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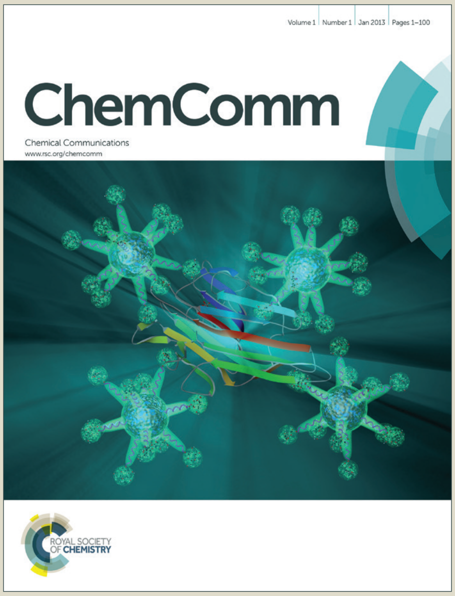
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Efficient Multiple Healing Conductive Composite via Host-Guest Inclusion

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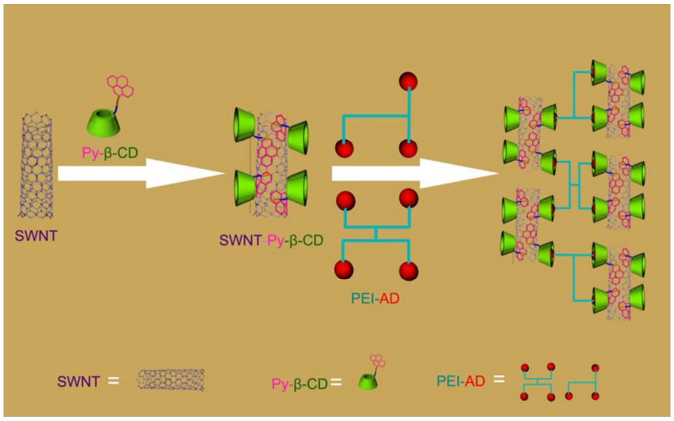
A self-healable conductive composite is developed by combining the small molecules and nanotubes through host-guest interactions. This material shows uniform conductivity, microwave absorption and humidity sensing properties, and can be rapidly healed to over 90% electrical and mechanical properties with the aid of water for multiple times. In addition, the produced material is also remouldable and recyclability.

Driven by the motivation of developing advanced reliable and durable materials, there has been intense research into self-healing materials.[1] But up to now, most self-healing materials are structural materials.[2] The research about functional materials with self-healing property is relatively rare.[3]

Electrically conductive materials are a kind of functional materials and are indispensable in the development of various modern electronics.[4] Restoration of conductivity of an electronic component could be of great significance for building advanced electronics.[5] A few healable conductive materials have been developed.[6] For example, Bielawski etc. firstly fabricated self-healing conductor by introducing reversible bonds into conductive polymers which were consist of N-heterocyclic carbenes and transition metals,[7] but the healing process requires high temperatures and solvent vapor. Polymeric microcapsules incorporated with conductive species as healing agent were also explored to create self-healing conductive materials.[8] When a mechanical damage was exerted to the capsules, these capsules were ruptured and the conductive species were released to the damaged region. Hence, the conductivity was restored. This capsule-based method is fast, efficient, and the healing process is autonomous.[9] But the healing is not repeatable at a given place and does not allow simultaneous structural healing. Another alternative method is to impart the self-healing ability of polymers to inorganic conductive materials (such as Ag, μNi, and nanotube).[10] These materials heal themselves either by manually bring the broken conductors into contact or with the aid of stimuli.[11] However, among these materials, hydrogen-bonded materials suffer from the slow healing speed and poor tolerance to moisture, and multilayer films deposited silver nanowires show nonuniform electrical properties from interior to surface. Developing conductive materials that possess parameters including uniform conductivity, fast self-healing speed, both electrical and mechanical healing capability, and repeatable healing capability is still a challenge.

In this paper, we design a composite material by combining the small molecules and nanotubes through host-guest interactions. The resultant composite shows uniform conductivity, and can be rapidly healed to over 90% electrical and mechanical properties with the aid of water for multiple times. In addition, the produced material is also remouldable and recyclability. β-Cyclodextrin-decorated single-walled carbon nanotubes (β-CD-SWNT) acted as macro-crosslinker, and endowed the composite with mechanical strength and conductivity. The host-guest interactions between β-CD-SWNT and adamantine acetic modified polyethylenimine oligomer (PEI-Ad) are the healing motifs.



Scheme 1. Schematic illustration of the preparation of SWNTs-β-CD/PEI-Ad complex.

β-CD-SWNTs were obtained by using π-π interaction between SWNT and pyrene modified β-CD (Py-β-CD, scheme 1). The FT-IR spectroscopy (Fig. S7) indicated that SWNTs -β-CD showed similar curve to the Py-β-CD. UV-VIS-NIR spectra (Fig. S8) showed that the pyrene absorption peaks of SWNTs-β-CD were slightly red shifted (2-3 nm) compared with that of Py-β-CD, suggesting π-π stacking between SWNTs and pyrene moieties of Py-β-CD.[12] Thermogravimetry analysis (TGA) results (Fig. S9) showed that the weight percentages of Py-β-CD in SWNTs -β-CD hybrid were 68 wt%.

Ad-PEI was prepared by the reaction of 1-adamantaneacetic acid with low-molecular-weight PEI (Mw=1800). ^{1}HNMR data (Fig. S10) indicated that the degree of substitution were 24.1%, which meant that each PEI-Ad chain containing 3.6 Ad groups.

SWNTs-β-CD/PEI-Ad complex was prepared by mixing SWNTs-β-CD and PEI-Ad aqueous solution (the molar ratio of β-CD and Ad was 1:5). After fully mixing, we got a plasticine-like compound, which can be moulded. Dry the product 48 h in vacuum at 40 ºC, a homogenous stiff material was obtained. It is known that β-CD could interact with adamantane and its derivatives to form stable inclusion complexes.[13] Therefore, the SWNTs-β-CD/PEI-Ad complex probably had two kinds of non-covalent interactions: the hydrogen bonding between N-H and O-H, and interactions between Ad and β-CD. In order to confirm the role of the Ad-β-CD inclusion on the formation of supramolecular materials, we mixed PEI-Ad and SWNTs using the same method as a control sample. It was found that SWNTs/PEI-Ad was a pile of powder, which can't be moulded and form supramolecular aggregates, indicating that the inclusion between Ad and β-CD played a key role on the formation of SWNTs-β-CD/PEI-Ad complex. It has been reported that the free β-CDs could act as competitive molecules to dissociate the complex of β-CD derivatives and guests.[14] So in another control test, SWNTs-β-CD/PEI-Ad samples were soaked in saturated β-CD solution and aqueous solution respectively for 48 h. It was found that the sample soaked in β-CD solution was dissociated after dried in vacuum, while the sample soaked in aqueous solution kept compact and can realize self-healing (Fig. S12). This result also demonstrated the host-guest interactions between SWNTs-β-CD and PEI-Ad are the key factors for the formation of supramolecular composite.

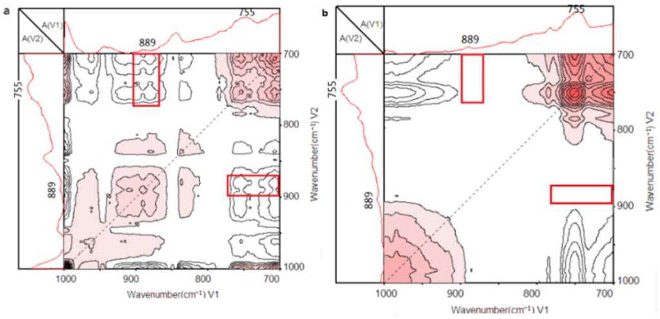


Fig. 1 Synchronous 2D IR correlation spectra is corresponding to the region of 1000-700 cm^{-1}. (a) SWNTs-β-CD/PEI-Ad complex; (b) Physical mixture of SWNTs-β-CD and PEI-Ad.

The interaction between Ad and β-CD in the SWNTs-β-CD/PEI-Ad complexes was investigated by two-dimensional infrared spectroscopy (2D-IR), which has been proved a powerful tool for studying the molecular interactions in many systems.[15] According to the theory of 2D-IR developed by Noda et al.,[16] a cross-peak is generated when two dipole-transition moments associated with the molecular vibrations of different functional groups are reorienting simultaneously. Such cooperative motion of the local structures is expected when strong interactions exist among different groups.[17] Fig. 1 showed the synchronous 2D correlation spectra of SWNTs-β-CD/PEI-Ad complex (a) and physical mixture of SWNTs-β-CD and PEI-Ad (b) in the 700–1000 cm^{-1} region constructed from 25 to 160 ºC. It can be seen that in the case of SWNTs-β-CD/PEI-Ad complex, feature of Ad at 889 cm^{-1} showed correlation with the feature of β-CD (755 cm^{-1}).[15] While this cross-peak almost disappeared in the physical mixture of SWNTs-β-CD and PEI-Ad map. These results meant that Ad and β-CD groups in the SWNTs-β-CD/PEI-Ad complex strongly interacted with each other due to the formation of inclusion complexes. On the contrary, in the physical mixture, it did not exist interaction between Ad and β-CD (Fig. 1b). And it further demonstrated that the SWNTs-β-CD/PEI-Ad complexes were supramolecular materials containing Ad-β-CD cross-links.

The cross-sectional scanning electron microscopy (SEM) images (Fig. 2A) of SWNTs-β-CD/PEI-Ad complex revealed that the SWNTs randomly entangled to form a high density of junction, which is the key factor in the conductivity of SWNTs-β-CD/PEI-Ad. The conductivity of samples was 0.15 $s \cdot m^{-1}$ in the ambient condition, slightly lower than that of SWNTs-β-CD (0.57 $s \cdot m^{-1}$). It was found that the conductivity of SWNTs-β-CD/PEI-Ad sample was almost keep constant whatever variation of the distance between the probes, implying the homogenous and a lack of phase aggregation of nanotubes in the composite.

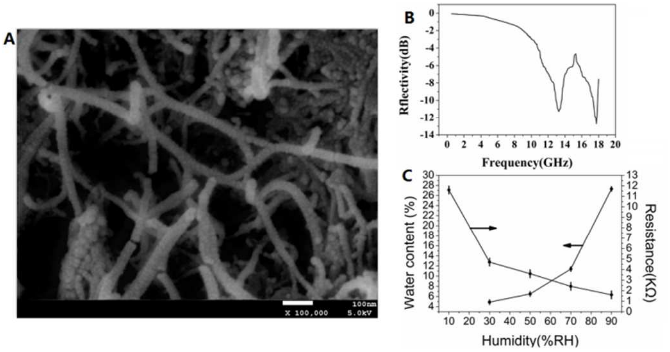


Fig. 2 (A) SEM images of the fracture surface of the SWNTs-β-CD/PEI-Ad complex (scale bar of 100 nm （× 100000）); (B) The reflection loss of the SWNTs-β-CD/PEI-Ad complex as a function of frequency, for the thickness d=3 mm; (C) The relationship between relative humidity and water content and the influence of humidity on resistance.

Large amount of nanotubes also endowed SWNTs-β-CD/PEI-Ad composite with good microwave absorption properties. Recent studies have demonstrated that nanotubes show strong microwave absorption with a matrix of polymer because of their capable of generating dielectric and magnetic losses when impinged by an electromagnetic wave.[18] In this study, we measured the permittivity and permeability of SWNTs-β-CD/PEI-Ad sample and calculated the reflection loss of samples (the thickness of sample was 3 mm).[19] As shown in Fig. 2B, SWNTs-β-CD/PEI-Ad samples showed two absorption peaks at 13.3 and 17.7 GHz. The frequencies range for absorbing values exceeds 5 dB (11-15, 15.4-18 GHz) is 7 GHz, which is approximately consistent with the results of CNTs/EP.[19b`]

It should be noticed that the SWNTs-β-CD/PEI-Ad composite showed moisture absorption capacity in the ambient condition due to the hydrophilicity of the amino groups. As shown in Fig. 2C, the water absorption of the SWNTs-β-CD/PEI-Ad composite increased with the relative humidity (RH) increasing. This moisture absorption capacity caused that the resistance of SWNTs-β-CD/PEI-Ad composite was sensitive to the RH of environment. It can be seen that the resistance of samples was around 11.6 kΩ in dry air (RH 10%), which was about 4 times that in 50% RH air and 8 times that in 90% RH air. On the basis of this humidity sensitive property, a humidity sensor based on SWNTs-β-CD/PEI-Ad composite should be further fabricated.

Unlike other humidity sensors, SWNTs-β-CD/PEI-Ad composite showed ability to restore electrical conductivity after damage. As shown in Fig. 3A, the as-prepared rectangular SWNTs-β-CD/PEI-Ad sample was connected in a circuit with a commercially available light emitting diode (LED) bulb. The LED bulb was lit with a DC voltage of 3.0 V to ensure appropriate brightness (Fig. 3A1). Then, the SWNTs-β-CD/PEI-Ad sample was cut into two pieces using a scissors and the LED bulb went off immediately (Fig. 3A2). When deionized water was dropped on the cut (Fig. 3A3), the opposite halves of the samples self-healed and the healing time was less than 5 min. This healed sample made the LED bulb bright again (Fig. 3A4, ESI Movie 1). We defined the conductive healing efficiency as the proportion of conductivity restored relative to the original one. Fig. 3B and Fig. 3C showed that successive cuts at the same location were also healed with conductive healing efficiency near 100 %, indicating excellent repeatable restoration of electrical performance of SWNTs-β-CD/PEI-Ad composite.

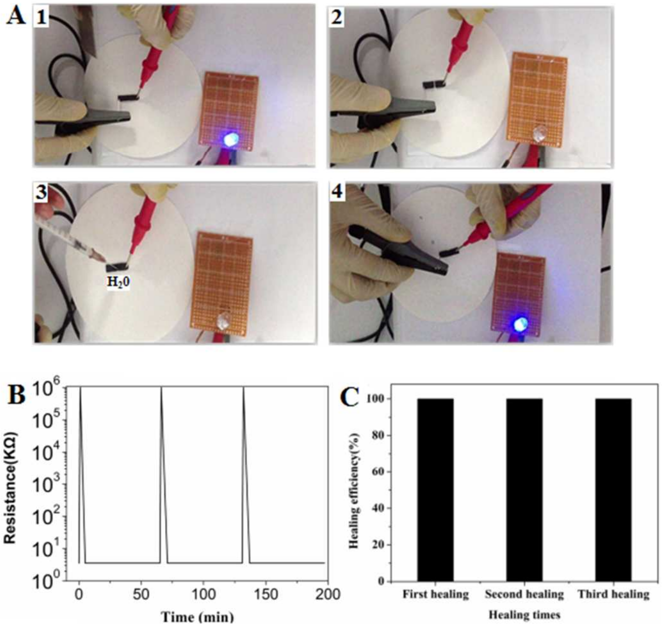


Fig. 3 (A) Demonstration of the healing process for the SWNT-βCD/PEI-Ad (1) As-prepared sample; (2) The sample was cut; (3) Deionized water was dropped on the cut; (4) The sample was healing. The whole movie is also available in the ESI; (B) Repeated electrical healing for three cuts at the same severed location; (C) The conductive healing efficiencies of the sample for the first, second and third healing. (50-60% RH, room temperature)

The mechanical self-healing property of SWNTs-β-CD/PEI-Ad composite was investigated by comparing the tensile strengths of composite as-prepared and after self-healing. The mechanical healing efficiency (η_{mech}) was defined as the proportion of tensile stress at break relative to that of the original sample. As shown in Fig. 4A, the mechanical properties were healed very well. After the first self-healing cycle, the η_{mech} of the composite is 93% at room temperature. After the third cycle, the η_{mech} was still 86%. The slightly strength loss during the healing cycles was possibly due to remnant defects at the site of initial fracture.

Both hydrogen bonds and Ad-β-CD host-guest interactions may benefit to the self-healing of SWNTs-β-CD/PEI-Ad composite. Hydrogen bonding self-healing behavior always need long time (over hours) to heal to 90% of its original tensile strength and the self-healing efficiency drop rapidly if the damage surfaces are left in ambient air due to absorption of moisture.[11b,20] But the self-healing relies on inclusion interactions between host and guest has quite high healing rate and is positively affected by moisture.[15, 21] For SWNTs-β-CD/PEI-Ad sample, moisture was benefit for the healing and the self-healing was quite quickly. Therefore, the Ad-β-CD interactions played a key role in the self-healing of SWNTs-β-CD/PEI-Ad composite. As shown in Fig. 4B, when a SWNTs-β-CD/PEI-Ad sample was cut into pieces, many Ad-β-CD links were dissociated near the fracture surface because the strength of the inclusion interactions had to be lower than that of covalent bonds. These non-associated groups are 'eager' to link together, therefore, Ad-β-CD reformed across the interface when broken pieces were pressed together. As a result, the sample self-healed. It should be noted that the water is also able to "glue" the other parts of material together (detail discussion was provided in Supplementary Information), just like other water-healing materials.[22]

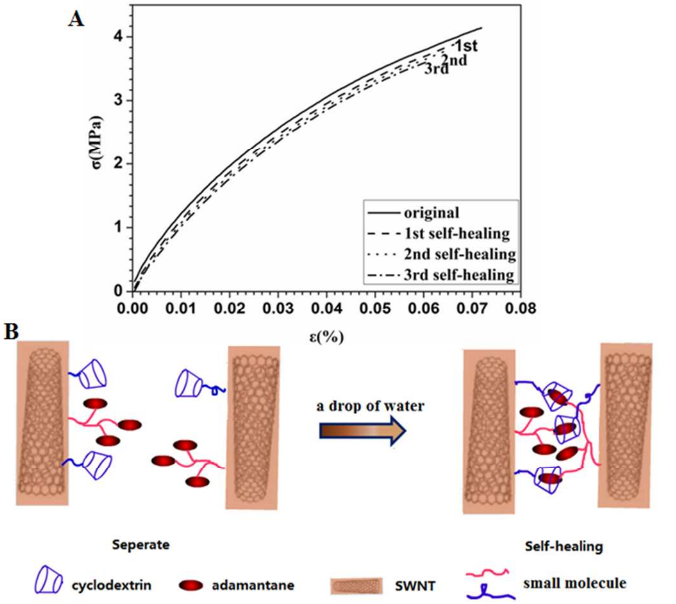


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Fig. 4 (A) Stress–strain curves of SWNTs-β-CD/PEI-Ad as-prepared sample and healed samples on different healing times at room temperature,50-60% RH; (B) Schematic representation of water-enabled healing of the sample.

Nowadays, conductive polymer composites have been found wide applications in many areas, however, the recycling at the end of their life cycle is a very big challenge. Most of the conductive polymer composites products end up in landfills and result in serious environmental pollution. Even for self-healing conductive polymers developed very recently, although they have longer working life, only few materials are remouldable and recyclability. In the present work, SWNTs-β-CD/PEI-Ad composite was found full recyclability and reworkability. It has been reported that Ad-β-CD is easily decomplexation at high temperature in water.[23] As shown in Fig. 5, the SWNTs-β-CD/PEI-Ad composite easily disassembled into small granulates by heating above 60 ºC in water due to the dissociation of β-CD-Ad. Then, at room temperature, the small granulates can be remended into rectangular bars. This cycle can be repeated several times.

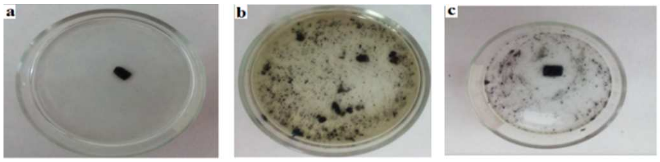

Fig. 5 The recycling of the SWNTs-β-CD/PEI-Ad complex. (a) As-prepared sample; (b) The sample was heated in 60 ºC water bath; (c) Out of the solvent in the samples and remended the granulates at room temperature.

In summary, a supramolecular composite with conductivity, wave absorption properties, and humidity sensitivity has been achieved through host-guest interactions between SWNTs-β-CD and PEI-Ad. This material shows good electrical and mechanical self-healing capability in fast healing rate in ambient environment. Furthermore, SWNTs-β-CD/PEI-Ad are full remouldable and recyclability. It is the first time to use host-guest interactions as healing motif for the self-healing conductive materials. Compared to hydrogen-bonding based self-healing systems, the host-guest systems may offer advantages of having much slower healing decay rate in ambient conditions. We anticipate that other self-healing polymer systems might also benefit from such a functional composite strategy to enable new electronic functionalities.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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