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A NEW MAGNETIC NANOPEAPOD: ENCAPSULATION OF MAGNETITE NANOPARTICLES IN POLYTHIOPHENE NANOTUBES

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Abstract – Template-based electropolymerization of cyclohexanedioxythiophene (CDOT) gave the corresponding polythiophene nanotubes (PNTs). A new hybrid polymer nanopeapod was constructed by introducing magnetite nanoparticles into the CDOT PNTs.

Recently, polymer nanotubes produced by polymerization of monomeric organic molecules have gotten a lot of attention.[1] Generally, polymer nanotubes are prepared by electropolymerization of monomers with electropolymerizing ability such as thiophene and pyrrole, grown in the templates.[2] And by using porous alumina as a template, for whose pore size and depth are resizable, various sized polymer nanotubes are possible to be prepared (Figure 1). The development is expected for the application of polymer nanotubes such as nanosize container and reaction field by using their internal space.[3]

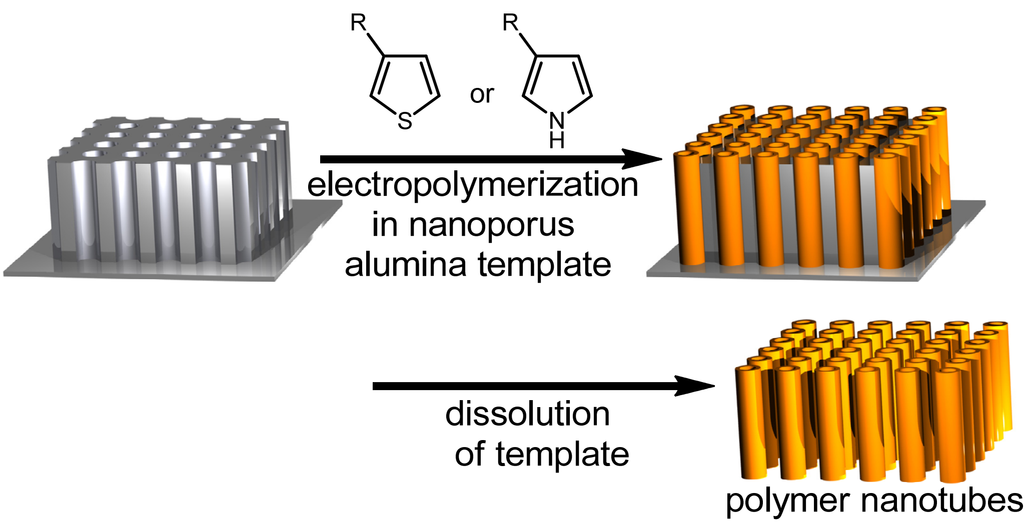

Figure 1. Synthesis of polymer nanotubes by template-based electropolymerization

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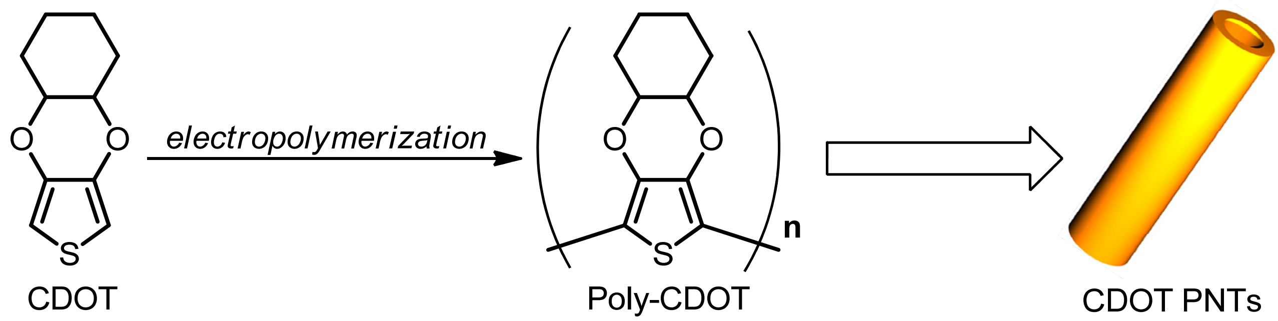
Dedicated with respect to Professor Dr. Ei-ichi Negishi on the occasion of his 77th Birthday.

As a new approach to nanomaterials, lately the study for preparing nanocomposite materials produced by combining several nanomaterials has been progressing. There is one such example as fullerene-combined carbon nanotubes, which are prepared by introducing fullerenes, guest molecules, into host nanotubes.[4] This was found by Luzzi *et al*. and named "Peapod" for its shape like a peapod containing peas inside. In addition, recently it was reported that endohedral metallofullerenes could be also introduced into carbon nanotubes and such peapods are expected for the application to the quantum computer and the electronic devices such as transistor or diode.[5] However, at the moment, the foremost problem is that only limited size of molecules are able to be introduced so that only limited minute hosts, i.e. carbon nanotubes with small diameter, are able to be synthesized. Consequently, to solve such a problem, we suggest the flexible polymer nanotubes with controllable diameter size. Using polymer nanotubes as the host has merit of taking in various sized nanomaterials impossibly taken in by carbon nanotubes and moreover, expressing unique properties not seen at peapod with carbon nanotubes. Nevertheless, presently, any studies have not been reported for preparing peapod with polymer nanotubes or establishing the method to introduce the guest molecules into such a peapod. Therefore, in this study, we examined the preparation of the peapod with polymer nanotubes as the host and the method to introduce nanomaterials into polymer nanotubes.

Polymer nanotubes (PNTs) of cyclohexanedioxythiophene (CDOT)[6] were synthesized by electropolymerization of CDOT in a porous alumina (Scheme 1).[7]



Scheme 1. CDOT PNTs composed of Poly-CDOT were synthesized by template-based electropolymerization of CDOT

The SEM image of the CDOT PNTs revealed an outer diameter of about 200 nm which corresponds to the pore diameter of the alumina membrane (Figure 2). The elemental composition of the CDOT PNTs was confirmed by the EDX analysis; its EDX spectrum (Figure 3) shows the presence of C, O, and S elements in the PNTs, which confirms that these tubular materials are composed by poly-CDOT that has been generated during the template-based electropolymerization.

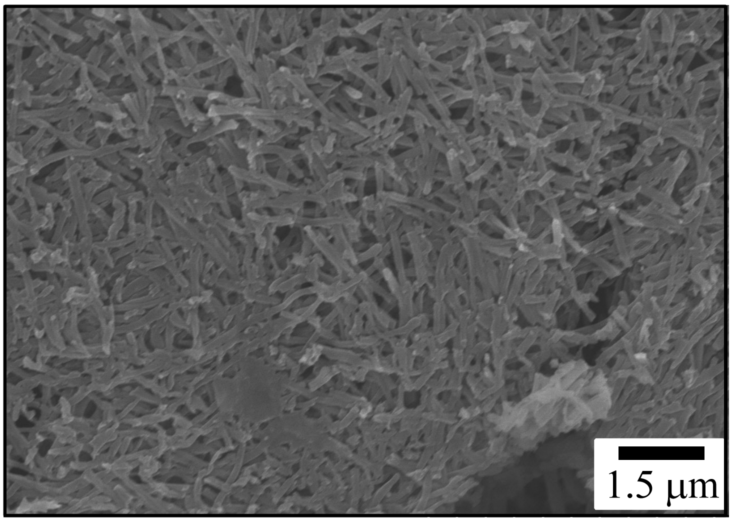


Figure 2. SEM image of CDOT-PNTs

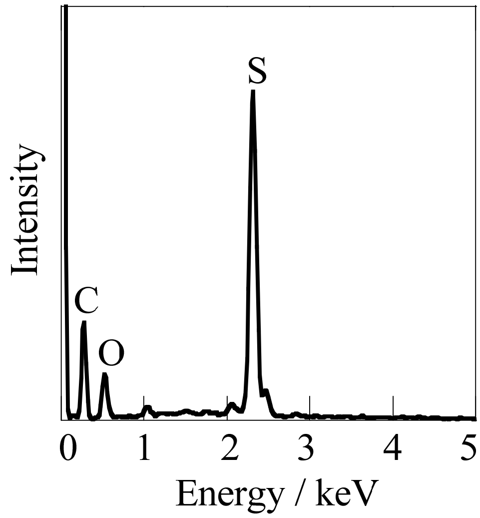


Figure 3. EDX spectrum of CDOT-PNTs

Magnetite nanoparticles (MGNPs),[8] "peas", were introduced into the synthesized CDOT-PNTs, "pod" and in this way, new type nanopeapods were prepared. And moreover, the characterization was performed for them.[9] To confirm the existence of the MGNPs inside/outside of the CDOT-PNTs, the transmission electron microscope (TEM) and scanning electron microscope (SEM) observations were performed respectively (Figure 4). By TEM observation, the presence of nanoparticles was confirmed in the inner space of CDOT-PNTs. On the other hand, by SEM observation, the presence of nanoparticles was not confirmed on the outside surface of CDOT-PNTs at all. Consequently, the nanoparticles only existed in the inner space of the CDOT-PNTs.

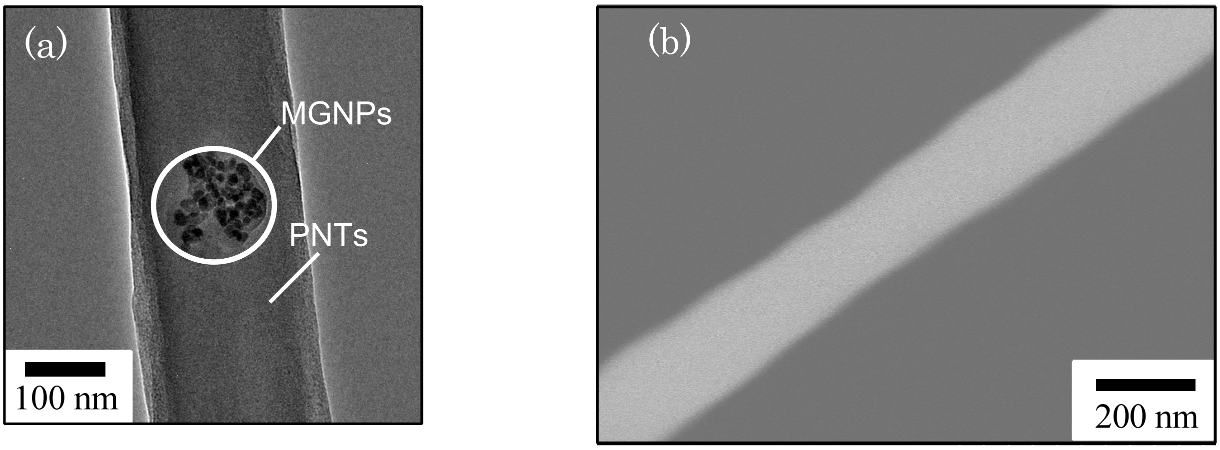


Figure 4. (a) TEM image of MGNPs@CDOT-PNTs (b) SEM image of MGNPs@CDOT-PNTs

Scanning transmission electron microscope (STEM) observation was performed at the same site of SEM observation. Subsequently, for elemental analysis of MGNPs@CDOT-PNTs, energy dispersive X-ray spectroscopy (EDX) mapping was performed (Figure 5).

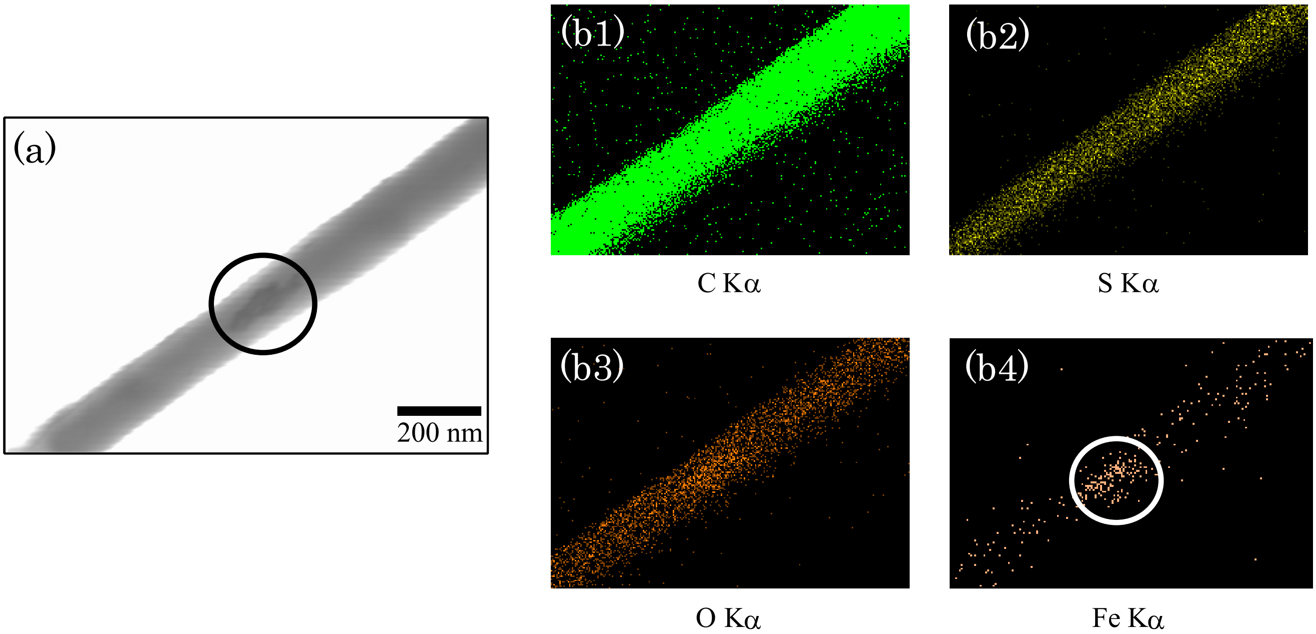


Figure 5. (a) STEM image and (b1-4) EDX mapping of MGNPs@CDOT-PNTs

The EDX measurement resulted in indicating that the MGNPs were introduced in the CDOT-PNTs so that plenty of iron was detected especially at the site where some kind of nanoparticles existed. Furthermore, the existence of magnetism was confirmed by putting a magnet close to MGNPs@CDOT-PNTs in water (Figure 6).

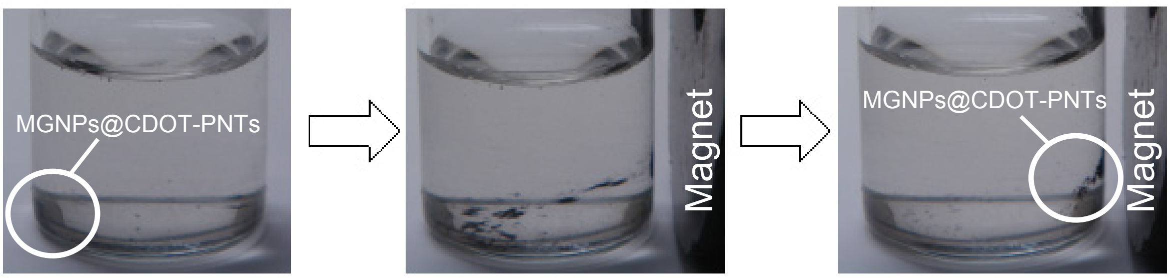


Figure 6. Photographs of MGNPs@CDOT-PNTs in water (left) and their response to a magnet (middle & right)

Figure 6 shows that the MGNPs@CDOT-PNTs were attracted towards the external magnetic field located on the right side of the sample vial, demonstrating the high magnetic sensitivity of our new polymer nanotube peapods.

In conclusion, we have succeeded in the preparation of the polymer nanopeapod. It was confirmed that magnetite nanoparticles were introduced in polymer nanotubes.

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. M. Mitsumori, T. Nakahodo, and H. Fujihara, *Nanoscale*, 2012, **4**, 117.
2. R. Xiao, S. Il Cho, R. Liu, and S. B. Lee, *J. Am. Chem. Soc*., 2007, **129**, 4483.
3. K. Sato, T. Nakahodo, and H. Fujihara, *Chem. Commun.*, 2011, **47**, 10067.
4. B. W. Smith, M. Monthioux, and D. E. Luzzi, *Nature*, 1998, **396**, 323.
5. K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. Lett.*, 2000, **85**, 5384.
6. CDOT was prepared by transetherification of 3,4-dimethoxythiophene with (*trans*/*cis*)-1,2-cyclohexanediol in 35%; D. Caras-Quintero and P. Bäuerle, *Chem. Commun*., 2004, 926.
7. Electrochemical synthesis was performed by attaching porous alumina (pore diameter of 200 nm) to platinum electrode (another platinum electrode was used as the counter electrode and Ag/0.1 M $AgNO_3$ was used as the reference electrode). The electrolysis solution contains 50 mM CDOT and 0.1 M Bu_4NPF_6 in MeCN. A voltage of 1.2V was applied. After the electrochemical synthesis, the electrode was rinsed with MeCN. The porous alumina was removed by dissolving in 1 M NaOH. These polymer nanotubes with pore diameter of 200 nm were characterized by SEM and TEM.
8. The magnetite (Fe_3O_4) nanoparticles with an average diameter of about 10 nm were prepared by thermal decomposition of the iron-oleate complex.
9. The construction of MGNPs@CDOT-PNTs peapod is as follow. A water suspension of MGNPs was poured into polymer nanotubes with porous alumina. After introduction of MGNPs into polymer nanotubes, the porous alumina was removed by dissolving in 1M NaOH. MGNPs@CDOT-PNTs were characterized by SEM, TEM, STEM, and EDX.