by measuring 1600 nanotubes on the 60 TEM images.

3 Results and discussion

In the relatively low magnification, TEM images show that there are large amounts of CNTs growing along the edge of the microgird (Fig. 1a). Most of them are relatively straight and 6–10 μm long (Fig. 1b and c), indicating their relatively uniform growth rate from the microgrid. As examining the CNT tip far from the microgrid, there are about 70% CNTs with tips free of metal catalyst and 30% CNTs with large metal particles at the tip (Fig. 1b and d). These results indicate that 70% CNTs grow following the base growth mode and other 30% CNTs grow in tip growth mode, similar to the growth of CNTs form a $Fe/Mo/Al_2O_3$ catalyst obeying different growth mode simultaneously [13]. However, most CNTs have larger tip as compared with its diameter (Fig. 2), which so far is not well understood and needs further investigation.

Notably, regardless of their different growth modes, most CNTs are totally hollow or are totally filled by copper, (Figs. 1c, d and 3). Since the filled materials (in black color) inside the CNTs are continuous, the channel of CNTs, after removing the filled materials, will also be totally hollow, without any inside carbon layers perpendicular to the nanotube axis. The result indicates an unprecedented growth of CNTs from copper in the present work, significantly different from those from iron [13], nickel, cobalt and even other copper catalysts [19, 20].

To understand this, we firstly compare the CNTs grown on the pure copper catalyst and the Fe–Cu catalyst. Grown on the Fe–Cu catalyst by the intentional addition of iron to the copper catalyst, the CNTs are bamboo-like with nearly no hollow channels (Fig. 4a). The EDS characterization indicates that the Fe–Cu alloy catalyst has an atomic ratio of iron of 3% (Fig. 4b) and the catalyst, responsible for CNTs

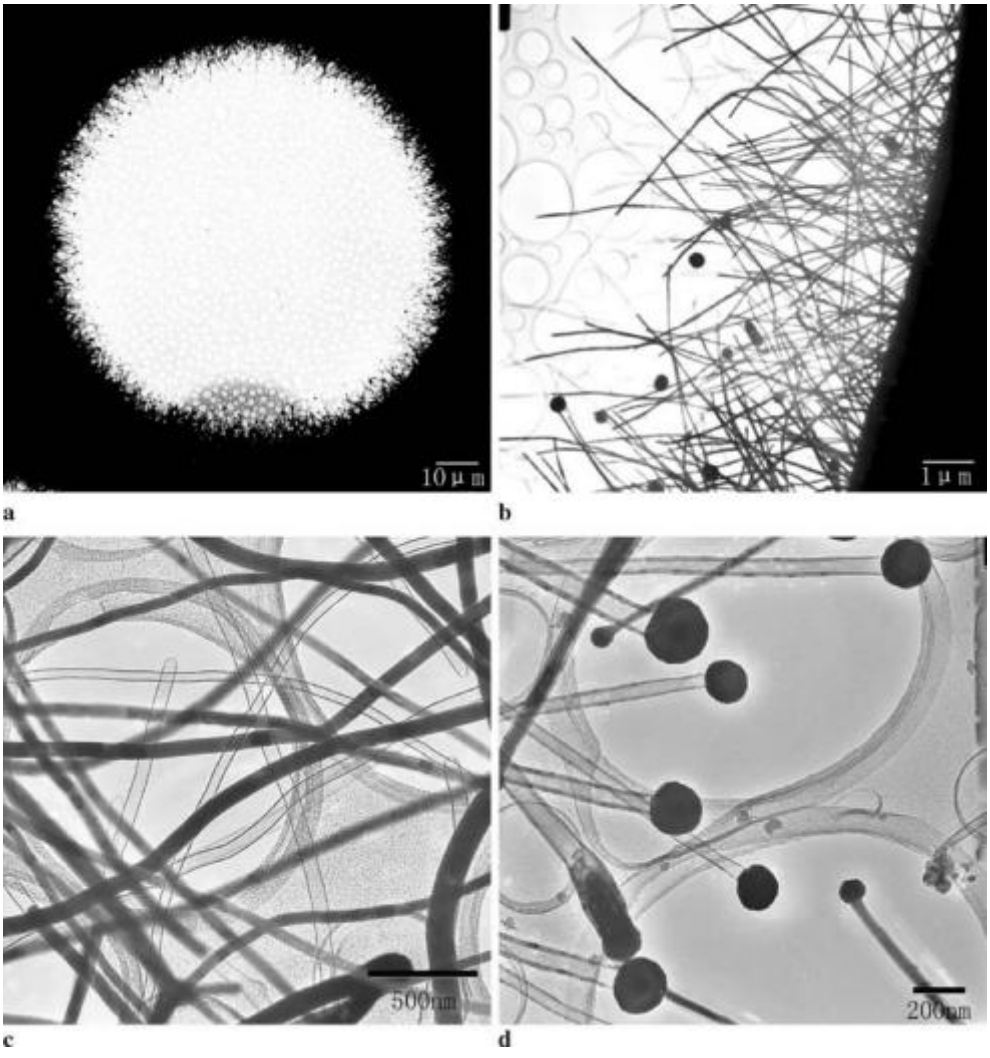

FIGURE 1 (**a**) Low magnification TEM image of CNTs on the edge of a microgrid; (**b**) TEM image of 70% CNTs following base growth mode; (**c**) Local image of the relatively straight CNTs filled or unfilled with copper in (**b**); (**d**) TEM image of CNTs with totally hollow core and large copper tips, following tip growth mode

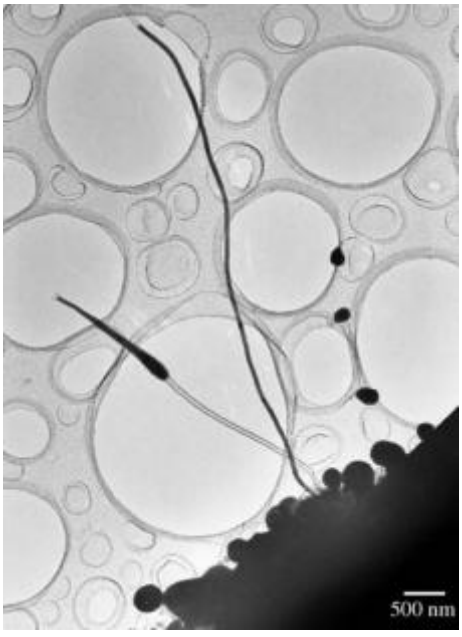

FIGURE 2 The sintering of copper nanoparticles on the microgrid and the CNTs following the tip growth mode or base growth mode

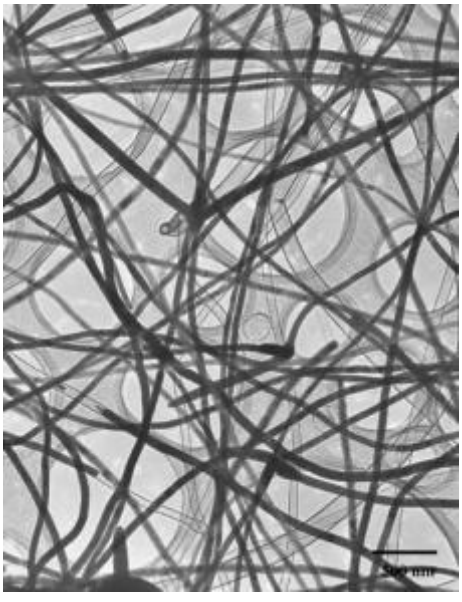

FIGURE 3 Detailed TEM image of large amount of Cu-filled CNTs and CNTs with totally hollow channel, without amorphous carbon on the outer wall

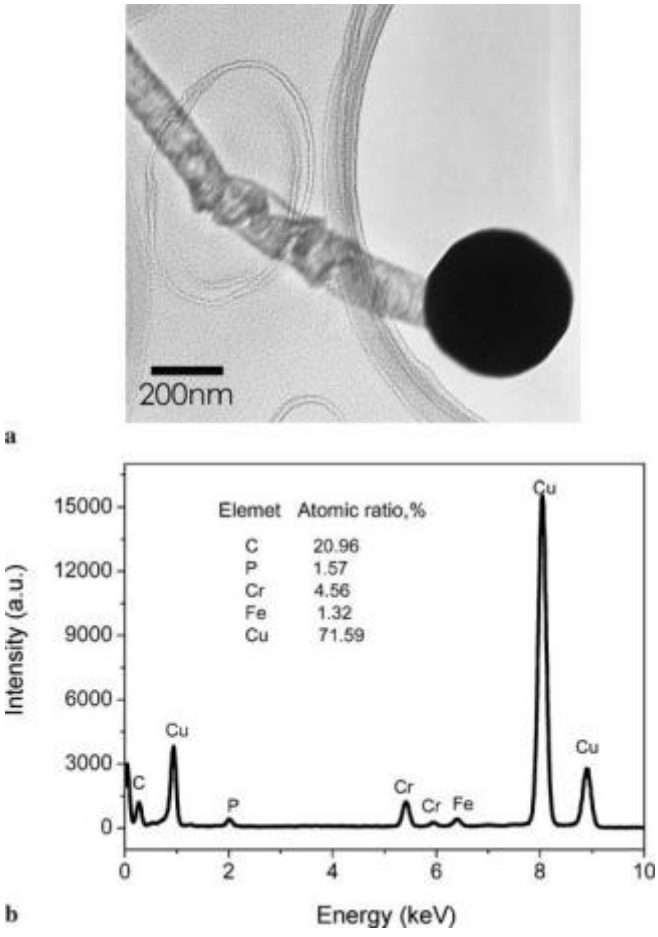

FIGURE 4 (**a**) TEM image of bamboo-like CNTs prepared from copper catalyst containing 3% iron; (**b**) EDS pattern of copper-iron nanoparticles in (**a**)

with totally hollow channels, is pure copper (Fig. 5). Since the difference between CNTs with or without hollow channels is mainly due to the formation of inner carbon layers of CNTs, it is essential to discuss the precipitation mode of the outer wall and inner carbon layers of CNTs. So far, it is generally accepted that the formation of the outer wall of the CNTs depends on the diffusion and precipitation of carbon mainly along the outer surface of metal particles. While the formation of the inner carbon layer of the CNTs with a bamboo-like structure is mostly attributed to the carbon diffusion via the bulk phase of metal dominantly [16, 17, 23] and the precipitation at the carbon-metal interface far from the outer surface of metal particles [16, 17, 23]. Only in the case of sufficient carbon supply can it be formed by the carbon diffusion along the outer surface of metal particles [18]. In previous work, we have proved that if we decrease the carbon supply, the CNTs with large hollow channels can be highly selectively formed [23]. Thus it is also effective to inhibit the formation of the inner carbon layer perpendicular to the tube axis by decreasing the carbon supply rate. Definitely, Fe–Cu catalyst with higher activity results in the high carbon supply rate, enhancing the carbon diffusion in the bulk phase of metal and the precipitation across relatively longer distance to form bamboo-like CNTs (Fig. 4b) [16–18]. Comparatively, a copper catalyst with lower activity of decomposed carbon source is effective for controlling the carbon supply rate in a small value, as compared with iron, cobalt and nickel. Furthermore, copper, with weak interaction with carbon, form copper carbide more difficultly [3, 19–22]. Thus the bulk phase of the particles maintains a pure metallic state, not a carbide state, as shown in HRTEM image (Fig. 7) and confirmed by the totally low atomic ratio of copper to carbon in the CNT tip by EDS (Fig. 5). These two factors are both favorable for the preferable diffusion and precipitation of carbon along the outer surface of copper, resulting in the formation of CNTs with totally hollow channels. The above results also indicate that the purity control of copper is important. High purity copper nanoparticles can be obtained by the physical evap-

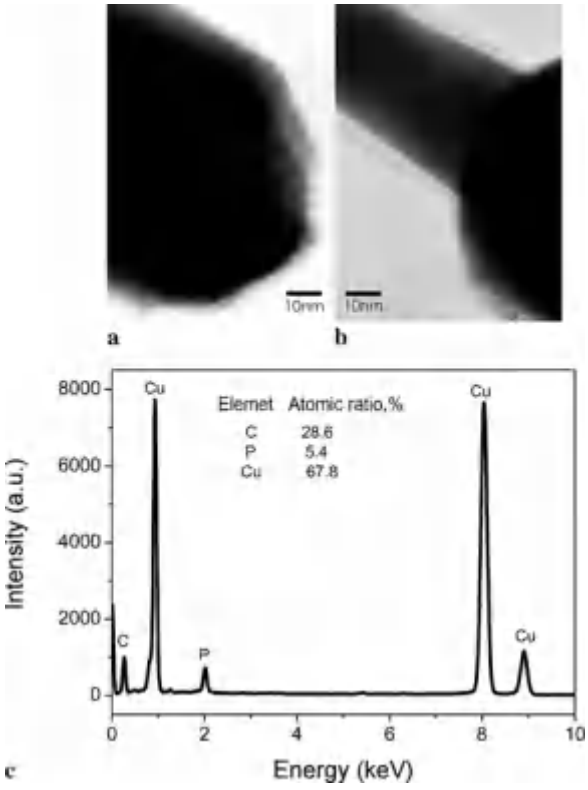

FIGURE 5 (**a**) Copper nanoparticles for the growth of CNTs in tip growth mode, with thin carbon layer smaller than 2 nm; (**b**) The thin carbon layer formed at the carbon-copper interface via the outer-surface diffusion mode of carbon; (**c**) EDS of the copper tip with high purity in (**b**)

oration of copper on the microgrid as in the present work or directly in the plasma condition [21]. Comparatively, the copper catalysts – prepared from the liquid phase crystallization, calcinations and the subsequent reduction – contain relatively more impurities, possibly including some high active metal species, which also result in the formation of bamboo-like CNTs [19, 20], similar to the results of our intentionally adding iron to the catalyst.

Furthermore, it is also proved that the feed gas containing some hydrogen is also important for producing CNTs with totally hollow channels. The comparison study indicates that, absent of hydrogen, CNTs with certain carbon layers perpendicular to the tube axis is produced, even using the pure copper catalyst (Fig. 6). The reason lies in the fact that hydrogen is one of the products of methane decomposition. Hydrogen in the feed gas will inhibit the formation of carbon. Thus the carbon supply rate for the deposition of CNTs is decreased effectively, allowing the preferable carbon outer surface diffusion and precipitation. Consequently, CNTs with totally hollow channels in high selectivity are achieved. This is confirmed by the thin carbon layer on copper tips (Fig. 5a) and the small atomic ratio of carbon to copper (Fig. 5b, EDS) in the presence of hydrogen. From the above comparison, it is clear that it is necessary to add hydrogen into feed gas and to increase the purity of copper catalyst for the synthesis of desirable CNTs with totally hollow channels.

Beside the CNTs with totally hollow channels, the copper filled CNTs are another dominant product. In many cases,

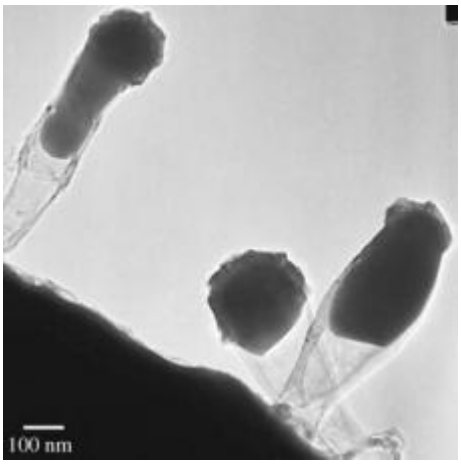

FIGURE 6 CNTs prepared from pure copper catalyst but using feed gas absent of hydrogen

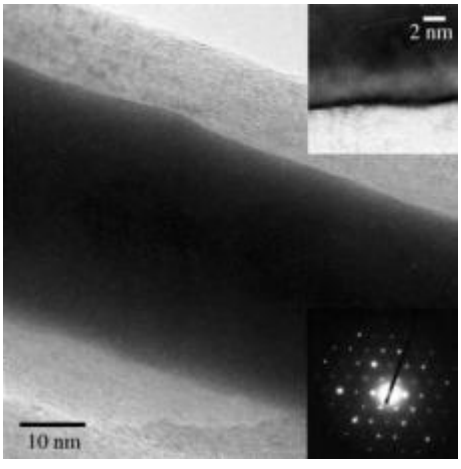

FIGURE 7 HRTEM image of the nanotubes filled with copper . The *upper insert* shows the detailed copper lattice and carbon layer; the *lower insert* is the SAED pattern of the single crystalline copper nanowires with fcc structure

copper occupies the whole channel (Figs. 1b, c and 3). And the filling volume ratio of copper is up to 50% of channel volume of the whole nanotube products, significantly higher than that (10%–30%) in other works [21, 22]. It may rank as one of the highest values reported so far. As to the state of copper in the nanotube, HRTEM image confirms its single crystalline form (the upper insert of Fig. 7) and the face-centered-cubic (fcc) structure by SAED (the lower insert of Fig. 7), in good agreement with that of molecular dynamic simulation [24]. Since the species have poor wetting ability with carbon, including copper, it is difficult to fill the CNTs with high filling ratio [3, 14]. For deeper understanding, it is, therefore, necessary to determine the state of copper. Notably, the melting point of bulk copper is 1356 K and the melting point of many nanoparticles (including Cu) may be 100–250 K lower than that of the bulk materials [25–28]. Thus the copper nanoparticles are in liquid or the quasi-liquid state at 1173 K in the present work. Meanwhile, the temperature of 1173 K is not high enough to produce large amounts of copper vapor, as in a plasma condition [21]. Thus the copper filling is predominantly via the liquid state or quasi-liquid capillary adsorption, similar to the wet chemical mechan-

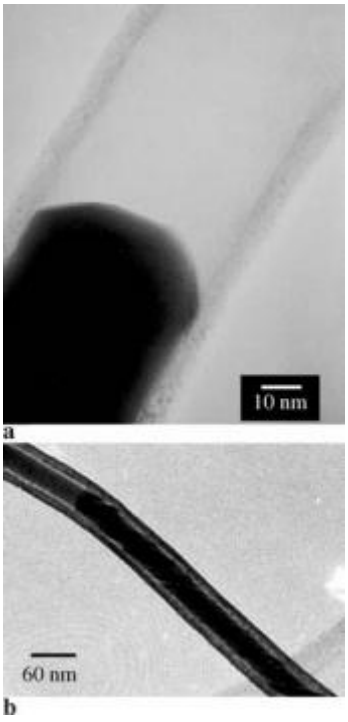

FIGURE 8 (**a**) The contact angle of the copper tip with the carbon layer is 120–135°, indicating the poor wetting of copper with carbon; (**b**) Long copper nanowires having no contact with the CNT wall

ism of filling other materials with poor carbon wetting ability [2]. Here, the contact angle between copper and the inner carbon wall is 120–135° (Fig. 8a), which provides a direct evidence of the relatively poor wetting characteristics of copper on the carbon surface and the liquid or quasi-liquid state capillary adsorption analysis. In special cases, the inside of the copper nanowires (with several micrometers long) have nearly no contact with the around carbon layers (Fig. 8b), which may be an interesting structure having potential applications such as the nano-channel catalytic reactor. After entering into the CNTs, the formation of continuous and single crystalline copper nanowires naturally occurs by the melting of copper nanoparticles or sections under the thermal driving force, similar to the formation of Ga or Fe nanowires in the CVD process [6, 13]. Specifically, the continuous copper nanowires are up to 8–10 μm long, a very useful material formed in the case of sufficient copper supply from the microgrid. The present method is simple, easily repeatable and at low cost.

4 Conclusions

CNTs with totally hollow channels and/or with totally filled copper nanowires in high selectivity have been prepared from methane decomposition using a copper catalyst with high purity and the feed gas containing hydrogen. The key lies in the control of the carbon supply rate and its diffusion mode over the metal particles. The in situ filling of copper into the CNTs by the liquid or quasi-liquid state capillary adsorption, confirmed by the HRTEM, is an effective way to fill materials with poor carbon wetting ability. The sufficient supply of copper source allows the formation of continuous coaxial copper-carbon nanowires up to 8–10 μm long under the thermal driving force. The total filling volume ratio of copper in CNTs for the first time is increased to about 50%. These results are useful for the further controlled synthesis of these desirable nanostructured materials.

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