

Aligned carbon nanotube/polymer composite fibers with improved mechanical strength and electrical conductivity†Wenhan Guo,^a Chao Liu,^a Xuemei Sun,^a Zhibin Yang,^a Hamid G. Kia^b and Huisheng Peng^{*a}

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In order to improve their practical applications, carbon nanotubes (CNTs) have been widely spun into fibers. However, both mechanical strength and electrical conductivity of the CNT fibers are far from the applications. Therefore, a second phase such as polymer has been introduced to increase their strength, but their conductivity further decreases due to the insulating or the low-conductivity action of the incorporated polymer. In this work, we have developed a general and effective route to fabricate CNT/polymer fibers through the introduction of monomers during an easy solution process followed by an *in situ* polymerization. The resulting composite fibers show an increased tensile strength and an improved electrical conductivity compared with either the pure CNT fibers or the CNT/polymer fibers prepared by the direct incorporation of polymers. This work demonstrates a fabrication methodology to design and synthesize high-quality CNT/polymer composite materials.

Introduction

Due to their unique structure and excellent physical and chemical properties,^{1–3} carbon nanotubes (CNTs) have been extensively studied for over twenty years and found to be very useful in a wide variety of application fields.^{4–8} However, the large-scale applications of individual CNTs have been limited by the difficulty in their structure control. As a solution, more and more attention has been paid to assemble CNTs into macroscopic fibers in which the CNTs are highly aligned to maintain the remarkable properties of individual nanotubes, *e.g.*, their high mechanical strength and electrical conductivity.^{9–11} The slight differences among individual CNTs may be neglected for applications such as high-performance structural materials and flexible electrodes.^{12–14} In order to further improve the CNT fiber properties, a second phase such as inorganic molecules or nanoparticles,^{15,16} organic molecules,¹⁷ or polymers,^{18–30} has been recently incorporated to produce composite fibers. For instance, a CNT fiber easily breaks under tensile forces mainly due to the sliding action of neighboring CNTs, which are bundled by the weak van der Waals force. Therefore, polymers are used to interconnect CNTs to decrease this slippage and improve the mechanical strength of the spun

fibers. The CNT/polymer fibers are typically prepared by dipping the pure CNT fibers into polymer solutions, followed by the evaporation of solvents.^{21–30} Accordingly, polymer molecules are infiltrated into CNTs through the solution diffusion. However, for the small voids of typically several nanometres among CNTs of the fiber, it is very difficult for the large polymer molecules to efficiently interpenetrate. Therefore, the resulting composite fibers are not uniform and show limited strength improvements. Furthermore, the introduction of polymers into the spun fiber generally increases their strength but decreases their conductivity due to the insulating or low-conductivity action of the incorporated polymer. For more practical applications, however, both strength and conductivity are expected to be further enhanced. To this end, the replacement of large polymer molecules with much smaller monomers followed by an *in situ* polymerization appears to overcome the above challenges. Compared with the direct incorporation of polymers, the monomers can infiltrate into the small voids to further increase the fiber strengths after polymerization, and the resulting polymer chains can pack the CNTs more closely in the spun fiber and decrease the electrical contact resistance resulting in a higher conductivity.

Herein, we show such an efficient and easy route to fabricate aligned CNT/polymer fibers by using acrylic acid (AA) as a model monomer. As expected, the resulting CNT/PAA composite fibers show both much improved tensile strength and electrical conductivity compared with the pure CNT fibers and CNT/PAA fibers fabricated by direct incorporation of PAA under the same experimental conditions. This work demonstrates a fabrication methodology to design and synthesize high-quality CNT/polymer composite materials.

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Experimental section

Preparation of the precursor solution

Acrylic acid (AA) was obtained from Shanghai Dahe Chemical, the initiator, ammonium persulfate (APS), and the crosslinker, *N,N*-methylene bisacrylamide (BIS), were purchased from Sigma Aldrich. In the preparation of the precursor solution, BIS (ranging from 0 to 320 mg) was first mixed with AA (7.77 g) in distilled de-ionized water (5 g) to form a stable solution, followed by addition of 1 mL initiator solution with a concentration of 40 mg mL⁻¹. The final mixture solution was gently sonicated for a few seconds to ensure the uniformity. The crosslinking degree was defined as the molar ratio of BIS to AA.

Fabrication of the CNT/PAA composite fiber

A chemical vapor deposition method was used to synthesize CNT arrays from which pure CNT fibers were spun directly at a rotating rate of 2000 rpm. More details can be found elsewhere.¹⁵ The pure CNT fibers were immersed into the precursor solution for 5 min and then placed in an oven at 50 °C for 2 days. The composite fibers were obtained after *in situ* free radical polymerization.

Characterization

Structures of composite fibers were characterized by scanning electron microscopy (Hitachi FE-SEM S-4800) and transmission electron microscopy (JEOL JEM-2100F operated at 200 kV). Raman measurements were made on a Renishaw inVia Reflex spectrometer with laser wavelength of 512 nm. Fourier transform infrared spectra were obtained from a Thermofisher NEXUS 470 spectrometer using KBr as the pelletizing material. Differential thermal analysis was performed on a DTG-60H (Shimadzu) from room temperature to 250 °C, with a heating rate of 10 °C min⁻¹. The DTG-60H was also used to determine the weight ratio between CNT and PAA in the composite fiber. For the mechanical measurements, the composite fibers were stabilized on a hard paper with the gauge length of 5 mm (typically used for the CNT fibers)^{33–35} and tested on an HY0350 Table-top Universal Testing Instrument. Electrical measurements were made using a two-probe method. An Olympus BX51 optical microscope was used to determine the fiber diameters as required for the mechanical and electrical measurements.

Results and discussion

We have first grown spinnable CNT arrays using a chemical vapor deposition process. Briefly, Fe/Al₂O₃ was used as the catalyst with ethylene serving as the carbon source, and a gas mixture of Ar and H₂ was used to carry the precursor to a tube furnace where the growth took place. The reaction temperature was typically controlled at 750 °C with a reaction time of about 10 min. The pure CNT fibers were then spun from the high-quality array (Fig. 1).

Diameter of the spun pure CNT fibers was controlled in a range of 5 to 15 μm. Fig. 2a shows a typical scanning electron microscopy (SEM) image of a pure CNT fiber with a diameter of ~8.6 μm. The fiber diameter is uniform along the axial direction.

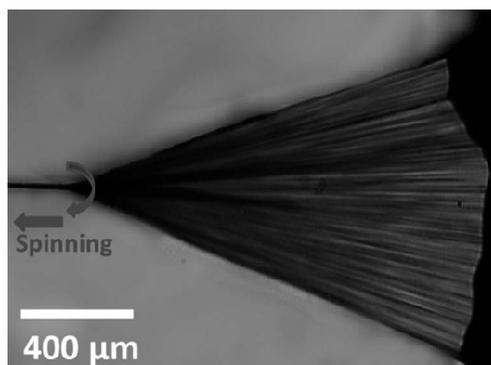


Fig. 1 Optical micrograph of the fiber fabrication from a CNT array. The right arrow shows the rotating direction.

Under a higher magnification, it is found that many CNT bundles wind together to form the fiber (Fig. 2c). These bundles are composed of highly aligned individual CNTs from the arrays. After the incorporation of the AA monomers followed by *in situ* polymerization, the resulting CNT/PAA composite fiber shrinks in diameter compared with the pure CNT fiber (Fig. 2b). In addition, the distances between the CNTs obviously decrease under high-magnification SEM (Fig. 2d). High-resolution transmission electron microscopy had further confirmed that the PAA molecules were successfully attached onto the CNT surfaces. As compared in Fig. 3, a thin polymer layer with thickness of ~2.5 nm is observed around a CNT in the composite fiber. The weight ratio between CNT and PAA was determined to be 5.44:1 by a thermogravimetric analysis.

Formation of the high-quality composite fibers has also been investigated by Raman spectroscopy and Fourier transform infrared spectroscopy. According to a typical Raman spectrum, the intensity ratio of the D-band at ~1345 cm⁻¹ to the G-band at ~1577 cm⁻¹ is calculated to be 0.63 for a pure CNT fiber (Fig. 4). After incorporation of the PAA, the resulting composite fiber shows a similar Raman spectrum in shape, however, the intensity ratio of D-band to G-band rises to 0.70 due to the introduction of defects on the CNTs by bombardment of free radicals produced during the polymerization (Fig. 4).³¹ Note that although PAA

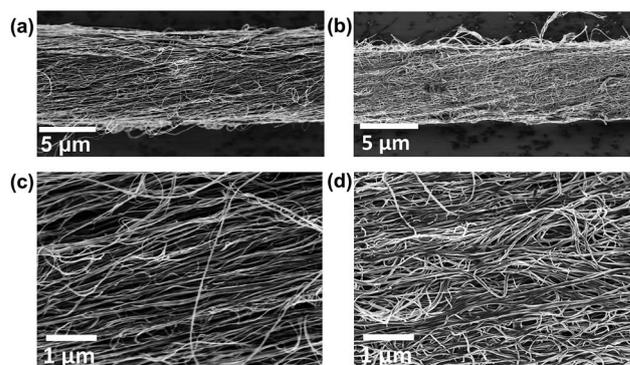


Fig. 2 Scanning electron microscopy (SEM) images of (a) a pure CNT fiber, (b) a CNT/PAA composite fiber, (c) higher magnification of (a), and (d) higher magnification of (b). For the CNT/PAA composite fiber, the monomer concentration and crosslinking degree in the precursor solution are 8.05 mol L⁻¹ and 0.48%, respectively.

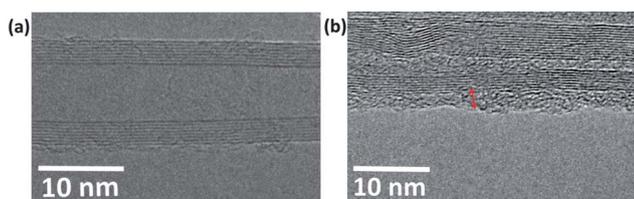


Fig. 3 Transmission electron microscopy (TEM) images of (a) a pure CNT, (b) a CNT coated with PAA in the composite fiber. The double-headed arrow in (b) shows that the thickness of PAA is ~ 2.5 nm.

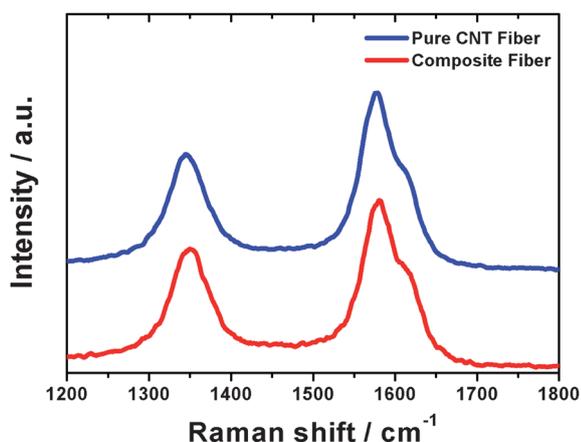


Fig. 4 Raman spectra of a pure CNT fiber and a CNT/PAA composite fiber.

typically serves as an electron donor and induces an upshift in the G-band, here no obvious shift had been found due to the relatively weak molecular interactions between CNT and PAA.³² Fig. 5 compares typical infrared spectra of CNTs, PAA, and CNT/PAA composite fibers. The characteristic peaks at ~ 1720 cm^{-1} which corresponds to C=O of PAA and ~ 1630 cm^{-1} which corresponds to C=C of CNTs are observed with the same intensity ratio at different locations of the CNT/PAA fibers. In other words, the uniform structure has been formed in these composite fibers.

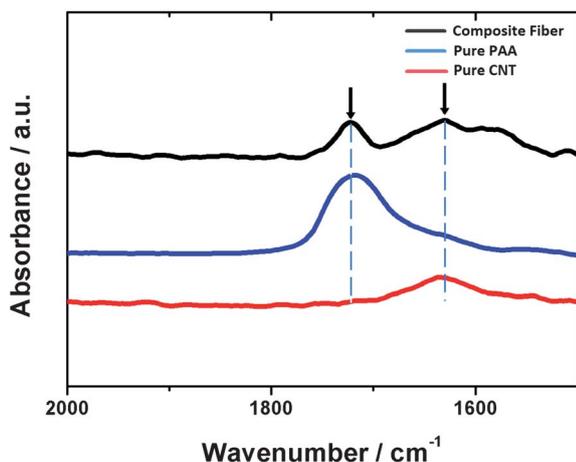


Fig. 5 Fourier transform infrared spectra of pure CNTs, PAA, and a CNT/PAA composite fiber.

Due to the high alignment of CNTs, the resulting fibers show excellent mechanical and electrical properties. For instance, the CNT fibers have been found to be stronger and stiffer than the current engineering fibers.¹⁴ The electrical conductivities of CNT fibers have achieved the level of 10^2 S cm^{-1} at room temperature. Here we have studied the improvement of mechanical strengths after the introduction of the polymer with and without a cross-linker by tracing the stress–strain curves. It was found that the curve shape appeared similar after the formation of the composite fibers. Fig. 6 shows a typical stress–strain curve. However, as shown in Fig. 7, the tensile strength of the CNT/PAA fibers has been increased by up to 220% compared with the as-prepared pure CNT fibers and up to 60% compared with the water-treated pure CNT fibers. Note that the water-treated pure CNT fiber showed a much higher tensile strength than the as-prepared pure CNT fiber because the fiber shrank and the interactions among the CNTs were increased after the water treatment. In addition, here the CNT/PAA composite fibers showed a higher strength (up to 31%) than those prepared by the direct incorporation of PAA under the same experimental conditions. It should also be noted that, based on the same fabrication procedures, some silica precursors have been physically incorporated into CNT fibers followed by their hydrolysis and condensation reactions to produce CNT/silica composite fibers.¹⁵ The tensile strengths of the resulting CNT/silica composite fibers were improved to 0.37–0.42 GPa from 0.32 GPa of the pure CNT fibers. As a comparison, the CNT/PAA fibers prepared by the *in situ* polymerization method showed much more improved tensile strengths of up to 0.8 GPa from 0.21 GPa of the pure CNT fibers. In addition, the CNT/silica fibers were not flexible due to the rigid nature of silica, while the CNT/PAA fibers maintained their high flexibility.

Fig. 7a also shows that the tensile strength of the CNT/PAA composite fibers first increases and then decreases with increase in the monomer concentration. The critical concentration point appears to be at 8.05 mol L^{-1} . As previously reported, polymer chains are introduced to decrease the slippage of the CNTs by interconnecting them. At first a higher amount of monomers increases the molecular weight of the polymer, which improves the interconnecting function and affects a higher strength.

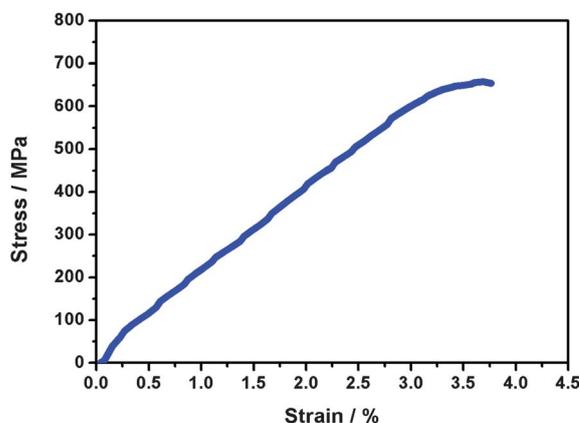


Fig. 6 A typical stress–strain curve of a CNT/PAA composite fiber with the monomer concentration of 8.05 mol L^{-1} and crosslinking degree of 0.24%.

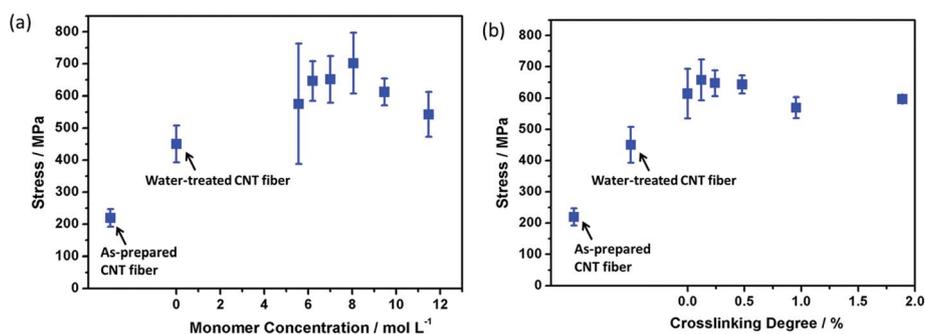


Fig. 7 (a) Dependence of the tensile strength on the monomer concentration with the same crosslinking degree of 0.12%. The monomer concentration of 0 mol L⁻¹ corresponds to the CNT fiber after a treatment of pure water. (b) Dependence of the tensile strength on the crosslinking degree with the same monomer concentration of 8.05 mol L⁻¹.

However, with the further increase in the monomer concentration beyond a critical point, more PAA chains with higher molecular weights aggregate and hinder the effective coating of CNTs (Fig. S1†). Some of them may even disturb the original alignment of CNTs. As a result, the strength of composite fibers gradually decreases with further increase in the monomer concentration. Therefore, a peak value was observed for the monomer concentration.

The dependence of the tensile strength on crosslinking degree was also carefully investigated, and representative data are compared in Fig. 7b. It was found that the tensile strength first increases with the increase in the crosslinking degree and then decreases. A strong peak typically appeared at the crosslinking degree of 0.12%. This phenomenon may be explained by the following reasons. Polymer chains are introduced to decrease the slippage among CNTs by interconnecting them, so the addition of the crosslinker improves the above interconnecting effects. The higher the crosslinking degrees, the larger the forces needed to cause the slippage. As a result, the tensile strength increases with increase in the crosslinking degree. On the other hand, the polymer crystallinity decreases at higher crosslinking degrees, which reduces the tensile strength of a composite fiber. In fact, the absolute values of the crystallization enthalpies of PAA decreased from 130.81, 111.41, 53.44, 13.44, to 8.47 J g⁻¹ with the increasing crosslinking degrees from 0, 0.12%, 0.24%, 0.48%, to 0.95%, respectively. These two opposite effects lead to a peak value at a critical crosslinking degree.

It should be noted that for the same group of samples, the critical concentration of ~8.05 mol L⁻¹ and optimal crosslinking degree of ~0.12% were always observed, and the above data could be reproduced. However, for different groups, the values of tensile strength for the composite fibers under the same concentration and crosslinking degree slightly varied as the parameters such as number density and organization of the CNTs in the building array were changed a little during the synthesis by chemical vapor deposition.

Electrical properties of the pure CNT and CNT/PAA composite fibers had also been studied in this work. For a pure CNT fiber, the electrical resistance decreased after a water treatment as the produced capillary forces during the evaporation of the water increased the contacts among the CNTs. In other words, the CNTs packed closer and decreased the contact resistance which has been shown to be the main contribution to

the CNT fiber electrical resistance.¹¹ In fact, the pure CNT fibers shrink by ~16% in diameter after water treatment. To better demonstrate the impact of PAA on the fibers electrical properties, comparisons have been made between the CNT/PAA fibers prepared by the *in situ* polymerization method and the water-treated pure CNT fibers.

It was found that the composite fibers show a decreased electrical resistance compared with the water-treated pure CNT fibers (Fig. 8a). Generally, the introduction of insulating polymers increases the electrical resistance of the resulting CNT composite fibers. The unexpected decrease in our observations is due to the interconnecting effects of the PAA molecules to bundle the CNTs more closely, which decreases the contact resistance of CNTs in the composite fibers. In fact, the CNT/PAA composite fibers further shrank by 8–18% in diameter compared with the water-treated pure CNT fibers. Fig. 8b has transformed the electrical resistance to electrical conductivity. Although the electrical conductivity of the CNT/PAA composite fibers generally increases compared with the water-treated pure CNT fibers, no obvious dependence of the conductivities on the monomer concentration has been observed. The electrical conductivity of CNT/PAA fibers has on average increased by 110% compared with the as-prepared pure CNT fibers, and by 50% compared with the water-treated pure CNT fibers. Currently, the CNT/PAA fibers prepared by the *in situ* polymerization method easily achieve 350 S cm⁻¹ at room temperature. As a comparison, the conductivity of a CNT/PAA fiber prepared by the direct incorporation of PAA obviously decreased compared with the water-treated pure CNT fibers. As another comparison, the CNT/silica fibers showed a much decreased electrical conductivity such as 121 S cm⁻¹ from 256 S cm⁻¹ of the building pure CNT fibers.¹⁵ Fig. 8c and d show the relationships between the electrical resistance and conductivity and the crosslinking degree, respectively. No obvious dependence of the electrical property on the extent of crosslinking was observed either.

It should be emphasized that the synthesized CNT/polymer fibers by this *in situ* polymerization method have not been optimized with regard to the used pure CNT fibers, the selections of monomers and/or crosslinkers, and the structures of the composite fibers. Both mechanical strength and electrical conductivity of the composite fibers can be further greatly increased by optimizing the above parameters. For instance, if

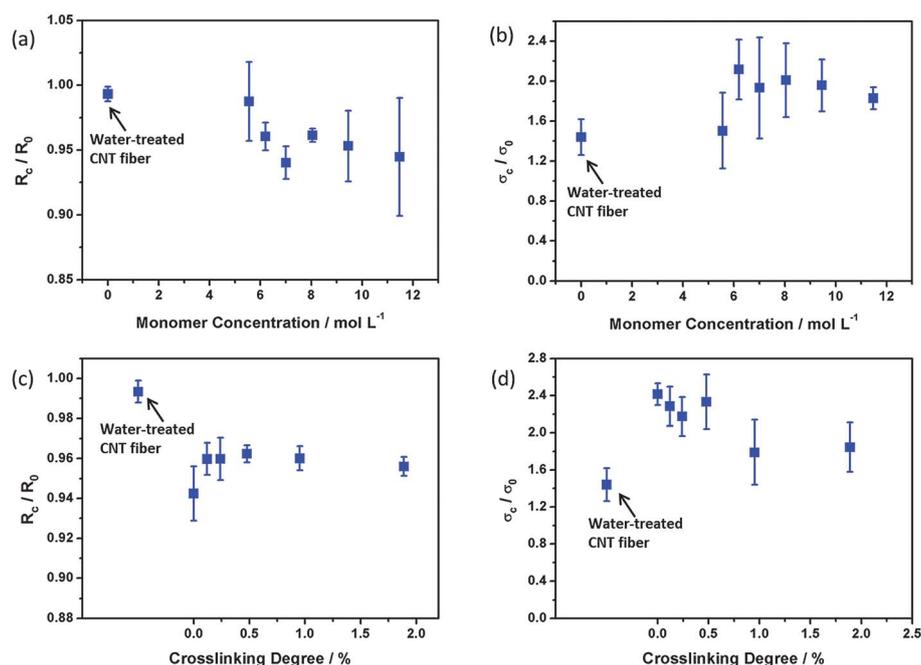


Fig. 8 (a) Dependence of the resistance ratio on the monomer concentration with the same crosslinking degree of 0.12%. (b) Dependence of the conductivity ratio on the monomer concentration with the same crosslinking degree of 0.12%. (c) Dependence of the resistance ratio on the crosslinking degree with the same monomer concentration of 8.05 mol L⁻¹. (d) Dependence of the conductivity ratio on the crosslinking degree with the same monomer concentration of 8.05 mol L⁻¹. R_0 and R_c correspond to the electrical resistance of a pure CNT fiber and the resulting composite fiber, respectively. σ_0 and σ_c correspond to the electrical conductivities of a pure CNT fiber and the resulting composite fiber, respectively.

a diacetylenic acid was used as the monomer followed by the *in situ* polymerization, the resulting composite fiber showed a mechanical strength up to 1.3 GPa. More efforts are under way to further improve their mechanical and electrical properties.

Conclusions

In summary, as widely reported, it remains challenging to simultaneously increase the mechanical strength and the electrical conductivity of the CNT fibers by the introduction of a second phase. The direct incorporation of polymers increases strength but decreases conductivity, while the acidic treatment or metal nanoparticle coating increases conductivity but decreases strength.³⁰ Here we have developed a simple fabrication methodology to synthesize CNT/PAA fibers through the incorporation of a monomer followed by *in situ* polymerization. The resulting composite fibers show both an increased mechanical strength and an improved electrical conductivity compared with either the pure CNT fibers or the CNT/polymer fibers fabricated by the direct incorporation of polymers. The combined excellent mechanical and electrical properties prove them as a new family of electrodes for various optoelectronic and electronic devices. The dye-sensitized solar cell based on such a fiber structure had been found to exhibit high efficiency (Fig. S2†), and a detailed study on this issue will follow soon.

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