

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Benzoxazine as a Reactive Noncovalent Dispersant for Carbon
Nanotubes

Chih-Feng Wang^{a,*}, Shiao-Wei Kuo^b, Ching-Hsuan Lin^c,
Hou-Guang Chen^a, Chih-Siang Liao^a, Pei-Rung Hung^a

^aDepartment of Materials Science and Engineering, I-Shou University, Kaohsiung,
840, Taiwan

^bDepartment of Materials and Optoelectronic Science, Center for Nanoscience and
Nanotechnology, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan

^cDepartment of Chemical Engineering, National Chung Hsing University, Taichung,
402, Taiwan

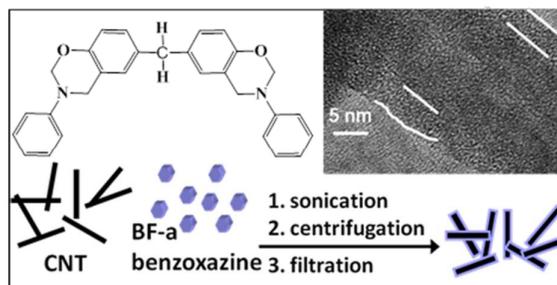
*To whom all correspondence should be addressed

E-mail: cfwang@isu.edu.tw

Tel: 886-7-6577711-3129

Fax: 886-7-6578444

Table of Contents (TOC) Image



Benzoxazines can be used as reactive noncovalent dispersant for carbon nanotubes (CNTs). The benzoxazine coatings improved the compatibility of the CNTs with various organic solvents and retained their reactivity.

Abstract

The dispersion of carbon nanotubes (CNTs) into individual particles or small bundles has remained a challenge and, thereby, has limited their applicability. Reactive noncovalent dispersion is an attractive option for changing the interfacial properties of nanotubes; the CNTs retain their graphene structure while the reactive functionalities of the dispersant moieties allow the dispersion of the CNTs within a thermosetting polymer matrix. Nevertheless, that approach typically requires multistep syntheses and the expensive reactants. In this study, we used two commercially available benzoxazine monomers as reactive noncovalent dispersants of CNTs. We used transmission electronic microscopy and thermogravimetric analysis to study the morphologies and thermal properties, respectively, of the resulting benzoxazine-modified CNTs. The presence of benzoxazine coatings improved the compatibility of the CNTs with various organic solvents; in addition, the adsorbed benzoxazines retained their reactivity. Such benzoxazine-modified CNTs have potential application in the preparation of a variety of CNT/polymer composites.

Introduction

Carbon nanotubes (CNTs) are materials of interest for both academic research and industrial applications because of their unique chemical and physical properties. Exceptional mechanical properties and excellent thermal and electrical conductivities render CNTs as ideal reinforcing fillers in polymer nanocomposites. Nevertheless, the poor solubility and difficult manipulation of CNTs in organic solvents and aqueous solutions have greatly limited their utility.¹⁻⁸ Two general approaches have been developed to enhance the solubility of CNTs: covalent functionalization and noncovalent adsorption of organic molecules on CNT surfaces. The first method involves covalently bonding surface-modifying groups or molecules onto the CNTs to improve their solubility as well as their dispersion in solvents and polymeric matrices.^{4, 5} The covalent functionalization of a CNT can, however, change the hybridization of its carbon atoms from sp^2 to sp^3 , thereby disrupting its electrical properties. The second approach, which typically involves van der Waals interactions between organic molecules/polymers and CNTs, generally preserves nearly all of the intrinsic features of the CNTs. Although much progress has been made in noncovalent strategies involving nonreactive organic molecules or polymers,^{7, 9-15} only a few studies have addressed reactive dispersants. When a reactive noncovalent dispersant binds tightly to a CNT surface through van der Waals interactions, its reactive

functional groups remain available for reactions with other molecules or through the formation of a thermosetting polymer matrix. In the latter case, the reactive functional groups of the reactive noncovalent dispersant enable seamless connection of the CNTs to the thermosetting polymer network, thereby allowing them to become an integral part of the resultant composite.¹⁶⁻¹⁹ Nevertheless, multistep syntheses processes, stringent preparation specifications, and expensive reactants have heretofore limited their practical applications.

Benzoxazine resins, which have been developed recently as new types of phenolic resins, are attracting academia and industrial interest because of their low cost, ease of processing, and high performance. In addition to these features, which they share with traditional phenolic resins, polybenzoxazines also possess several unique properties: low degrees of water absorption (despite a large number of hydroxyl groups in their backbone structure), high moduli, excellent resistance to chemicals and UV light, near-zero volumetric shrinkage/expansion upon polymerization, low surface free energies, and high glass transition temperatures.²⁰⁻²⁶ Recent studies of CNTs and benzoxazine resins have focused mainly on incorporating CNTs into polybenzoxazines to enhance the properties of the resultant nanocomposites.²⁷⁻³² In this paper, we report the use of a commercially available benzoxazine as a reactive noncovalent dispersant for CNTs, leading to functionalized

CNTs exhibiting high dispersibility in organic solvents as well as thermal reactivity.

Furthermore, the commercial availability of the raw materials and the simple fabrication and operation processes described herein suggest that such dispersants have great potential for further use in academic research and industrial applications..

Experimental Section

Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (BA-a benzoxazine) was supplied by Shikoku Chemicals. Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane (BF-a benzoxazine) was obtained from Huntsman. Multiwalled CNTs (average diameter: 10–20 nm; length: 5–15 μm) were purchased from Centron Biochemistry Technology. These materials were used as received.

Typical experimental procedure for solubilization of CNTs: Benzoxazine monomer (2.0 mg) was added to suspension of CNTs (2.0 mg) in a solvent (10.0 mL) and then the resulting mixture was sonicated for 30 min in a water bath maintained at a temperature of approximately 20 °C. The tested solvents included ethyl acetate (EA), ethyl-3-ethoxypropionate (EEP), methyl ethyl ketone (MEK), propylene glycol monomethyl ether acetate (PGMEA), and tetrahydrofuran (THF). After sonication, the insoluble CNTs were removed through centrifugation. Scanning electron microscopy (SEM) images were recorded using a Hitachi-S-4700 microscope operated at 15 kV. Sample of CNT/polybenzoxazine composites for SEM imaging were prepared by depositing a drop of the CNT/benzoxazine suspension (in THF) onto a silicon wafer (10 mm \times 10 mm) and then curing in an oven at 240 °C for 1 h. Transmission electron microscopy (TEM) images were recorded using a Philips Tecnai 20 microscope operated at 200 kV. The polybenzoxazine-modified CNT

samples for TEM imaging were prepared through a three-step process: (i) a CNT/benzoxazine suspension (in THF) was filtered through a 0.2 μm PTFE membrane to remove the free benzoxazine; (ii) the collected benzoxazine-modified CNTs were dispersed in THF followed by ultrasonication in a water bath for 30 min; (iii) a drop of the benzoxazine-modified CNT suspension was deposited on a holey carbon-coated copper grid (Ted Pella, USA) and then cured in an oven at 240 $^{\circ}\text{C}$ for 1 h. Thermogravimetric analysis (TGA) was performed under N_2 using a TA Instruments Q50 apparatus (heating rate: 20 $^{\circ}\text{C min}^{-1}$; temperature range: from room temperature to 800 $^{\circ}\text{C}$. N_2 flow rate: 60 mL min^{-1}).

Results and Discussion

We used two typical bifunctional benzoxazine monomers—BA-a and BF-a—as target dispersants for this study (Figure 1a). To compare the dispersion abilities of the benzoxazines BA-a and BF-a for CNT in various organic solvents, we dispersed CNTs separately in solution of BA-a and BF-a through ultrasonication for 30 min and then centrifugation. Both the BA-a- and BF-a-treated CNTs exhibited excellent stabilities for up to three months (Figure 1b and 1c). The pristine CNT in EA, MEK, and THF (i.e., in the absence of a benzoxazine) underwent rapid aggregation and precipitated completely from these organic solvents after centrifugation; furthermore, the supernatant was transparent and colorless. The CNT/benzoxazine solutions were highly stable and did not precipitate after three months under ambient conditions. Thus benzoxazines significantly improved the solubility of CNTs in various organic solvents and provided stable dispersions for long periods of time.

In previous paragraph, it was shown that benzoxazine monomers may have been adsorbed onto the surfaces of CNT, thereby separating larger CNT agglomerates into highly stable dispersion. To further explore the interactions between CNTs and benzoxazines BA-a and BF-a, we used SEM to observe the structures of the CNT/polybenzoxazine composites (Figures 2a–d). First, we deposited the CNT/benzoxazine suspension onto a silicon wafers and then them cured to form

corresponding CNT/polybenzoxazine composites. Figures 2a and 2b present top-view SEM images of the CNT/BA-a polybenzoxazine composites at different magnifications. The BA-a polybenzoxazine coating was present over the entire surface (Figure 2a), with the branch-like CNT nanostructures connected together by the polybenzoxazine film (Figure 2b). Figures 2c and 2d display SEM images of the CNT/BF-a polybenzoxazine composites at different magnifications. The morphology of the CNT/BF-a polybenzoxazine composite was very different from that of the CNT/BA-a polybenzoxazine composite. The CNT/BF-a polybenzoxazine composites were deposited on the silicon wafer individually (Figure 2c), with no evidence for the presence of any polybenzoxazine film between each pair of CNT/BF-a polybenzoxazine nanostructures (Figure 2d). Moreover, the diameters of the CNT nanostructures in the CNT/BF-a polybenzoxazine composites were greater than those of the CNT nanostructures in the CNT/BA-a polybenzoxazine composites. According to these SEM images, it appears that the two benzoxazine monomers possess different absorption capacities toward the CNTs. Scheme 1 provides an illustration of a suggested mechanism of formation of the CNT/BA-a polybenzoxazine and CNT/BF-a polybenzoxazine composites. In the CNT/BA-a system, only a few of BA-a monomers absorbed onto the CNTs. During the drop-coating process, the unabsorbed benzoxazine monomers combined together to form benzoxazine films. Finally, the

CNT nanostructures became embedded in the polybenzoxazine films during the curing process. In contrast, in the CNT/BF-a system, a great amount of BF-a monomers absorbed onto the CNTs, thereby increasing the diameter of the CNT nanostructures. To further investigate the dispersion ability of benzoxazine-modified CNTs, we filtered the CNT/benzoxazine suspension in THF through a PTFE membrane to remove the free benzoxazine and obtain benzoxazine modified-CNT. We then evaluated the dispersion stability of these benzoxazine-modified CNTs in organic solvents through visual observation at different periods of times after sonication (Figure 3). Immediately after sonication, the solutions of both BA-a- and BF-a-modified CNTs were black (Figure 3a); we could not tell whether any nanotube aggregates were present in these solutions because of their darkness. After two days, the BA-a-modified CNTs had precipitated (Figure 3b, vials I-III). In contrast, the suspensions of the BF-a-modified CNTs suspensions were stable and did not precipitate after two days (Figure 3b, vials IV-VI); indeed, they remained suspended after two months of standing at room temperature. Thus, the benzoxazine BF-a significantly enhanced the solubility of CNTs in organic solvents and extended their long-term dispersion stability.

Figures 4a-d display TEM images of the pristine CNTs and the BF-a polybenzoxazine-modified CNTs. At low magnification, the pristine CNTs appeared

highly entangled, with a non-uniform bundle size (Figure 4a). After modification with the BF-a polybenzoxazine, the bundle size decreased significantly (Figure 4b), with most of the CNTs appearing to have dispersed as individual tubes or in small bundles. A higher-resolution TEM image of the pristine CNTs (Figure 4c) reveals that the surfaces of CNTs were clean. In contrast, Figure 4d reveals that a coating of polybenzoxazine covered the CNTs of the BF-a polybenzoxazine–modified CNTs, such that the individual nanotubes were separated from one another. We used TGA under a N₂ atmosphere to determine the thermal properties of BF-a benzoxazine, the BF-a polybenzoxazine, the pristine CNTs, the BF-a benzoxazine–modified CNTs and the BF-a polybenzoxazine–modified CNTs. Figure 5a reveals that the thermal stability of the BF-a polybenzoxazine was higher than that of the BF-a monomer, consistent with its cross-linked network structure. The pristine CNTs did not undergo any obvious weight loss during their TGA analysis (Figure 5b). Hence, we can attribute the weight losses observed for the BF-a benzoxazine–modified CNTs and BF-a polybenzoxazine–modified CNTs to the decomposition of their dispersants. The thermal properties of the BF-a benzoxazine–modified CNTs and the BF-a polybenzoxazine–modified CNTs follow were similar to those of the BF-a monomer and the BF-a polybenzoxazine, respectively; that is, the thermal stability and char yield of the BF-a polybenzoxazine–modified CNTs were higher than those of the

BF-a benzoxazine-modified CNTs because of the cross-linked network structure in the former. Thus, the BF-a monomer units that had adsorbed on the CNTs retained their reactivity, allowing homo-crosslinking and, potentially, reactions with other functional groups (e.g., epoxy, isocyanate, oxazoline, maleimide, cyanate ester)²⁶ under suitable conditions.

Conclusions

Benzoxazine monomers have intrinsic affinity for pristine CNTs. When using such monomers as reactive noncovalent dispersants, we found that CNTs could be dispersed well in several organic solvents. The strength of the interactions between the CNTs and the benzoxazines was dependent on the chemical structure of each monomer. A coating of the benzoxazine BF-a on a CNT surface greatly enhanced its dispersibility in organic solvents; the monomer units remained reactive for crosslinking and, presumably, for reactions with other functional groups in other polymeric systems (e.g., polybenzoxazine, polyimide, polyurethane, epoxy resin, phenolic resin). Accordingly, BF-a benzoxazine-modified CNTs appear to be promising candidates for use in the preparation of various CNT/polymer composites.

Acknowledgment

This study was supported financially by the National Science Council, Taiwan, Republic of China, under contracts NSC 99-2221-E-214-005 and NSC 102-2221-E-214 -056.

References

1. L. Hu, D. S. Hecht and G. Gruener, *Chem. Rev.*, 2010, **110**, 5790-5844.
2. S. W. Kim, T. Kim, Y. S. Kim, H. S. Choi, H. J. Lim, S. J. Yang and C. R. Park, *Carbon*, 2012, **50**, 3-33.
3. P.-C. Ma, N. A. Siddiqui, G. Marom and J.-K. Kim, *Composites Part A*, 2010, **41**, 1345-1367.
4. N. G. Sahoo, S. Rana, J. W. Cho, L. Li and S. H. Chan, *Prog. Polym. Sci.*, 2010, **35**, 837-867.
5. Y. P. Sun, K. F. Fu, Y. Lin and W. J. Huang, *Acc. Chem. Res.*, 2002, **35**, 1096-1104.
6. D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105-1136.
7. J.-M. Yuan, Z.-F. Fan, X.-H. Chen, X.-H. Chen, Z.-J. Wu and L.-P. He, *Polymer*, 2009, **50**, 3285-3291.
8. H. K. F. Cheng, Y. Pan, N. G. Sahoo, K. Chong, L. Li, S. H. Chan and J. Zhao, *J. Appl. Polym. Sci.*, 2012, **124**, 1117-1127.
9. T. Ogoshi, T. Saito, T.-a. Yamagishi and Y. Nakamoto, *Carbon*, 2009, **47**, 117-123.
10. S. Srinivasan, S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Angew. Chem. Int.*

- Ed.*, 2008, **47**, 5746-5749.
11. Y.-L. Zhao and J. F. Stoddart, *Acc. Chem. Res.*, 2009, **42**, 1161-1171.
 12. H.-S. Oh and H. Kim, *Adv. Funct. Mater.*, 2011, **21**, 3954-3960.
 13. N. Berton, F. Lemasson, A. Poschlad, V. Meded, F. Tristram, W. Wenzel, F. Hennrich, M. M. Kappes and M. Mayor, *Small*, 2014, **10**, 360-367.
 14. Y. S. Chen, A. Malkovskiy, X. Q. Wang, M. Lebron-Colon, A. P. Sokolov, K. Perry, K. More and Y. Pang, *Acs Macro Lett.*, 2012, **1**, 246-251.
 15. Y. S. Chen, R. N. Gunasinghe, X. Q. Wang and Y. Pang, *RSC Adv.*, 2013, **3**, 25097-25102.
 16. Y. Dong, R. Wang, S. Li, H. Yang, M. Du and Y. Fu, *J. Colloid Interface Sci.*, 2013, **391**, 8-15.
 17. Y. Yan, J. Cui, S. Zhao, J. Zhang, J. Liu and J. Cheng, *J. Mater. Chem.*, 2012, **22**, 1928-1936.
 18. W. Yuan, J. Feng, Z. Judeh, J. Dai and M. B. Chan-Park, *Chem. Mater.* 2010, **22**, 6542-6554.
 19. S. Zhao, Z. Song, J. Cui, C. Li and Y. Yan, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4548-4556.
 20. N. N. Ghosh, B. Kiskan and Y. Yagci, *Prog. Polym. Sci.*, 2007, **32**, 1344-1391.
 21. C. P. R. Nair, *Prog. Polym. Sci.*, 2004, **29**, 401-498.

22. C. H. Lin, Y. S. Shih, M. W. Wang, C. Y. Tseng, T. Y. Juang and C. F. Wang, *RSC Adv.*, 2014, **4**, 8692-8698.
23. C. F. Wang, Y. C. Su, S. W. Kuo, C. F. Huang, Y. C. Sheen and F. C. Chang, *Angew. Chem. Int. Ed.*, 2006, **45**, 2248-2251.
24. C.-F. Wang, H.-Y. Chen, S.-W. Kuo, Y.-S. Lai and P.-F. Yang, *RSC Adv.*, 2013, **3**, 9764-9769.
25. C.-F. Wang, T.-F. Wang, C.-S. Liao, S.-W. Kuo and H.-C. Lin, *J. Phys. Chem. C*, 2011, **115**, 16495-16500.
26. H. Ishida, Handbook of benzoxazine resins. Ishida, H., Agag, T., Ed. Elsevier: Amsterdam, 2011; Chapter 1, p 1.
27. Q. Chen, R. Xu and D. Yu, *Polymer*, 2006, **47**, 7711-7719.
28. C. Zuniga, L. Bonnaud, G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz and P. Dubois, *J. Mater. Chem. A*, 2014, **2**, 6814-6822.
29. L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman and P. Dubois, *Chem. Commun.*, 2013, **49**, 9543-9545.
30. M. Kaleemullah, S. U. Khan and J.-K. Kim, *Compos. Sci. Technol.*, 2012, **72**, 1968-1976.
31. Y. Liu, B. Wang and X. Jing, *Polym. Compos.*, 2011, **32**, 1352-1361.
32. Y.-H. Wang, C.-M. Chang and Y.-L. Liu, *Polymer*, 2012, **53**, 106-112.

Figure Captions

Scheme 1. Cartoon representation of the formation of CNT/BA-a polybenzoxazine and CNT/BF-a polybenzoxazine composites.

Figure 1. (a) Structures of the benzoxazines BA-a and BF-a (b, c) Photographs of CNTs dispersed with (b) BA-a benzoxazine and (c) BF-a benzoxazine in (I) EA, (II) EEP, (III) MEK, (IV) PGMEA, and (V) THF, after standing for three months.

Figure 2. (a, c) SEM images of the (a) CNT/BA-a polybenzoxazine composite and (c) CNT/BF-a polybenzoxazine composite. (b, d) Enlarged views of the microstructures in (a) and (c)

Figure 3. Photographs of the (I–III) BA-a benzoxazine–modified CNTs and (IV–VI) BF-a benzoxazine–modified CNTs in (I, IV) MEK, (II, V) EA, and (III, VI) THF at different periods of time after sonication: (a) immediately; (b) two days.

Figure 4. TEM images of the (a, c) pristine CNTs and (b, d) BF-a polybenzoxazine–modified CNTs.

Figure 5. (a) TGA traces of the BF-a benzoxazine (BF-a) and the BF-a polybenzoxazine (PBF-a). (b) TGA traces of the pristine CNTs, the BF-a benzoxazine-modified CNTs (CNT/BF-a), and the BF-a polybenzoxazine-modified CNTs (CNT/PBF-a).

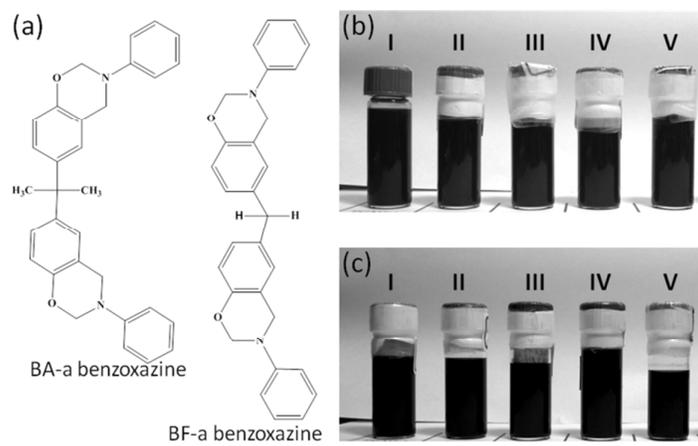


Figure 1

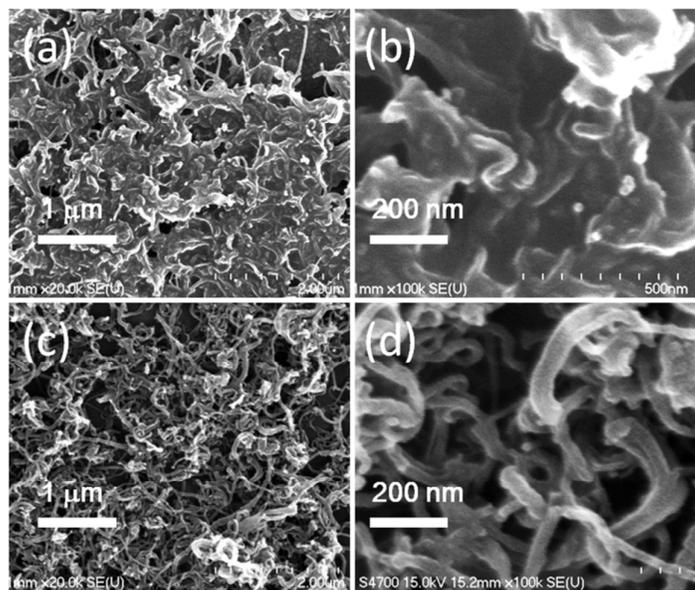


Figure 2

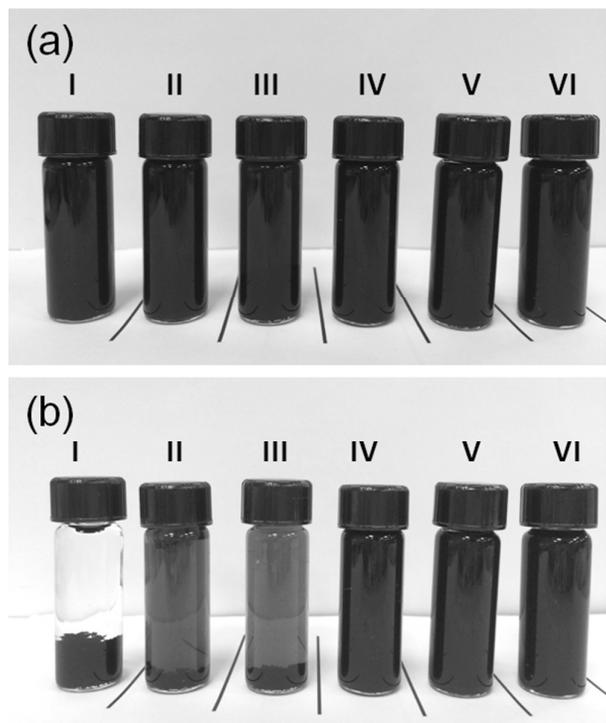


Figure 3

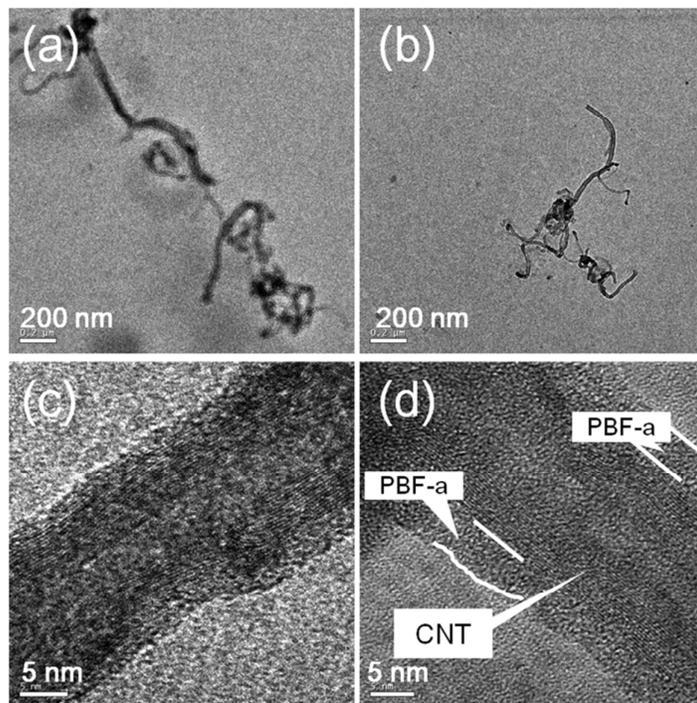


Figure 4

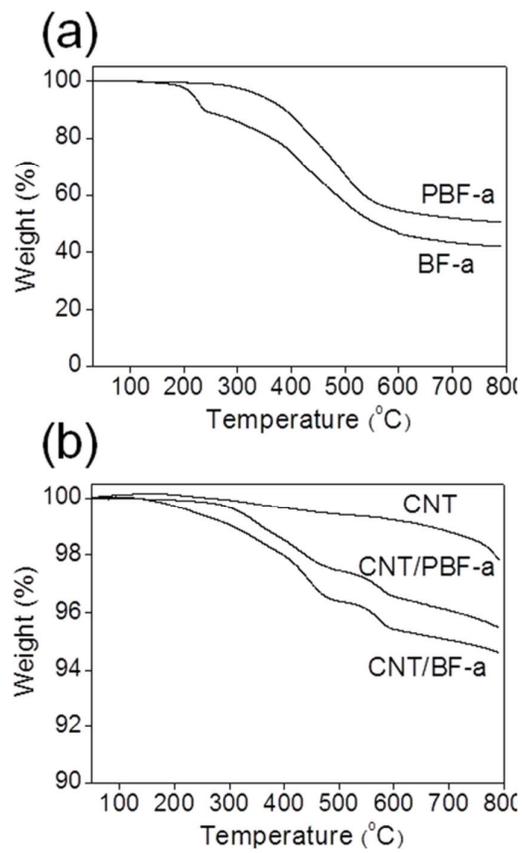
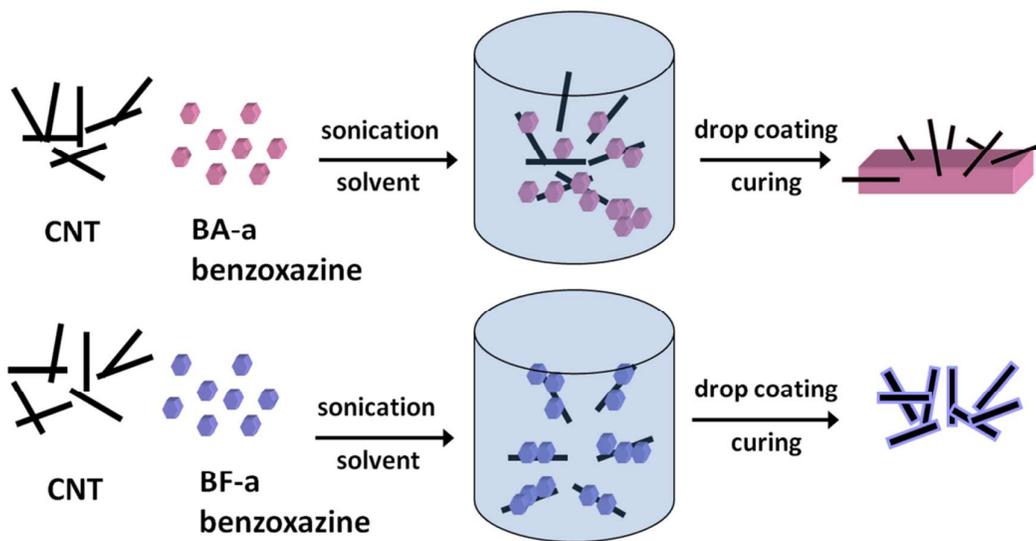


Figure 5



Scheme 1