Macromolecules

Article

Fabrication of PEO–OPV Templated Titania Nano-Hollow Rods and Their Aggregating Microspheres

Chi-Chun Hsieh, King-Fu Lin, and An-Ting Chien

Macromolecules, **2006**, 39 (8), 3043-3047 • DOI: 10.1021/ma052518z

Macromolecules is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Macromolecules **2006,** *39,* 3043−3047

Fabrication of PEO_{17}−OPV_3 Templated Titania Nano-Hollow Rods and Their Aggregating Microspheres

Chi-Chun Hsieh, King-Fu Lin,* and An-Ting Chien

Department of Material Science and Engineering and Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Received November 25, 2005; Revised Manuscript Received February 28, 2006

ABSTRACT: In this work, PEO_{17}−OPV_3, a light-emitting amphiphilic molecule, was served as a structure-directing agent to fabricate the nano-hollow rods and microspheres through self-assembling with titania precursors. FT-IR and EDX were employed to examine the composition of these hybrid materials. In the beginning, the microspheres of ∼1 μm composed of bundles of nanorods were observed by SEM. By grinding the microspheres, isolated hollow rods of ∼100 nm in diameter were observed and investigated by TEM and AFM. Two sets of crystalline planes, rutile (110) and (101), in the skin of hollow rods were resolved. As we stained the OPV_3 packing domains of hollow rods with RuO_4, the rutile layer of the skin was ripped off, and the stained inner layer of ∼20 nm diameter was clearly identified. On the basis of the experimental evidence, we proposed a cylinder with a core−shell skin model to explain the formation of nano-hollow rods.

Introduction

During the past two decades, titania (TiO_2) nanocrystals have attracted vast attention owing to their versatile applications, such as solar cells[1,2] and photocatalysts.[3] Various forms of TiO_2 nanostructures have been reported, including spheres,[4] wires,[5] tubes,[6] and rods.[7] However, the resulting morphologies are highly dependent on the synthetic routes and their associated preparation method, such as sol−gel processes,[8,9] template methods,[10,11] and hydrothermal treatments.[12] On the other hand, among the series of π-conjugated polymers, poly(phenylene−vinylene) (PPV)-based polymers have been widely studied since their optoelectronic properties were discovered.[13,14] Recently, their oligomers (OPV) to form supramolecular architectures have attracted great attention because of potential applications on the optoelectronic nanodevices.[15−17]

It is commonly accepted that the optoelectronic properties of π-conjugated molecules are affected not only by the primary molecular structure (π-conjugation) but also by the supramolecular organization (π-stacking).[18−21] Thus, amphiphilic molecules with a proper hydrophilicity or hydrophobicity are needed to proceed a self-assembly process, and people usually focus first on the design and synthesis of self-assembling amphiphilic molecules, followed by the investigation of their aggregation behavior.[22−31] In our previous study, we have synthesized a specifically designed amphiphilic PEO_{17}−OPV_3 molecule with a rigid OPV segment linking with a soft PEO segment through a sulfonate group that twists the molecule in between hydrophilic and hydrophobic segments.[32] It formed a ringlike supramolecular structure of ∼30 nm diameter on mica. As it hybridized with silica, a uniform ringlike disk of ∼150 nm in diameter and ∼0.65 nm in thickness was formed. The thickness is roughly equal to the width of rigid OPV segment, implicating that π−π stacking governs the self-assembly process during co-organization between PEO_{17}−OPV_3 molecules and silicates.

In this study, PEO_{17}−OPV_3 in tetrahydrofuran (THF) was mixed with the titanium tetraisopropoxide in an acidified aqueous/ethanol solution. The mixture, after aged for about a month at ambient temperature, afforded the PEO_{17}−OPV_3/titania microspheres of ∼1 μm in diameter composed of bundles of hollow rods. By grinding the microspheres, the isolated hollow rods with a rutile skin in overall diameter of ∼100 nm were obtained. As we stained the OPV_3 π−π stacking domains of the hollow rods with RuO_4, the rutile layer of the skin was ripped off and the stained inner layer of ∼20 nm in diameter was clearly observed by TEM. On the basis of the experimental evidence, a cylinder with a core−shell skin model was proposed to explain the formation of nano-hollow rods.

Experimental Section

Materials. All organics were purchased from the commercial suppliers (Acros or Aldrich). THF was dried and distilled over sodium. Water (ultrapure, 18.3 MΩ) was purified by the Barnstead Easy RF system. All solvents were degassed by sparking with nitrogen for 30 min prior to use. The synthetic route to prepare the PEO_{17}−OPV_3 was described elsewhere.[32]

Preparation of PEO_{17}−OPV_3/Titania Hybrid Samples. 115 mmol of ethanol, 55.6 mmol of water, and 12 mmol of HCl were mixed in a vial with stirring at room temperature and then added with 2.2 g (7.7 mmol) of titanium tetraisopropoxide (TTIP) under vigorous stirring to prevent gelation. The solution was kept stirring for 2 h to afford a titania source solution. All procedures were handled in a nitrogen-purged glovebox. Another solution of 0.09 g (0.078 mmol) of PEO_{17}−OPV_3 in 5 mL of THF was prepared and then added with the titania source solution dropwise. The resulting solution had a molar composition of 1.0 TTIP:15 EtOH:0.01 PEO_{17}−OPV_3:1.56 HCl:7.2 H_2O:9 THF. After vigorous stirring for 24 h at room temperature, the solution was transferred into a Petri dish and aged for about 1 month until a large amount of particles precipitated. The PEO_{17}−OPV_3/titania microspheres were afforded after filtration and drying at 60 °C in a vacuum oven for 24 h. The PEO_{17}−OPV_3/titania hollow nanorods were obtained by grinding the microspheres into a powder form.

Characterization. Fourier transform infrared (FT-IR) spectra of PEO_{17}−OPV_3 and its hybrid nanorods with titania were recorded on a JASCO-410E FTIR spectrometer with KBr pellets. Scanning electron microscopy (SEM) of the microsphere samples (sputtered with gold) was investigated using a JEOL JSM-6300 scanning electron microscope. For transmission electron microscopy (TEM)

---

* To whom correspondence should be addressed: Tel +886-2-2392-8290; Fax +886-2-2363-4562; e-mail kflin@ccms.ntu.edu.tw.

10.1021/ma052518z CCC: $33.50

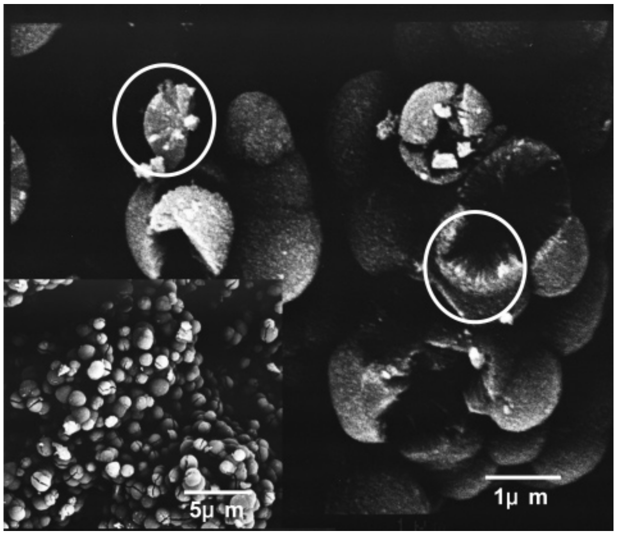


Figure 1. SEM micrographs of $PEO_{17}-OPV_3$-templated TiO_2 microspheres.

and atomic force microscopy (AFM), the microsphere samples were ground into a powder form and then suspended in methanol. A carbon-film-coated copper grid used for TEM investigation was then dip into the solution, withdrawn immediately, and dried under vacuum. The specimens were normally investigated using a JEOL JEM-1230 transmission electron microscope equipped with a Gatan dual vision CCD camera operating at 120 kV. High-resolution transmission electron microscopy (HR-TEM) and energy-dispersive X-ray spectroscopy (EDX) were investigated using a Philips/FEI Tecnai 20 G2 S-twin transmission electron microscope equipped with an EDX working at 200 kV. An automatically flat mica used for AFM investigation was also dip into the solution to collect the ground sample. The AFM specimens were investigated using a Digital Instruments Dimension-3100 multimode microscope in a tapping mode.

Results and Discussion

SEM micrographs of the $PEO_{17}-OPV_3$/titania microspheres are shown in Figure 1. The size of these spheres is rather uniform with a diameter of $\sim 1\ \mu$m, and almost all of them have flaws. It should be noted that no shear or other forces were applied during sample preparation. Therefore, these cracks should be created in connection to the formation of microspheres. Viewing along the flaw line from the magnified SEM image, it interestingly revealed that each spherical assembly was made up of bundles of rods. To investigate these rods, the microspheres were ground and then subjected to TEM, AFM, and FTIR analyses. From TEM micrographs in Figure 2a,b, we found that these rods were hollow. The rods have the external diameter of $\sim$100 nm, and their hollow region has a diameter of $\sim$10 nm (see Figure 3b). The AFM image of rods on mica also shows the hollow texture similar to that observed by TEM (see Figure 3). Figure 4 shows the FT-IR spectrum of nano-hollow rods along with that of neat $PEO_{17}-OPV_3$ for comparison. For the hybrid sample, the absorbance peak between 500 and 900 cm^{-1} originated from the Ti−O stretching.[33,34] The vibrational stretchings at 3400 and 1640 cm^{-1} were assigned to the −OH groups. Though the residual peaks are small due to the low feeding ratio of organic molecules to titania precursors, it is still distinguishable and could be compared to that of neat $PEO_{17}-OPV_3$. Absorbances at 2800−3000, 1460, and 936−965 cm^{-1} originated from the vibrations of aliphatic C−H, aromatic, and C=C double bonds, respectively. The 1100 and 1250 cm^{-1} peaks are the stretching modes of C−O bonds. Indeed, the FT-IR results confirm that the hollow nanorods are a $PEO_{17}-OPV_3$/titania hybrid material.

To enhance the contrast of OPV_3 portions, the samples were stained by RuO_4. Surprisingly, the stained rods are thinner (about 20 nm) and shorter than the unstained samples (see Figure 2c,d). It strongly suggested that RuO_4 could tear off the shell portion of the rods and remained the stained hollow cylinder core with

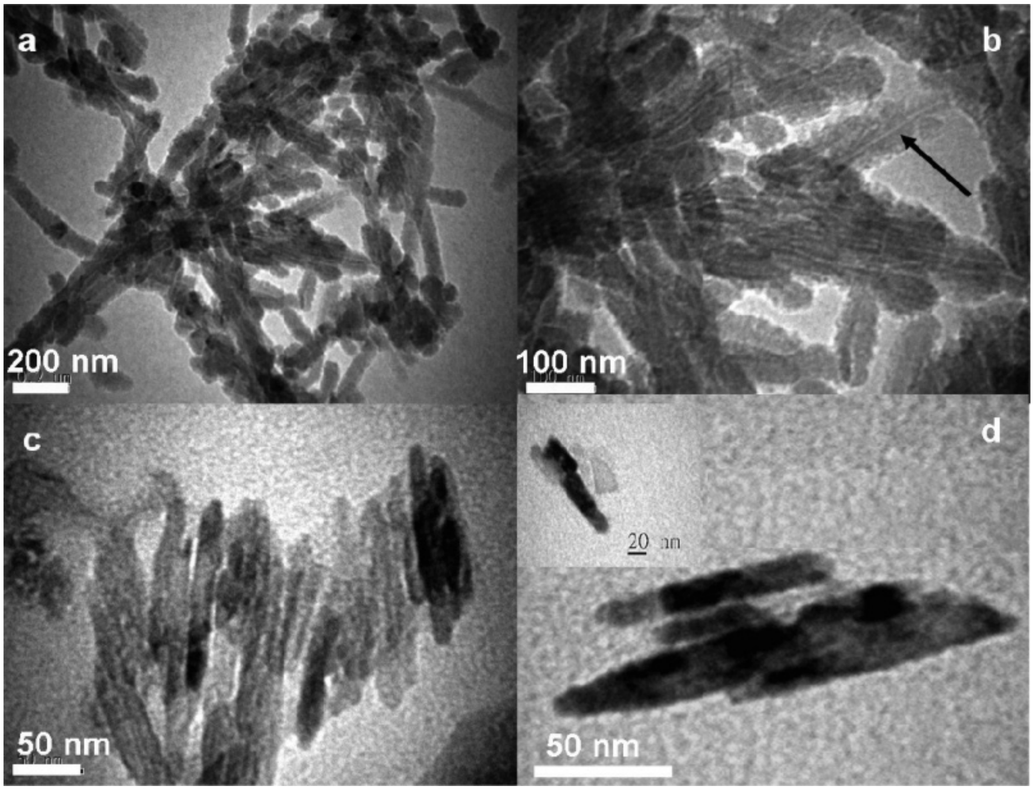


Figure 2. TEM micrographs of $PEO_{17}-OPV_3$-templated TiO_2 nano-hollow rods (a and b are unstained samples, c and d are RuO_4-stained samples).

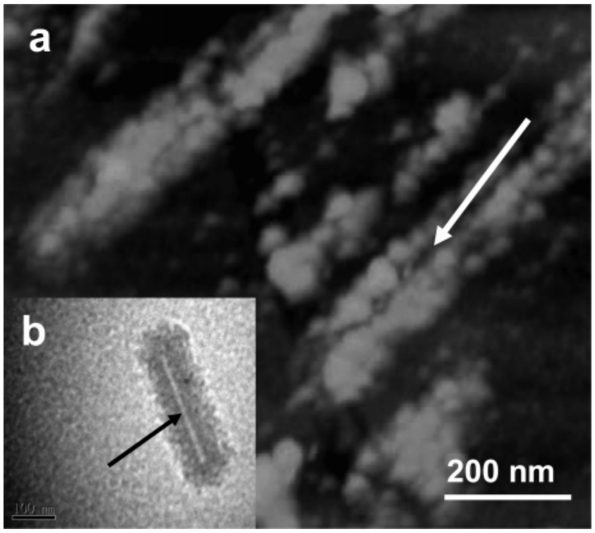


Figure 3. (a) AFM image of templated TiO_2 nano-hollow rods on mica and (b) their TEM image.

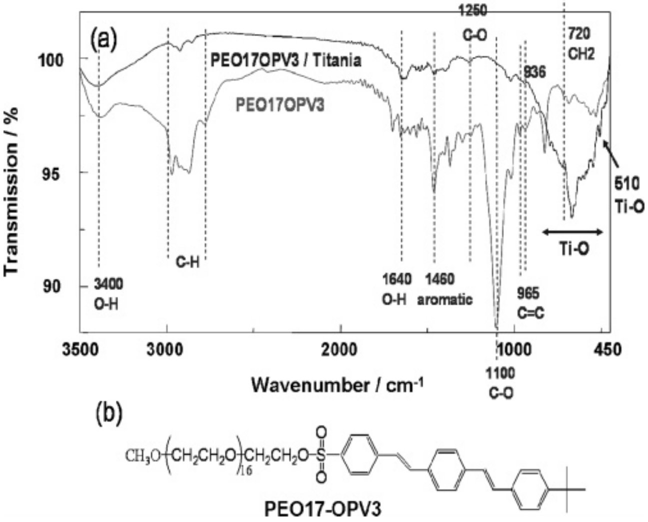


Figure 4. (a) FT-IR spectra of amphiphilic $PEO_{17}-OPV_3$ molecule and its hybrid with titania. (b) Chemical structure of $PEO_{17}-OPV_3$ molecule.

the external diameter of ~20 nm. Thus, a possible mechanism for the assembly process to form the nano-hollow rods, and their aggregating microspheres is suggested as follows.

In our previous study, we have shown that $PEO_{17}-OPV_3$ molecules tended to form a ring structure on the mica surface with the external diameter of ~30 nm.[32] It is because of the amphiphilic nature of $PEO_{17}-OPV_3$ and the twist of this molecule in between hydrophobic and hydrophilic segments (caused by the as-tetrahedral shape of sulfonate linking group); this renders them to have only one side with the same curvature to proceed the $\pi-\pi$ stacking of conjugated OPV_3 portions. Therefore, it is believed that as titania involved in the primary self-assembly of $PEO_{17}-OPV_3$ through interaction with the hydrophilic PEO_{17} segments, the ring structure would stack together to form a cylinder with skin consisting of the hydrophilic PEO_{17} and titania, as illustrated in Figure 5. As the RuO_4 stained the OPV_3 $\pi-\pi$ stacking regions, it created great strain on the interface between hydrophobic OPV_3 stacking and hydrophilic titania/PEO_{17} regions. As a result, the shell region in the skin of rods composed of titania/PEO_{17} portions was rip off as observed in the TEM image of Figure 2d (inset). Some of the partially stained samples also evidenced that the ringlike building blocks are inside the rods (see TEM images of Figure 5a,b). The driving force for these hollow rods to aggregate into microspheres is still not clear. However, it should be related to the minimized surface energy accompanied by the shrinkage during the latter stage polymerization of titania. It is believed that the dangling ~Ti−O−Ti−OH side chain originally connecting with PEO_{17} segments on the skin of rods plays an important role for the connection between adjacent rods during aging. These unpolymerized precursors with dangling Ti−OH function groups have high affinity to one another. Eventually, in the latter stage of polymerization, a series of nanorods were driven to form a microscale hybrid sphere. However, because of the rigidity of hollow rods, the uneven shrinkage to minimize the surface energy might result in flaws on the formed microspheres.

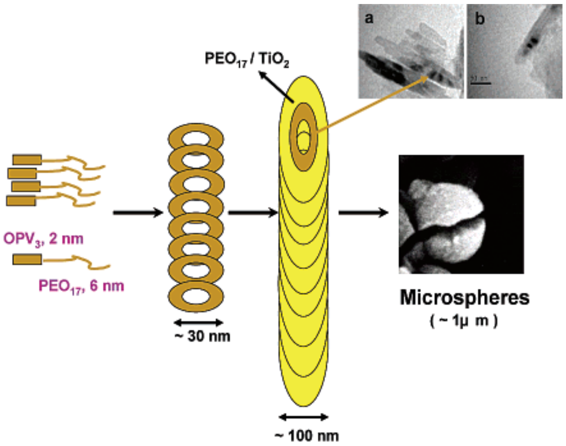
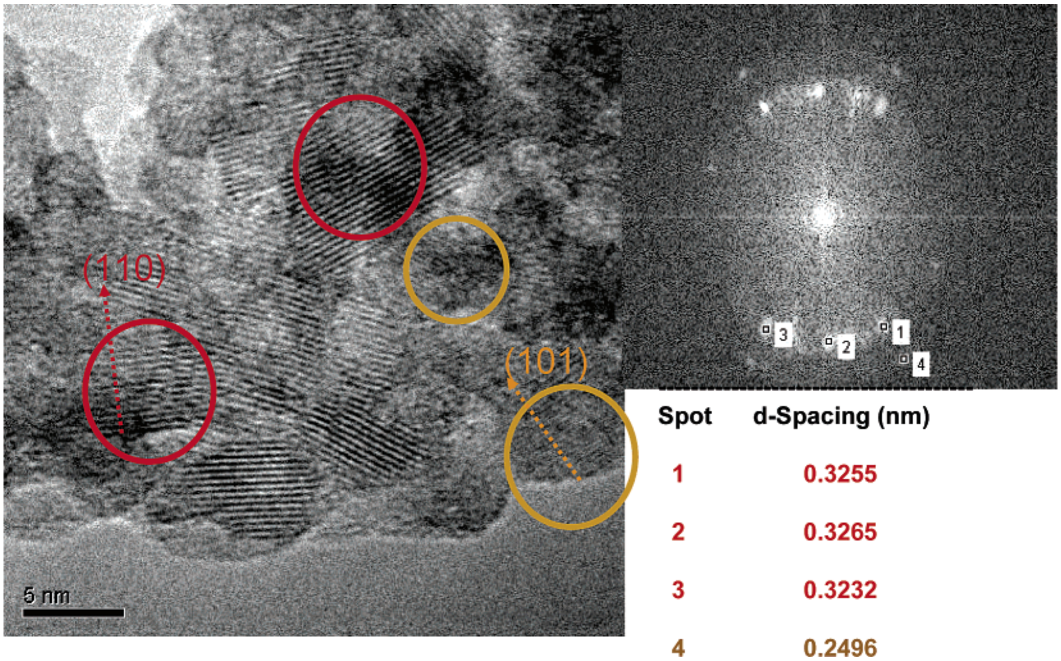


Figure 5. Illustration of assembly mechanism.

Figure 6 shows the HR-TEM image of titania/PEO_{17} shell region in the skin of $PEO_{17}-OPV_3$/titania nano-hollow rod. Lattice images were clearly observed, indicating that these PEO_{17}-templated titania had high crystallinity despite the small size. Two sets of crystalline planes were found, rutile (110) and rutile (101). The *d* spacing calculated by FFT pattern (see the tabulated data in Figure 6) was 0.325 nm for rutile (110) and 0.25 nm for rutile (101). Rutile structure is a thermodynamically stable phase of TiO_2. The anatase to rutile transformation occurs in the temperature range of 700−1000 °C, and the allowing temperature to grow anatase crystal is 670−680 °C.[35,36] In our case, however, all preparation procedures were performed at low temperature. It indicated that our amphiphilic molecule, $PEO_{17}-OPV_3$, could induce the crystallization of titania even at low temperature. A similar case was also reported by Han and co-workers.[37] They used a triblock copolymer, Pluronic P-123 ($PEO_{20}PPO_{70}PEO_{20}$), served as a surfactant to synthesize highly crystalline TiO_2 nanocrystals at room temperature.

It is noteworthy that the crystallization was not oriented along one direction (see Figure 6), although it ought to be influenced by the formation of supramolecular structure. The crystalline area in TEM image was indeed consisted of titanium, oxygen, and carbon as indicated by EDX (see Figure 7). It might be due to the fact that the PEO segments (mainly interacted with titania) are soft and coil in nature opposed to the well-ordered $\pi-\pi$ stacking of OPV_3 segments. Nevertheless, the crystallization of titanate should contribute to the final structure of $PEO_{17}-OPV_3$/titania microspheres. Since the core of nano-hollow rods is a photoharvest area ($\pi-\pi$ stacking of OPV_3 segments), the photoinjected electrons should be easier to transport through the shell of TiO_2 nanocrystals. Thus, the fabricated $PEO_{17}-OPV_3$/titania nano-hollow rods and their aggregating micro-



Spot	d-Spacing (nm)
1	0.3255
2	0.3265
3	0.3232
4	0.2496

Figure 6. HR-TEM micrograph and the corresponding FFT pattern of PEO_{17}−OPV_3-templated TiO_2 nano-hollow rod.

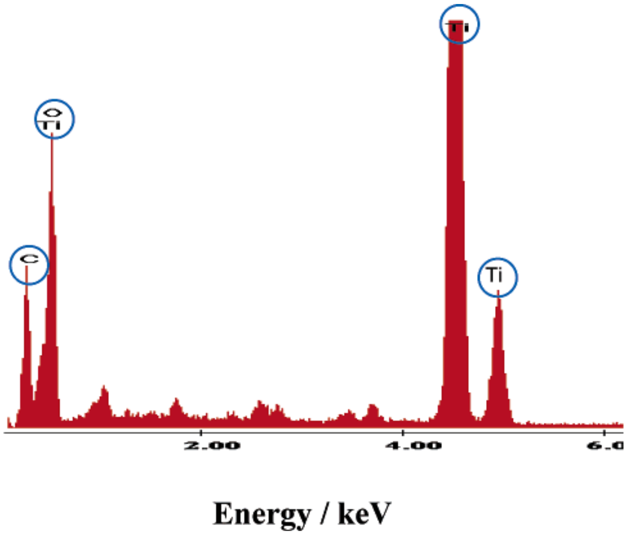


Figure 7. EDX analysis of PEO_{17}−OPV_3-templated TiO_2 nano-hollow rod.

spheres should be a promising material for application on the photocatalysts and organic solar cells. Further research on these subjects is ongoing.

Conclusions

In this study, we have successfully developed a facile method to prepare the PEO_{17}−OPV_3-templated titania microspheres of $\sim$1 μm in diameter and the nano-hollow rods of 100 nm in short axis. A cylinder with core−shell skin model is proposed for the formation of nano-hollow rods. The π−π stacking of conjugated OPV_3 portions governs the formation of primary ring structure.[32] Further stacking of the ring structure to form a cylinder with the skin consisting of the hydrophilic PEO_{17} and titania afforded the nano-hollow rods. Through the final stage of polymerization among the Ti−OH dangling chains and subsequent formation of TiO_2 nanocrystals, the adjacent nano-hollow rods were aggregated to form a microsphere. Because the core is a photoharvest material and the shell is an electron-transporting material, the fabricated PEO_{17}−OPV_3/titania nano-hollow rods and their aggregating microspheres are believed to be a promising material for application on the photocatalysts and organic solar cells.

Acknowledgment. The authors acknowledge the financial support of the National Science Council in Taiwan, Republic of China, through Grant NSC 93--2218-E-002-006.

References and Notes

(1) O'Regan, B.; Grätzel, M. *Nature (London)* **1991**, *353*, 737.
(2) Stergiopoulos, T.; Arabatzis, I. M.; Katsaros, G.; Falaras, P. *Nano Lett.* **2002**, *2*, 1259.
(3) Tang, J.; Wu, Y.; McFarland, E. W.; Stucky, G. D. *Chem. Commun.* **2004**, 1670.
(4) Zhou, Y.; Antonietti, M. *J. Am. Chem. Soc.* **2003**, *125*, 14960.
(5) Yi, D. K.; Yoo, S. J.; Kim, D.-Y. *Nano Lett.* **2002**, *2*, 1101.
(6) Tian, Z. R.; Voigt, J. A.; Liu, J.; Mckenzie, B.; Xu, H. *J. Am. Chem. Soc.* **2003**, *125*, 12384.
(7) Wu, J.-J.; Yu, C.-C. *J. Phys. Chem. B* **2004**, *108*, 3377.
(8) Nam, H.-J.; Amemiya, T.; Murabayashi, M.; Itoh, K. *J. Phys. Chem. B* **2004**, *108*, 8254.
(9) Polleux, J.; Pinna, N.; Antonietti, M.; Niederberger, M. *Adv. Mater.* **2004**, *16*, 436.
(10) Serrano, D. P.; Calleja, G.; Sanz, R.; Pizarro, P. *Chem. Commun.* **2004**, 1000.
(11) Ostomel, T. A.; Stucky, G. D. *Chem. Commun.* **2004**, 1016.
(12) Zhang, Q.; Gao, L. *Langmuir* **2003**, *19*, 967.
(13) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (b) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.
(14) (a) Cheng, H. L.; Lin, K. F. *Macromolecules* **2000**, *33*, 4961. (b) Cheng, H. L.; Lin, K. F. *Langmuir* **2002**, *18*, 7287. (c) Cheng, H.-L.; Lin, K.-F. *J. Mater. Chem.* **2002**, *12*, 2270. (d) Chiu, C.-C.; Lin, K.-F.; Chou, H.-L. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2180. (e) Cheng, H. L.; Lin, K. F. *Macromolecules* **2003**, *36*, 6949. (f) Fan, Y.-L.; Lin, K.-F. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2520.
(15) Kilbinger, A. F. M.; Feast, W. J. *J. Mater. Chem.* **2000**, *10*, 1777.
(16) Schenning, A. P. H. J.; Kilbinger, A. F. M.; Biscarini, F.; Cavallini, M.; Cooper, H. J.; Derrick, P. J.; Feast, W. J.; Lazzaroni, R.; Leclère, Ph.; McDonell, L. A.; Meijer, E. W.; Meskers, S. C. J. *J. Am. Chem. Soc.* **2002**, *124*, 1269.
(17) Henze, O.; Parker, D.; Feast, W. J. *J. Mater. Chem.* **2003**, *13*, 1269.
(18) Bucknull, D. G.; Anderson, H. L. *Science* **2003**, *302*, 1904.
(19) Peleshanko, S.; Jeong, J.; Gunawidjaja, R.; Tsukruk, V. V. *Macromolecules* **2004**, *37*, 6511.
(20) Huang, Y. Y.; Chen, H. L.; Hashimoto, T. *Macromolecules* **2003**, *36*, 764.

(21) Alam, M. M.; Zhu, Y.; Jenekhe, S. A. *Langmuir* **2003**, *19*, 8625.
(22) Brannan, A. K.; Bates, F. S. *Macromolecules* **2004**, *37*, 8816.
(23) Gehringer, L.; Bourgogne, C.; Guillon, D.; Donnio, B. *J. Am. Chem. Soc.* **2004**, *126*, 3856.
(24) Cho, B. K.; Jain, A.; Gruner, S. M.; Wiesner, U. *Science* **2004**, *305*, 1598.
(25) Koulic, C.; Jérôme, R. *Macromolecules* **2004**, *37*, 888.
(26) Zheng, S.; Tao, C.; He, Q.; Zhu, H.; Li, J. *Chem. Mater.* **2004**, *16*, 3677.
(27) Park, S.; Lim, J. H.; Chung, S. W.; Mirkin, C. A. *Science* **2004**, *303*, 348.
(28) Lee, M.; Lee, S. J.; Jiang, L. H. *J. Am. Chem. Soc.* **2004**, *126*, 12724.
(29) Kuang, M.; Duan, H.; Wang, J.; Jiang, M. *J. Phys. Chem. B* **2004**, *108*, 16023.
(30) Yan, D.; Zhou, Y.; Hou, J. *Science* **2004**, *303*, 65.
(31) Allcock, H. R.; Powell, E. S.; Chang, Y. *Macromolecules* **2004**, *37*, 7163.
(32) Hsieh, C.-C.; Lin, K. F. *J. Mater. Chem.* **2005**, *15*, 4154.
(33) Boettcher, S. W.; Bartl, M. H.; Hu, J. G.; Stucky, G. D. *J. Am. Chem. Soc.* **2005**, *127*, 9721.
(34) Wen, B.; Liu, C.; Liu, Y. *J. Phys. Chem. B* **2005**, *109*, 12372.
(35) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735.
(36) Kavan, L.; Grätzel, M.; Gilbert, S. E.; Klemenz, C.; Scheel, H. J. *J. Am. Chem. Soc.* **1996**, *118*, 6716.
(37) Han, S.; Choi, S.-H.; Kim, S.-S.; Cho, M.; Jang, B.; Kim, D.-Y.; Yoon, J.; Hyeon, T. *Small* **2005**, *1*, 812.

MA052518Z