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TIF Progress Report

Functionalized Carbon Nanotubes as Novel Supercapacitor Electrode Materials

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Contract Number: W7707-06-3363/001/HAL

Contract Project Manager: Dr. C. Cameron, 902-427-1367

Contract Scientific Authority: Dr. T. Huber, 250-363-5715

Defence R&D Canada – Atlantic

Contract Report
DRDC Atlantic CR 2007-272
December 2007

Canada

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Abstract

Significant progress has been made in the direction of nanotube functionalization with polymers. The initial approach, which involved the introduction of a non-conjugated polymer (poly(styrene sulfonate)) was found to result in films that were poorly conducting and would likely not be suitable for supercapacitor applications. We therefore turned our attention to the introduction of conjugated polymers on the nanotube surface. Using the Suzuki coupling protocol that was described in the previous report, we have prepared a series of nanotubes that are covalently functionalized with conjugated polymers. In addition we have begun the preparation of supramolecularly-functionalized nanotubes, in which the pristine nanotube structure is preserved. These materials have been used to produce thin films, and the conductivity of these films has been investigated.

Résumé

Des progrès importants ont été réalisés dans le domaine de la fonctionnalisation de nanotubes au moyen de polymères. Il a été établi que l'approche initiale, consistant à intégrer un polymère non-conjugué, soit le sulfonate de polystyrène, donne des pellicules de piètre conductibilité, qui ne pourraient vraisemblablement pas être utilisées pour fabriquer des supercondensateurs. Nous avons donc décidé d'étudier l'ajout de polymères conjugués à la surface des nanotubes. On a utilisé le protocole de couplage de Suzuki, décrit dans un rapport antérieur, pour préparer une série de nanotubes fonctionnalisés formant des liaisons covalentes avec des polymères conjugués. Nous avons aussi amorcé des travaux de préparation de nanotubes fonctionnalisés à l'échelle supramoléculaire qui permettent de préserver la structure initiale du nanotube. Ces matériaux ont servi à produire des couches minces qui ont fait l'objet d'études de la conductibilité.

Executive summary

TIF Progress Report: Functionalized Carbon Nanotubes as Novel Supercapacitor Electrode Materials

A. Adronov; DRDC Atlantic CR 2007-272; Defence R&D Canada – Atlantic; December 2007.

Introduction: The military has a requirement for high pulse power, which is not met by conventional energy storage devices. Supercapacitors are energy storage devices that exhibit higher power density than batteries and fuel cells, and higher energy density than conventional capacitors. These characteristics make supercapacitors promising as high pulse power sources. The goal of the Supercapacitor TIF, under which this contract falls, is to develop a supercapacitor device to be used in conjunction with a high energy density source, such as a battery or fuel cell. The resulting hybrid configuration is a relatively lightweight source of power, in which the supercapacitor component may be quickly discharged, delivering the transient power required, then quickly recharged by the high energy density component. Materials which are especially suited as electrodes in supercapacitors are those that exhibit high electrical conductivity and high surface area. Another critical characteristic for such materials is a favourable porosity distribution that maximizes surface area and allows for electrolyte ion mobility. The development of polymer □carbon nanotube composites that possess these properties is the focus of this contract. This contract report summarizes progress at McMaster University in the first year of the Supercapacitor TIF project.

Results: First generation materials, prepared with non-conjugated polymers, resulted in films that were poorly conducting, thus attention was turned to the introduction of conjugated polymers. A series of nanotubes covalently functionalized with conjugated polymers was prepared and investigated. In addition, the preparation of supramolecularly-functionalized nanotubes was achieved, and allowed the production of thin films with interesting conductivity properties.

Significance: The electrical conductivity of some of the materials made is surprisingly high and may indicate significant charge transfer between the polymer and the nanotubes. Maximizing the conductivity and microstructure, as a function of polymer packing, may result in the development of lightweight materials that function well as supercapacitor electrodes, for high pulse power applications.

Future plans: The capacitance of the films will be determined, as well as more accurate conductivity determination using thicker films. In addition, the films will be characterized more extensively, especially with respect to microstructure and surface area.

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TIF Progress Report: Functionalized Carbon Nanotubes as Novel Supercapacitor Electrode Materials

A. Adronov; DRDC Atlantic CR 2007-272; R & D pour la défense Canada – Atlantique; Décembre 2007.

Introduction ou contexte: Les dispositifs classiques de stockage d'énergie ne répondent pas aux besoins du secteur militaire en matière de sources d'énergie à impulsions élevées. Les supercondensateurs sont des dispositifs de stockage d'énergie qui offrent une puissance volumique supérieure à celle des accumulateurs et des piles à combustibles et une densité d'énergie supérieure à celle des condensateurs classiques. Les caractéristiques des supercondensateurs sont d'un grand intérêt, car ceux-ci pourraient constituer des sources d'énergie à impulsions élevées. Le projet du FIT portant sur les supercondensateurs, dans le cadre duquel les présents travaux sont réalisés, a pour but de mettre au point un dispositif de ce type pouvant être combiné à une source à forte densité d'énergie, par exemple un accumulateur ou une pile à combustible. L'ensemble hybride constitue une source d'alimentation relativement légère; dans un tel assemblage, le supercondensateur peut être rapidement déchargé pour fournir la puissance transitoire requise, puis être rapidement rechargé au moyen du composant à forte densité d'énergie. Les matériaux qui pourraient être utilisés pour fabriquer des électrodes de supercondensateurs sont ceux qui possèdent une conductivité électrique et une surface efficace élevées. Parmi leurs autres caractéristiques cruciales, on compte la répartition favorable de la porosité, qui optimise la surface efficace du matériau et favorise la mobilité ionique de l'électrolyte. Les travaux exécutés dans le cadre du présent contrat portent principalement sur l'élaboration de composites de polymères et de nanotubes de carbone qui possèdent les propriétés susmentionnées. Le présent rapport contient un résumé des progrès réalisés dans les installations de l'Université McMaster au cours de la première année du projet du FIT sur les supercondensateurs.

Résultats: Les matériaux de première génération préparés avec des polymères non-conjugués ont permis de produire des pellicules ayant une piètre conductibilité; notre attention s'est donc portée sur l'ajout de polymères conjugués dans les composites. On a préparé et étudié une série de nanotubes fonctionnalisés formant des liaisons covalentes avec des polymères conjugués. De plus, nous avons préparé des nanotubes fonctionnalisés à l'échelle supramoléculaire qui permettent de produire des couches minces possédant des propriétés de conductibilité d'un grand intérêt.

Importance: La conductivité électrique de certains des matériaux obtenus est étonnamment élevée, ce qui pourrait indiquer qu'il se produit un important transfert de charges entre le polymère et les nanotubes. En maximisant la conductibilité et la microstructure en fonction de la densité de l'arrangement des chaînes de polymère, on pourrait obtenir des matériaux légers pouvant servir à fabriquer des électrodes de supercondensateurs utilisés comme sources d'énergie à impulsions élevées.

Perspectives: Les travaux porteront sur la détermination de la capacité des pellicules, ainsi que sur la mesure plus exacte de la conductibilité de pellicules plus épaisses. On entreprendra aussi

une caractérisation plus poussée des pellicules, notamment au chapitre de leur microstructure et de leur surface efficace.

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1 Results

1.1 Preparation of films from nanotubes functionalized with poly(styrene sulfonate) (PSS)

Using previously reported methodology,[1] we prepared PSS-SWNTs, which are soluble in water. An aqueous solution of the PSS-SWNTs was used to prepare thin films by the vacuum filtration method. Briefly, this involves filtration of a solution containing SWNTs through a porous membrane (Figure 1).[2-5] A nanotube film is formed upon the surface of the membrane, and can be dried and transferred to a suitable substrate or, if mechanical strength allows, removed as a freestanding film. The filtration process favours the formation of homogeneous films as nanotubes deposited upon the filtration membrane impede the flow of solvent through that region encouraging deposition of nanotubes upon uncovered areas of the membrane. Since nanotubes have a high aspect ratio, the filtration process generally causes them to orient themselves flat against the surface of the membrane. This ensures a high degree of connectivity contributing to both the mechanical strength and conductivity of the resulting film. Using the vacuum filtration procedure nanotube density and film thickness can also be controlled easily by altering the concentration or volume of solution used.

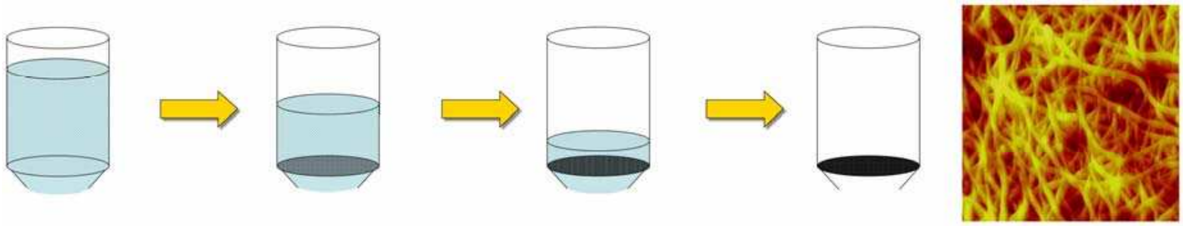


Figure 1. Schematic representation of nanotube thin film formation by filtration of a dilute nanotube solution through a porous membrane, with an AFM image of the resulting film at right.

This method was employed to prepare films of the PSS-SWNT material, which was compared to unfunctionalized nanotubes. It was found that the polymer-functionalized nanotube films are significantly more robust than films made from pristine nanotubes. The polymer-functionalized materials were highly flexible, while the ones from pristine nanotubes were brittle and would break if bent. To determine electrical conductivity properties, crude resistivity measurements were made using a multimeter. Unfortunately, the polymer-functionalized films exhibited high resistivity values, in the range of $\sim 10^5\ \Omega$. Compared to pristine nanotubes, for which the resistivities were measured to be in the range of $10\ \Omega$, the conductivity of the polymer-functionalized materials is quite poor. This result indicates that either the nanotubes become insulating due to their covalent functionalization (i.e., introduction of defects along the nanotube wall decreases conductivity significantly), or the insulating polymer that coats the nanotubes prevents electrons from hopping from one nanotube to the next, thereby diminishing conductivity.

These observations prompted us to investigate the use of conjugated polymers to functionalize the carbon nanotubes.

1.2 Preparation of SWNTs functionalized with conjugated polymers.

Using the Suzuki coupling protocol that we recently published,[6] we were able to covalently couple conjugated polymers to the nanotube surface via a conjugated linker, as depicted in Figure 2. This involved the initial use of the diazonium salt decomposition reaction to introduce iodophenyl functionalities onto the nanotube surface. The iodophenyl functionalities are highly reactive toward boronic esters, and initiate the polymerization from the nanotube surface. It should be noted that the aryl bromide monomers can also act react with the boronates, leading to the formation of free polymer in solution. However, the aryl iodides are much more reactive, leading to a significant degree of coupling to nanotubes. Any free polymer produced in solution as a result of this chemistry is easily removed by filtration through a 200 nm pore diameter Teflon membrane. The resulting materials (4 and 5) exhibited solubility in tetrahydrofuran (THF) of 100 and 350 mg/L, respectively.

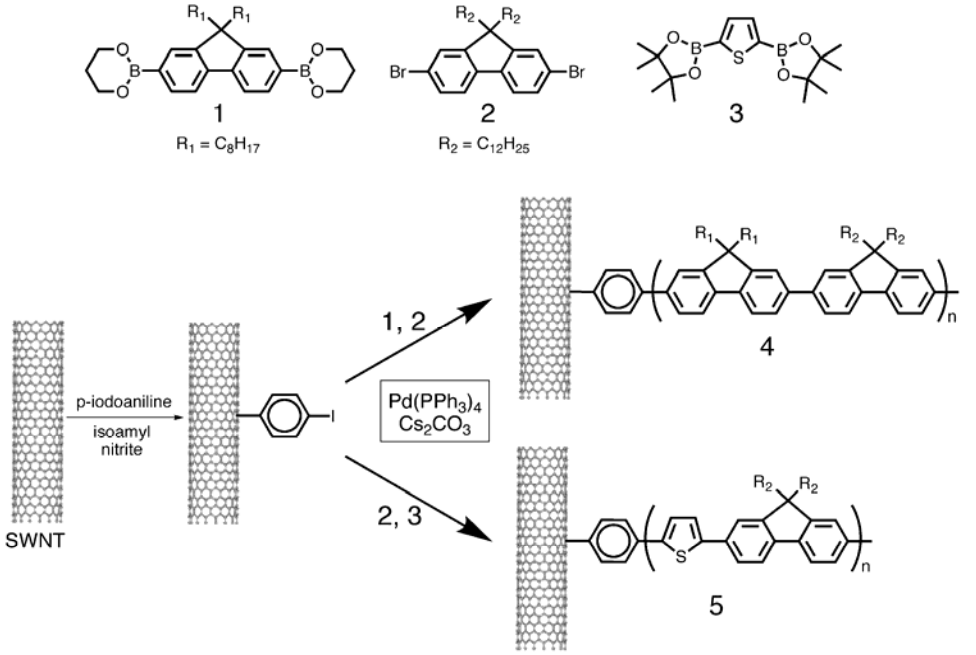


Figure 2. Suzuki polycondensation for the preparation of carbon nanotubes functionalized with conjugated polymers.

Films of these materials were also prepared by the filtration method and found to have similar mechanical properties (flexibility) to the PSS-SWNT sample (Figure 3). Similar conductivity measurements were made for these materials, and it was found that they also exhibit resistivities that are significantly higher than pristine nanotubes. Considering that the attached polymers in this case are conjugated, electron mobility between nanotubes through these polymers should not be impeded. It therefore seems that covalent functionalization of SWNTs leads to significantly diminished conductivity, and this is the main problem that must be overcome in achieving conductive materials.

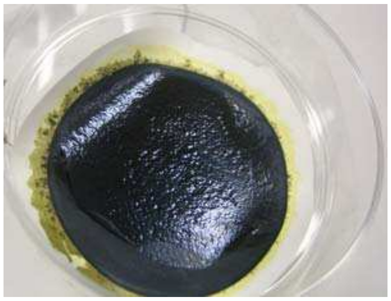


Figure 3. Photograph of nanotube film on membrane from sample 4.

1.3 Supramolecular functionalization of SWNTs with conjugated polymers.

To overcome the poor conductivity of covalently functionalized nanotubes, we have begun to prepare supramolecular assemblies of nanotubes with conjugated polymers (Figure 4). This has been found to result in irreversible binding of polymers to the nanotube surface, and produces highly soluble complexes. Thus far, four different conjugated polymers have been prepared and complexed to the nanotube surface. These include poly(fluorene) (6), poly(fluorene-co-thiophene) (7), poly(thiophene) (8), and a poly(porphyrin-diacetylene) (9). Polymers 6-8 were prepared by Suzuki coupling, while polymer 9 was prepared by the Glaser-Hay coupling of the alkyne-functionalized porphyrin. Using solutions of these compounds, we have prepared films by the filtration method and again found that they retain the flexibility properties of the previously mentioned polymer-functionalized materials. However, in this case, the conductivity of the films is practically identical to that of pristine nanotube films. These films will be used for supercapacitor applications in the coming months.

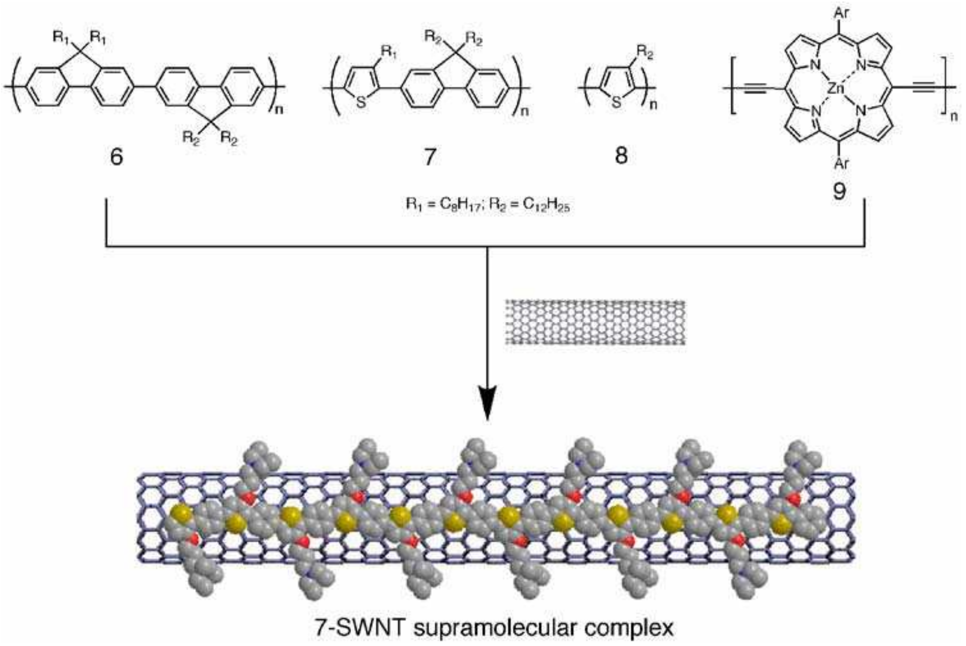


Figure 4. Supramolecular assembly of conjugated polymers onto the surface of SWNTs.

1.4 Conductivity measurements.

Samples of both covalent and non-covalent composites of polymers and nanotubes have been sent to Trish Huber for conductivity measurements. It was found that the conductivities of the supramolecular complexes was very good, as predicted by the crude measurements in our lab, but due to the extremely small thicknesses of these films, precise conductivity values could not be obtained (these require accurate thickness measurements that have not been accomplished yet). The measured values are provided below, along with the chemical structures of the compounds that correspond with each compound number (Figure 5).

Table 1. Conductivity data for nanotube thin films

Sample	**Sheet Resistance (Ω)**[*]	**Thickness (mm)**[†]	**Conductivity (S/cm)**
SWNT	0.70	0.09	160
Pt42-p	3.1	0.05	64
Pt42-s	6.5		
Pt40-s	1.4		
Fc22-s	40	0.04	6.2
Pt22	1.1×10^6		
Pt42 (glass slide)	1.4×10^3		
Pt40 (glass slide)	1.8×10^3		
Pt41 (glass slide)	37		
Pt41-s	3.9		

[*] technically the units are ohms per square

[†] (± 0.02 mm)

The results are reported in terms of sheet resistance because many of the films are so thin that the uncertainty is relatively very large, which can dramatically skew resistivity or conductivity values (which take thickness into account). In many cases, the thickness of the films is on the order of the uncertainty of the micrometer used, and varies across the sample. Thicker, more uniform films will be prepared in the near future so that more accurate conductivity measurements can be made.

For reference: the relationship between the sheet resistance (R_s) and conductivity (σ) is:

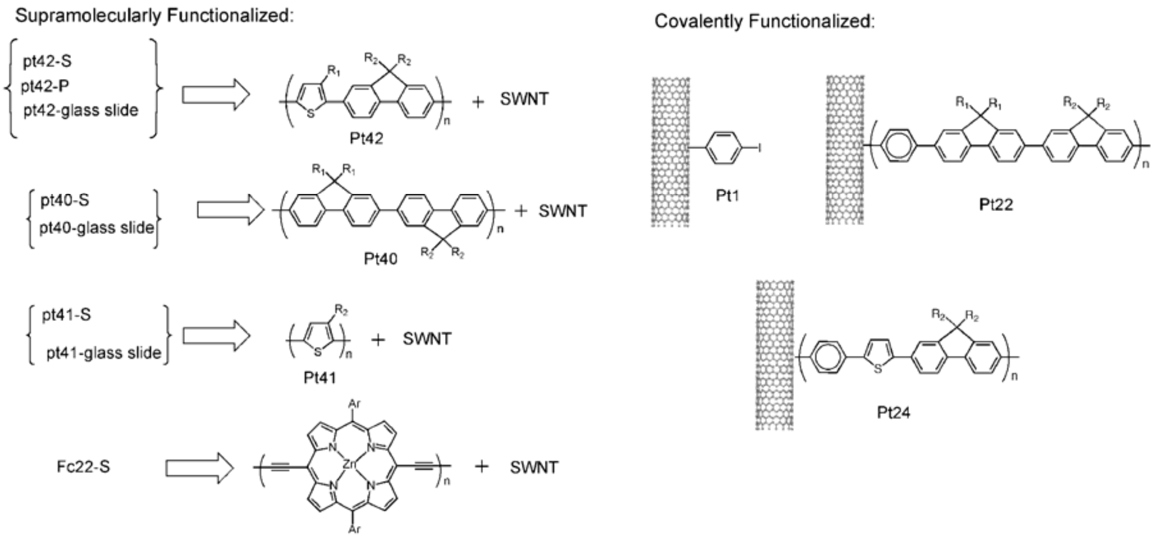
$$\sigma = \frac{1}{R_s \cdot t}$$

where t is the thickness in cm, thus σ has units of $(\Omega \cdot \mathrm{cm})^{-1}$, thus S/cm,

and $R_s = \frac{V}{I}(\text{size and shape correction factors})$

where V is the voltage drop between the inner two pins, and I is the current flowing between the outer two pins.

Therefore, a variation in thickness of ± 0.02 mm in sample Pt42-p can translate to a conductivity that ranges from 46 to 110 S/cm. Again, the small thickness introduces a large uncertainty, and this will need to be addressed in the near future.



S = soluble fraction; P = insoluble (precipitate) fraction
glass slide = sample transferred to a glass slide (very thin)

Figure 5. Compounds on which conductivity measurements were performed.

1.5 Future Work

Capacitance measurements will be performed on the films to assess the best candidates for further study. Either thicker films will be prepared, or more accurate means of measuring the thickness of the thin films will be investigated, in order to more accurately determine the electrical conductivity. Further characterization of the films is planned, including assessing the microstructure and surface area.

2 References

[1] Li, H. M.; Adronov, A. *Carbon* **2007**, in press.

[2] Wu, Z. C.; Chen, Z. H.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. *Science* **2004**, *305*, 1273-1276.

[3] Hennrich, F.; Lebedkin, S.; Malik, S.; Tracy, J.; Barczewski, M.; Rosner, H.; Kappes, M. *Phys Chem Chem Phys* **2002**, *4*, 2273-2277.

[4] Deheer, W. A.; Bacsa, W. S.; Chatelain, A.; Gerfin, T.; Humphreybaker, R.; Forro, L.; Ugarte, D. *Science* **1995**, *268*, 845-847.

[5] Malik, S.; Rosner, H.; Hennrich, F.; Bottcher, A.; Kappes, M. M.; Beck, T.; Auhorn, M. *Phys Chem Chem Phys* **2004**, *6*, 3540-3544.

[6] Cheng, F. Y.; Adronov, A. *Chem. Mater.* **2006**, *18*, 5389-5391.

[7] Li, H. M.; Cheng, F. O.; Duft, A. M.; Adronov, A. *Journal of the American Chemical Society* **2005**, *127*, 14518-14524.

List of symbols/abbreviations/acronyms/initialisms

AFM	Atomic Force Microscopy
Cs_2CO_3	cesium carbonate
DND	Department of National Defence
L	litre, volume unit
mg	milligram, mass unit
Ω	Ohm, resistance unit
$Pd(PPh_3)_4$	tetrakis(triphenylphosphine)palladium(0)
PSS	poly(styrene sulfonate)
SWNT	single-walled carbon nanotube(s)
THF	tetrahydrofuran

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Significant progress has been made in the direction of nanotube functionalization with polymers. The initial approach, which involved the introduction of a non-conjugated polymer (poly(styrene sulfonate)) was found to result in films that were poorly conducting and would likely not be suitable for supercapacitor applications. We therefore turned our attention to the introduction of conjugated polymers on the nanotube surface. Using the Suzuki coupling protocol that was described in the previous report, we have prepared a series of nanotubes that are covalently functionalized with conjugated polymers. In addition we have begun the preparation of supramolecularly-functionalized nanotubes, in which the pristine nanotube structure is preserved. These materials have been used to produce thin films, and the conductivity of these films has been investigated.

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nanotube, functionalization, conjugated polymer, supramolecular, conductivity

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