

A Novel Route to Multiwalled Carbon Nanotubes and Carbon Nanorods at Low Temperature

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Multiwalled carbon nanotubes and carbon nanorods were produced through a novel route in the presence of different metallic particle catalysts at the extremely low temperature of 200 °C. In this process, tetrachloroethylene (C_2Cl_4) was used as the carbon feedstock, which can be reduced by metallic potassium to free C_2 in benzene at the temperature of 200 °C. Then the freshly formed free C_2 can assemble into the hexagonal carbon clusters, which can grow into nanotubes at the surface of the catalytic particles (Fe/Au). Transmission electron microscopy (TEM) images showed that the nanotubes had an average length of 1.8 μm , and the inner diameter of 60 nm, the outer diameter was 80 nm in average. The Y-junction carbon nanotubes were first observed in the solution reaction. In addition, the freshly reduced free C_2 can also form one-dimensional conjugate carbon chain clusters, and then they assemble into nanorods with the diameter of 70 nm and the length of 1000 nm in the presence of another catalytic particle (Ag). The catalyst and the reaction time play important roles in the nucleation and growth process of the nanotubes and nanorods.

Introduction

Carbon nanotubes (denoted as CNTs hereafter) and nanorods have attracted attention in recent years not only for their small dimension and unique morphologies, but also for their potential of applications in various technologies. Nanotubes¹ can be thought of as single graphite sheets wrapped into seamless cylinder. They can be either semiconducting, semimetallic, or metallic, depending on the wrapping angle and tube diameter.^{2–4} Their high mechanical strength,⁵ capillary properties,⁶ and remarkable electronic structure^{3,7–8} allow envisagement of potential uses. Another important use of CNTs is that some other important one-dimensional nanomaterials can be produced, such as tubular oxides,⁹ wire- or rodlike carbides,¹⁰ and rodlike GaN,¹¹ by using the CNTs as the preexisting templates. Most nanotubes consist of several concentric layers (multiwalled nanotubes), but single-walled tubes (SWTs) have also been found.¹²

Since Iijima¹ discovered CNTs in an arc-discharge apparatus, a worldwide research effort has been stimulated to improving their synthesis, determining their structure,^{13–18} and calculating their physical properties.^{19–23} In the following years, many methods have been used to produce CNTs, such as arc discharge in the absence or presence of metal,^{12,19,24} laser vaporization of a metal–graphite composite target,¹⁶ carbon monoxide disproportionation on a metal catalyst,²⁵ and hydrocarbon pyrolysis.²⁶ But they mainly fall into one category; furthermore, they also require elevated temperature. Very recently, Jiang²⁷ et. al reported a catalytic-assembly route to multiwalled CNTs at 350 °C using hexachorobenzene as the carbon feedstock. The temperature for producing CNTs reported by them is the lowest at that time.

In the past decade, many theoretical studies have been done in exploring the atomic structure and possible electrical properties of Y-junction CNTs.^{28–30} One of the most significant

findings is that the single-walled Y-junction CNT is theoretically the smallest molecular transistor.²⁸ Y-junction CNTs were first observed in arc-discharge produced carbon nanotubes, which exhibit a structure composed of three joining tubes.³¹ But to date, they have only been grown by the chemical vapor deposition (CVD) method, such as hot-filament chemical vapor deposition (HFCVD)³² and template growth method in thermal CVD,³³ and no solution method has been used to prepare Y-junction CNTs.

Herein, we report a novel benzene-thermal-reduction-catalysis route to produce multiwalled carbon nanotubes (MWTs) and carbon nanorods in the presence of different catalysts at 200 °C (so-called BTRC route). The temperature reported here is much lower than the lowest one reported previously. In the previous work on carbon nanotubes, apart from arc-discharge and laser evaporation methods, the sources of carbon atoms are small molecules of hydrocarbons, such as CH_4 , C_2H_2 , and C_2H_4 , which can be used to produce CNTs at relatively high temperature.³⁴ While in the present route, we use tetrachloroethylene as the carbon feedstock, which can be reduced to free C_2 by metallic potassium at a low temperature of 200 °C, and then the freshly formed free C_2 may assemble into hexagonal carbon clusters or one-dimension carbon chain clusters. Finally, these clusters can grow into the corresponding nanotubes²⁷ and nanorods in the presence of different catalysts. In the experiment, we discovered that when using Fe/Au as catalysts, the products were mainly nanotubes with the existence of the amorphous carbon, and when using Ag as catalyst, the products were mainly carbon nanorods. The reaction process can be represented by Scheme 1. In addition, we first observe Y-junction CNTs in the solution reaction.

Experimental Section

In our experiment, all reagents were of analytical grade. The catalyzer precursor was prepared by refluxing the metal chlorides, which are the mixture of $FeCl_3 \cdot 6H_2O$ and $HAuCl_4 \cdot 3H_2O$ (Au:Fe molar ratio of 1:1), in thionyl chloride ($SOCl_2$)

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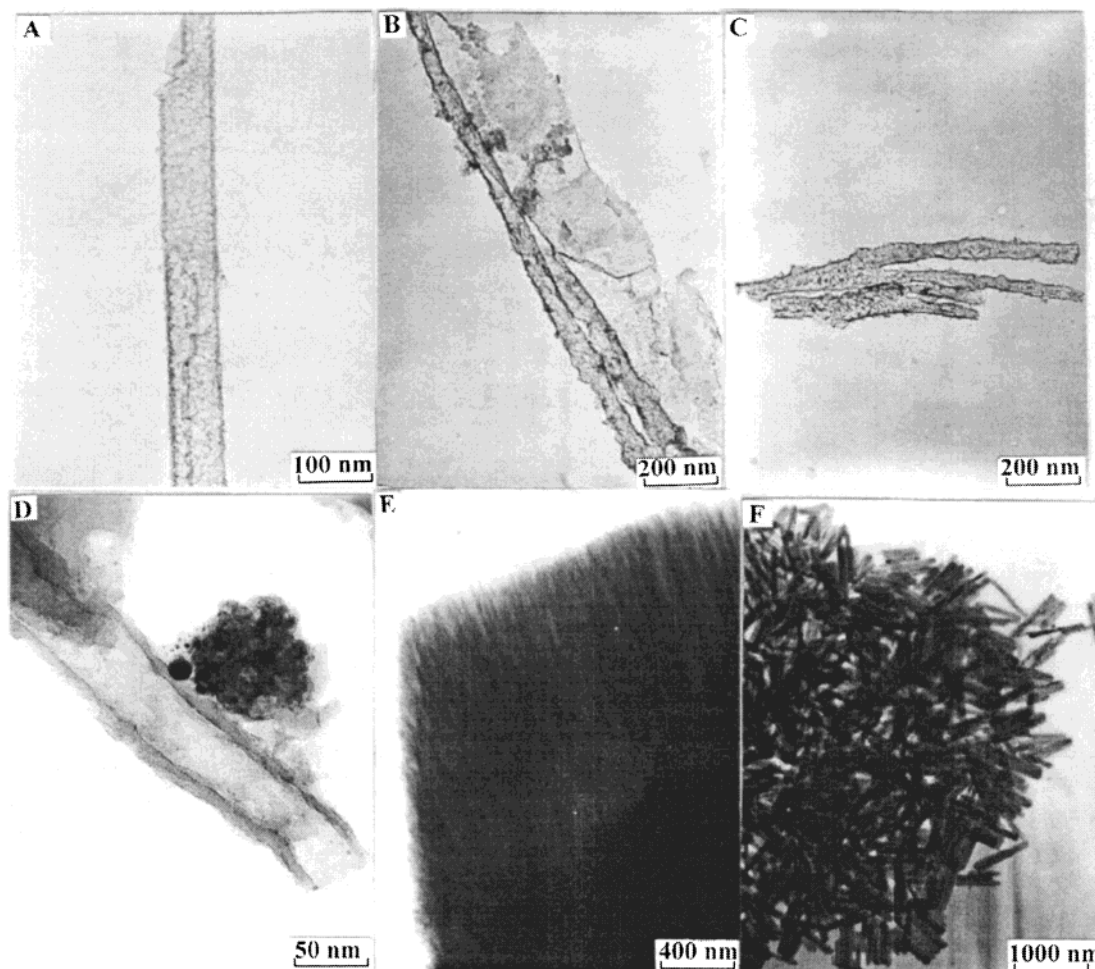
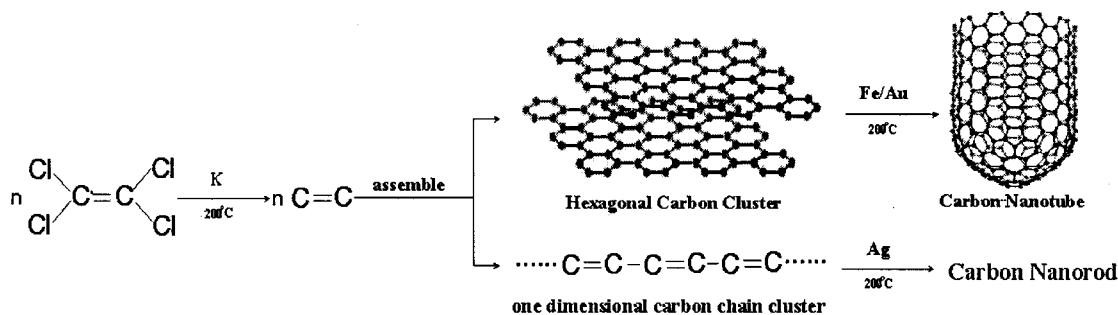


Figure 1. Transition electron microscopy (TEM) images of multiwalled carbon nanotubes (A, B, C, D, E) and carbon nanorods (F). Most nanotubes have straight-line morphology (A, E) and some nanotubes are shown with a bamboo-like structure (B) or branching structure (C).

SCHEME 1: The Formation Mechanism of Carbon Nanotube and Carbon Nanorod by Benzene-Thermal-Reduction-Catalysis Route in the Presence of Different Catalysts at Low Temperature.



for 45 min. AgCl was prepared according to the reaction of AgNO₃ and NaCl, and dried in a vacuum for 4 h. A typical synthesis is as follows: 8 mL of tetrachloroethylene (C₂Cl₄) was placed into a stainless steel autoclave with 30 mL capacity, and then 10 mL of benzene and 5 g of potassium were added. After that, 6 mL of benzene was added until about 80% of the autoclave's capacity. Finally, 100 mg of catalyzer precursor was added. The sealed autoclave was kept at 200 °C for 27 h, and then cooled to room temperature in the furnace naturally. The products were filtered out; washed with absolute ethanol, dilute acid, and distilled water in subsequence; and then dried in a vacuum at room temperature for 4 h.

The morphologies of the samples were observed through transmission electron microscope (TEM) measurements, which were made on a Hitachi H-800 transmission electron microscope

with an accelerating voltage of 200 kV. The microstructure of carbon nanotubes was analyzed by high-resolution electron microscopy (HRTEM) images, which were taken on a JEOL-2010 transmission electron microscope. Samples for the electron microscope were deposited from ethanol solution of the products onto thin amorphous carbon films supported by copper grids. Raman spectra were recorded with a Spex 1403 Raman spectrometer at ambient temperature.

Discussion

Transmission electron microscopy (TEM) images for the products are shown in Figure 1. From Figure 1A, it can be seen that nanotubes are straight with an average length of 1.8 μm, their inner diameters of 60 nm and outer diameters of 80 nm in

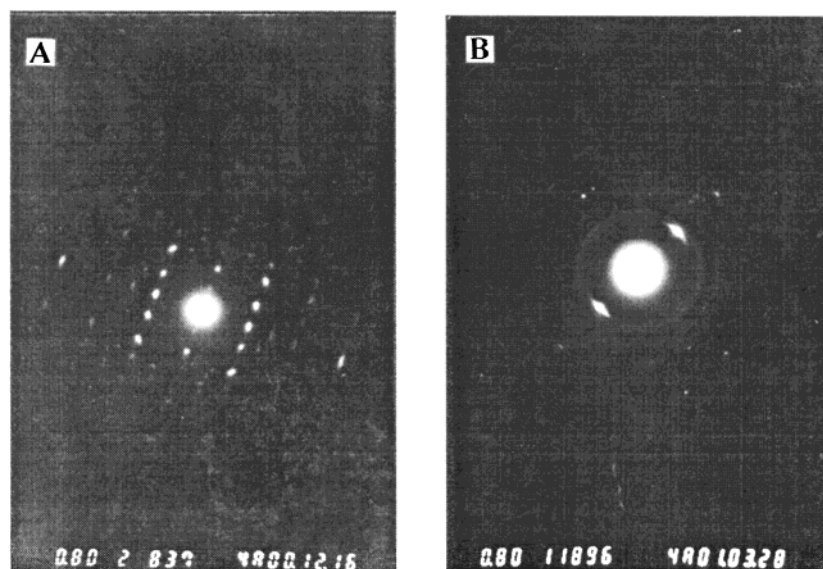


Figure 2. The electron diffraction patterns: (A) of carbon nanorods prepared in the presence of Ag particle catalyst; (B) of a carbon nanotube prepared in the presence of Fe/Au particle catalyst.

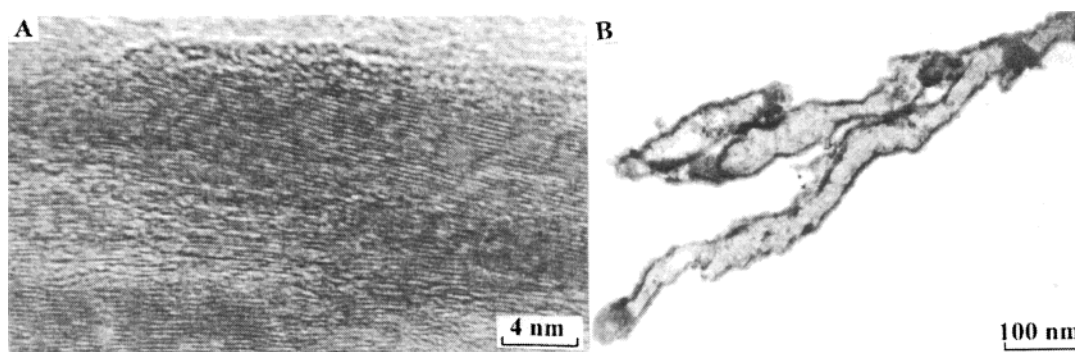


Figure 3. High-resolution TEM images of multiwalled carbon nanotubes. Image of nanotube wall (A), spacing between the fringes is about 0.34 nm corresponding to the (002) lattice parameter of graphite. Figure 3B is the low-magnification image of nanotube. Catalyst metal particle exists in the close end.

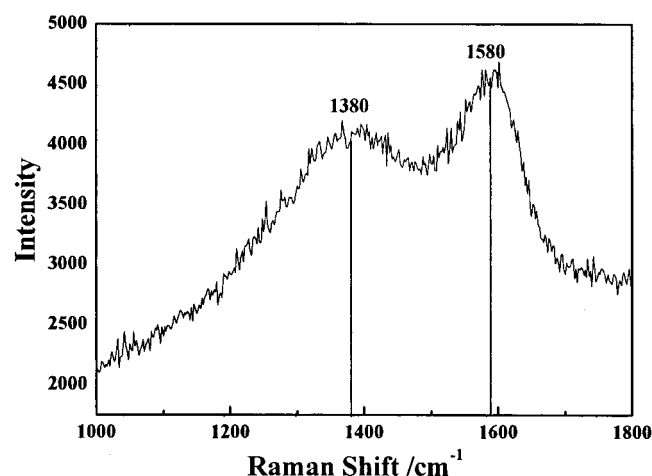


Figure 4. Raman spectra at room temperature of the obtained multiwalled carbon nanotubes

average. Figure 1B shows a bamboo-like structure of CNTs. The inner tube is subdivided by single-graphite or multi-graphite layers, which may be caused by the surface diffusion of carbon clusters on the large catalytic particles across the nanotube's wall.³⁵ Most of the nanotubes have open ends, without amorphous carbon coating.

Branching structures in CNTs (Y-junction carbon nanotubes) are also observed in the products. The TEM image of an

individual Y-junction CNT is shown in Figure 1C. It is observed that a straight carbon nanotube stem is split downward into two thinner carbon nanotube branches, both continuing to grow. The metal particle might have catalyzed the central part of the Y-junction and adsorbed carbon atoms from the freshly formed hexagonal carbon clusters to supply for the upward growth of the stem carbon nanotube.

Other electron micrographs (Figure 1D and 1E) show the nanotube's bundle and sphere-like nanoparticles. From Figure 1E, one can more clearly see that the carbon nanotubes are arrayed orderly on the surface of the catalyst. The HRTEM image shown in Figure 3B indicates that some carbon nanotubes have bending structure. From this image and Figure 1E, one can clearly see that the catalytic metal particles exist at the close end of the tubes. It suggests that the metal particles are responsible for the nucleation of the multiwalled carbon nanotubes. As previously reported,³⁶ the outer diameter of the fibers depends on the size of metal particles. We also noticed a dependence of the thickness of the nanotubes on the diameter of the metal crystallites. The current chemical and physical environments do not ensure the stability of the metal particles, and some aggregates up to 90 nm in diameter were observed (Figure 3B).

Figure 1F shows the carbon nanorods with the diameter of 70 nm and the length of 1000 nm, which was prepared in the presence of Ag particle catalyst. From this figure, we can see

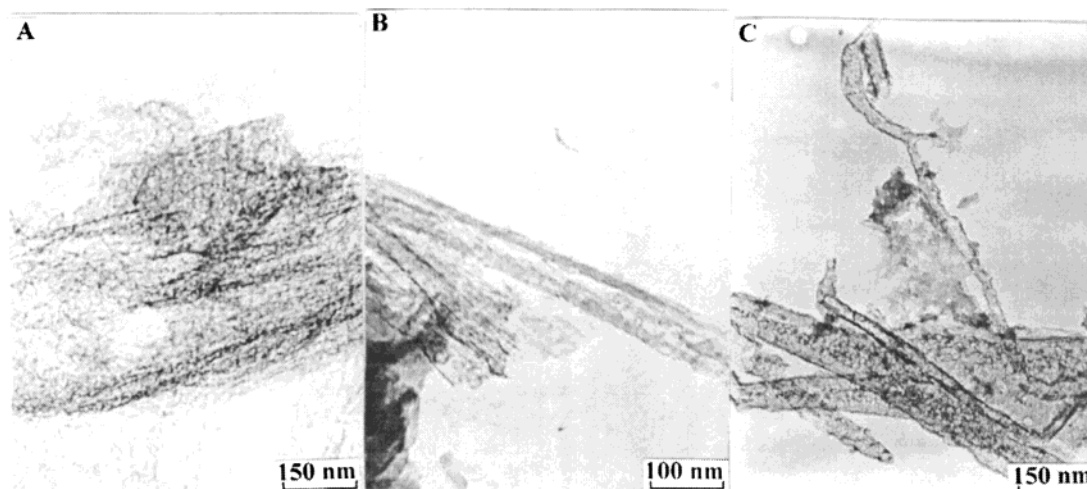


Figure 5. TEM images of carbon nanotube growth process. (A) Obtained after 9 h at 200 °C, (B) obtained after 18 h at 200 °C, (C) obtained after 27 h at 200 °C.

that the nanorods are extremely uniform. The electron diffraction (ED) pattern shown in Figure 2A was obtained from a selected area of carbon nanorods shown in Figure 1F, and it revealed that the carbon nanorods are very crystalline.

The HRTEM image of the nanotubes shown in Figure 3A indicates that the CNT wall is very graphitic, and which can also be proved by a typical ED pattern of the nanotubes that was obtained by focusing the beam on an individual nanotube (shown in Figure 2B). The interlayer spacing in the multiwalls is about 0.34 nm, which corresponds to the (002) plane lattice parameter of graphite carbon.¹ The Raman spectrum of the product prepared in the presence of Fe/Au particle catalyst is shown in Figure 4. The D-band at around 1360 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite or glassy carbon. The peak at 1580 cm^{-1} (G-band) corresponding to an E_{2g} mode of graphite and is related to the vibration of sp^2 bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite layer.³⁷ Nanotubes with concentric multiwalled layers of hexagonal carbon lattice display the same vibrations.³⁸ Due to the higher level of amorphous carbon in the final products, the I_D intensity is larger than that in pure carbon nanotubes. The above analysis indicates the graphite structure of the nanotubes. According to the analysis of Kasuye et al.,³⁸ the complex structure of $1540\text{--}1600\text{ cm}^{-1}$ can be understood by z1-folding of the graphite phonon dispersion relation.

The walls of CNTs, the cylinder stories of multiwalled nanotubes, and the planar sheet of single-walled nanotubes are all built from the hexagonal lattice of sp^2 bonded carbon.²⁴ During the reaction producing CNTs, represented by Scheme 1, tetrachloroethylene is reduced by metallic potassium through deleting chlorine group to free C_2 , and the freshly formed free C_2 then may assemble into hexagonal carbon clusters. At the same time, the chlorides of Fe and Au are reduced to Fe/Au catalyzer particles by potassium. The hexagonal carbon clusters diffuse to the growth sites through constant surface diffusion when the nucleation of CNT from a freshly reduced metal particle has finished, and then assemble into nanotubes and cause the axial growth. Furthermore, the oriented growth of newly formed hexagonal carbon clusters on the nanotubes wall is favorable because the geometry structure of hexagonal carbon clusters is similar to that of carbon nanotube walls built from the hexagonal lattice of sp^2 bonded carbon. It results in the formation of multiwalled nanotubes under such a relatively low temperature benzene-thermal process. In fact, for multiwalled

carbon nanotubes, it is quite likely that the presence of the outer wall stabilizes the inner wall, keeping it open for continuous growth.³⁹ The growth mechanism here is different from that of ideal single-walled nanotubes⁴⁰ because of the absence of single-wall carbon nanotubes in our observation. From the scheme, we can see that the freshly reduced free C_2 may also assemble into one-dimension conjugate carbon chain clusters. They may grow into nanorods in the presence of Ag particles used as the catalyst.

The reaction time is another key role for the growth process of CNTs. The micrographs of the products prepared at various time are shown in TEM images (Figure 5 A–C). From the figure, one can see that the products are nanofibers after reaction for 9 h at 200 °C (Figure 5A), and when prolonging the growth process time to 18 h, the products grow into the rudiment of carbon nanotubes, but they are not well crystallized (Figure 5B). When the time is prolonged to 27 h, the well crystallized carbon nanotubes are produced (Figure 5C).

The yield of nanotubes is about 15% from the original reagents through electron microscope observation of the prepared samples, and the other contents of the obtained products are amorphous carbon and some sphere-like nanoparticles. We find it is easy to get individual nanotubes under electron microscope observation although the yield here is about 15%. It is said, this may be useful to utilize and operate single carbon nanotubes. But the yield of carbon nanorods is relatively higher than that of nanotubes, which is nearly 60%. The reason causing such different yields of nanotubes and nanorods is still not clear. We suppose that it is the influence by different catalysts.

Improvements in the process of producing carbon nanotubes are still needed. Much work is required to understand the reaction kinetics and control the aligning of carbon nanotubes. It is very critical to find a better catalyst for the formation and growth of carbon nanotubes. Transition metals, such as Ni, Co, Fe, Au, and Pt, their alloys, and their carbides may be the favorable catalysts. It is reasonable to suppose that selecting the more suitable catalyst may increase the yield of carbon nanotubes in the present benzene-thermal growth process. This method may provide a new means to produce carbon nanotubes or nanorods and other carbide nanotubes or nanorods, such as SiC, WC, NC_x , TiC, and so forth.

Conclusion

Multiwalled carbon nanotubes and carbon nanorods were obtained through a novel method, called benzene-thermal-

reduction-catalysis (BTRC) route, in the presence of different metallic particle catalysts at the extremely low temperature of 200 °C. TEM images shows that the nanotubes have an average length of 1.8 μm , and inner diameters of 60 nm, and outer diameters of 80 nm in average. The nanorods have an average diameter of 70 nm and length of 1000 nm. In this process, the free C_2 can be released by reducing tetrachloroethylene (C_2Cl_4) using the metallic potassium as the reductant in benzene at the temperature of 200 °C. Then the freshly formed free C_2 can assemble into the hexagonal carbon clusters or one-dimension carbon chain clusters. Finally, these clusters can grow into the corresponding nanotubes and nanorods in the presence of different catalysts. The Y-junction carbon nanotube was first observed in the solution reaction. The catalyst and the reaction time play important roles in the nucleation and growth process of the nanotubes and nanorods.

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