Supramolecular Carbon Nanotube Films Adaptive to Thermoelectrics

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Abstract. We present a rational route to stable carbon nanotubes, where supramolecular chemistry is important for stabilizing ionic bonding between charged nanotubes and counter ions. Developed SWNT materials, which are stable in air, at 100 °C, could readily be implemented to thermoelectric power generators.

1. Introduction
Some challenges in sustainable energy supply and powering remain to be solved in the near future. Thermoelectrics is a technique that immediately converts temperature difference into electric potential difference. Unlike conventional turbine generators with high pressure gases and large facilities, thermoelectric generators can produce power from small temperature differences and therefore can be widely applied in the recovery of waste heat from currently untapped sources such as commercial buildings and industrial plants. In addition, it can be expected that a lot of waste heat is potentially used as supplementary power for mobile vehicles (cars, buses, etc.) and information technology (IT) equipment including security and medical devices. In particular, the application of flexible and lightweight thermoelectric generators will be expanded in applications above. Importantly, for practical thermoelectric power conversion materials in a temperature range lower than 400 K, flexibility is crucial to cover and adhere closely to the heat sources that emit low thermal radiation.

Single-walled carbon nanotubes (SWNTs) are promising active thermoelectric materials owing to their narrow bandgap energy and high charge carrier mobility. Indeed, single-walled carbon nanotubes (SWNTs) show relatively high thermopower at room temperature. Thermoelectric modules mostly require both p-type and n-type materials. However, it has long been difficult to prepare air-stable n-type SWNTs because negatively-charged carbons, called carbanions, are highly reactive to electron acceptors such as oxygen. Additionally, the tuning of doping level is inevitable for optimizing thermoelectric properties. In order to solve these issues, here we introduce several approaches to the reliable doping of SWNTs.

2. Results and discussion

2.1. A general concept
A large positive charge over
a large molecular complex

Negative charges over
a long-range carbon framework

Figure 1. A schematic illustration of charge balanced n-type SWNT anion-metal cation complexes

We investigate the chemical doping of SWNTs in terms of non-covalent molecular interactions. Particularly, we attribute charged SWNTs to molecular ions, which enables the rational design of stable ion-pair complexes (Fig. 1) [2-6]. A charge could be delocalized over several carbon atoms through $\pi$-conjugation. Such charge is then compensated by a counter charge; for example, a negative charge doped into SWNTs can be stabilized by complexation with cations. In this situation, charge density balance between positive and negative charges is important for the stabilization; the “hard/soft acids/bases (HSAB)” rule is adopted [7].

2.2. Phosphine functionalization

Figure 2. Prototype, flexible thermoelectric power generators equipped with p-type and n-type doped SWNT films. (a) flexibility. (b) Temperature-dependent thermovoltage generation.

Strategies for conventional molecular doping mostly rely on the use of amine-functional compounds. However, SWNTs functionalized with amines readily lose their n-type characteristics in air. We here
used phosphines [1]; phosphonium generated after charge transfer could be a counter ion for n-type SWNTs. A series of phosphine derivatives successfully formed n-type SWNTs and their SWNT composites showed moderate air-stability. The encapsulation of molecular dopants inside the hollow inner space of SWNTs leads to the progression of n-type doping [3]. Furthermore, they can be integrated into flexible thermoelectrics that can recover any waste heat (Fig. 2).

2.3. The functionalization of crown ether complexes

![Figure 3](image)

**Figure 3.** Time-course measurement of thermoelectric properties of n-type doped SWNTs with potassium (K⁺)-benzo-18-crown complexes.

Molecularly-doped n-type SWNTs coordinated with large cationic complexes show unprecedented air- and thermal stability [2]. We used supramolecular complexes based on crown ethers as counter cations to n-type SWNTs; they spontaneously form complexes with alkali metal ions such as sodium (Na⁺) and potassium (K⁺) ions in polar solvent. Particularly, potassium complexes with benzo-18-crown ethers gave a SWNT composite showing air-stability above 100 °C (Fig. 3).

2.4. Organic dye supramolecular systems

Triarylmethane derivatives in their basic and reduced forms show excellent n-type doping ability against SWNTs, resulting in their stabilization in air [4,5].

2.5. Hole doping

![Figure 4](image)

**Figure 4.** (a) A schematic of electrolyte-SWNT interactions. (b) Anion-dependent thermoelectric properties of polyelectrolyte-SWNT composites.
The p-type doping of SWNTs, and its stabilization are demonstrated by the complexation with charge-delocalized complex anions such as bis(trifluoromethanesulfonyl)imide (TFSI) (Fig. 4). The stable p-type doping of SWNTs is also developed using polyelectrolytes [6]; solid-state absorption and photoelectron spectroscopy reveal that the adsorption of electrolytes induces hole transfer to SWNTs.

3. Conclusion
We have demonstrated a rational strategy for successful amphoteric chemical doping to SWNTs. Additionally, these stable doped SWNTs were integrated into flexible and robust power modules enabling thermal-to-electricity conversion below 100 °C. The flexible thermoelectric power generator is, in near future, expected to harness electrical power from industrial plants and many other heat sources such as vehicles, and buildings, boosting energy-saving efforts in the fight against global warming.

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