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Layer-by-Layer Assembly of Multiwall Carbon Nanotubes on Spherical Colloids

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Multiwall carbon nanotubes (CNTs) have been assembled on various types of colloidal templates using the well-known polyelectrolyte-assisted layer-by-layer (LBL) assembly technique. Dense mono- and multilayers of CNTs were successfully deposited on silica, polystyrene, and melamine spherical colloids of different size, showing that relatively short CNTs completely wrap the surface of the spheres, while long nanotubes stick out of the surface, allowing them to contact various spheres at the same time. Decomposition of the colloidal template leads to formation of hollow CNT spheres, which was demonstrated through treatment of melamine@CNT particles with HCl. The deposition was also carried out on ordered arrays of polystyrene particles, leading to nanostructured, conducting CNT assemblies. Rupture of the assemblies with ultrasound shows that the assembly only takes place on one-half of the colloid spheres, so that "Janus" particles with asymmetric functionalities can be easily prepared.

Introduction

Carbon structures have been the subject of extensive research since the discovery of fullerenes[1] and carbon nanotubes (CNTs)[2] because of their unique structure-dependent electrical and mechanical properties. In recent years, considerable efforts have been made to fabricate different carbon morphologies and explore their application[3] in various fields including composites,[4] electrochemical devices,[5] field emission devices,[6] nanoscale electronic devices,[7] and sensors,[8] among others. Strategies for functionalizing carbon nanotubes and limitations in processing and assembly methods are important barriers for the pursuit of these potential applications, and for this reason new developments to assemble and align carbon nanotubes are needed.

In particular, the availability of high quality, homogeneous, thin films is a fundamental prerequisite for investigating their optical, optoelectronic, and electrical properties at a macroscopic scale. There have been a number of reports on the preparation of CNT thin films, including the spraying of CNT dispersions onto substrates,[9] stretching polymer films loaded with CNTs,[10] monolayer deposition by horizontally transferring surfactant-dispersed or chemically derivatized CNTs spread on water,[11] electrophoretic[12] and Langmuir−Blodgett deposition,[13] and layer-by-layer (LBL) assembly.[14,15]

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(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Iijima, S. *Nature* **1991**, *354*, 56.

(3) Frank, S.; Poncharal, P.; Wang, Z. L.; de Heer, W. A. *Science* **1998**, *280*, 1744. Kim, P.; Lieber, C. M. *Science* **1999**, *286*, 2148. Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127. Kyotani, T.; Tsai, L. F.; Tomita, A. *Chem. Mater.* **1996**, *8*, 2109. Zhu, H. W.; Xu, C. L.; Wu, D. H.; Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Science* **2002**, *296*, 884. Benito, A. M.; Maniette, Y.; Munoz, E.; Martinez, M. T. *Carbon* **1998**, *36*, 681. Fan, S. S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M.; Dai, H. J. *Science* **1999**, *283*, 512. Alekseyev, N. I.; Dyuzhev, G. A. *Carbon* **2003**, *41*, 1343.

(4) Biercuk, M. J.; Llaguno, M. C.; Radosavljevic, M.; Hyun, J. K.; Johnson, A. T.; Fischer, J. E. *Appl. Phys. Lett.* **2002**, *80*, 2767. Qian, D.; Dickey, E. C.; Andrews, R.; Rantell, T. *Appl. Phys. Lett.* **2000**, *76*, 2868. Haggenmueller, R.; Gommans, H. H.; Rinzler, A. G.; Fischer, J. E.; Winey, K. I. *Chem. Phys. Lett.* **2000**, *330*, 219. Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, *290*, 1331. Baughman, R. H. *Science* **2000**, *290*, 1310.

(5) An, K. H.; Kim, W. S.; Park, Y. S.; Moon, J.-M.; Bae, D. J.; Lim, S. C.; Lee, Y. S.; Lee, Y. H. *Adv. Funct. Mater.* **2001**, *11*, 387. Niu, C.; Sickel, E. K.; Hoch, R.; Moy, D.; Tennent, H. *Appl. Phys. Lett.* **1997**, *70*, 1480. Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; De Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *284*, 1340.

(6) de Heer, W. A.; Chatelain, A.; Ugarte, D. *Science* **1995**, *270*, 1179. Rinzler, A. G.; Hafner, J. H.; Nikolaev, P.; Lou, L.; Kim, S. G.; Tománek, D.; Nordlander, P.; Colbert, D. T.; Smalley, R. E. *Science* **1995**, *269*, 1550. Lee, N. S.; Chung, D. S.; Han, I. T.; Kang, J. H.; Choi, Y. S.; Kim, H. Y.; Park, S. H.; Jin, Y. W.; Yi, W. K.; Yun, M. J.; Jung, J. E.; Lee, C. J.; You, J. H.; Jo, S. H.; Lee, C. G.; Kim, J. M. *Diamond Relat. Mater.* **2001**, *10*, 265. Saito, Y.; Uemura, S.; *Carbon* **2000**, *38*, 169. Rosen, R.; Simendinger, W.; Debbault, C.; Shimoda, H.; Fleming, L.; Stoner, B.; Zhou, O. *Appl. Phys. Lett.* **2000**, *76*, 1668. Sugie, H.; Tanemura, M.; Filip, V.; Iwata, K.; Takahashi, K.; Okuyama, F. *Appl. Phys. Lett.* **2001**, *78*, 2578.

(7) Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. *Science* **2001**, *294*, 1317. Yao, Z.; Postma, H. Ch.; Balents, L.; Dekker, C. *Nature* **1999**, *402*, 273. Fuhrer, M. S.; Nygård, J.; Shih, L.; Forero, M.; Yoon, Y.; Mazzoni, M. S. C.; Choi, H. J.; Ihm, J.; Louie, S. G.; Zettl, A.; McEuen, P. L. *Science* **2000**, *288*, 494. Rueckes, T.; Kim, K.; Joselevich, E.; Tseng, G. Y.; Cheung, C.; Lieber, C. M. *Science* **2000**, *289*, 94. Franklin, N. R.; Li, Y.; Chen, R. J.; Javey, A.; Dai, H. *Appl. Phys. Lett.* **2001**, *79*, 4571.

(8) Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147. Kim, P.; Lieber, C. M. *Science* **1999**, *286*, 2148.

(9) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synth. Met.* **1999**, *103*, 2555. Kazaoui, S.; Minami, N.; Jacquemin, R.; Kataura, H.; Achiba, Y. *Phys. Rev. B* **1999**, *60*, 13339.

(10) Ichida, M.; Mizuno, S.; Kataura, H.; Achiba, Y.; Nakamura, A. *AIP Conf. Proc.* **2001**, *590*, 121.

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LBL assembly has attracted particular attention because of its enormous potential use in coatings, electronics, sensors, and controlled drug release.[16] Polyelectrolytes provided the first and most widely studied example of layer-by-layer self-assembly.[17] However, other charged compounds such as nucleic acids,[18] proteins,[16,19] multivalent metal ions,[20] ionic dyes,[21] nanoparticles,[16,22] and even viruses[23] also form layer-by-layer structures. In this way, not only thin films but also core−shell particles of tailored size and composition can be fabricated by using colloidal cores as templates onto which multilayers are assembled.[22,24] Subsequent removal of the core yields hollow capsules of polymer, inorganic, or organic−inorganic composites.[25] The composite particles and hollow capsules are attracting increasing interest in various fields, including materials science, catalysis, pharmaceutics, and medicine.[26] With few exceptions,[27] the thickness of the multilayer structure increases linearly with the number of layers,[28] which allows precise control over the thickness and properties of the film. These properties, along with a possibility of covalent linkage or electrostatic anchoring of various biomolecules to polymers, render layer-by-layer polyelectrolyte structures very attractive as building blocks for nanoscale device fabrication.

Kotov and co-workers have recently shown[15] that CNTs can be used in the LBL process upon surface charging, leading to ultrastrong, self-standing, thin films. In the work reported here, the LBL technique has been similarly used for the assembly of multiwall CNTs on various spherical colloids such as melamine (MF), polystyrene (PS), and silica, yielding colloidal nanocomposites with compact mono- or multilayers of carbon nanotubes. Such systems open up a plethora of possibilities to achieve new ways to assemble carbon nanotubes, and thereby to build more complicated structures. We introduce an approach toward fabricating conducting capsules based on the deposition of carbon nanotube shells on MF particles followed by removal of the organic cores. Also shown are preliminary results on the assembly of carbon nanotubes on hexagonally ordered arrays of polystyrene nanoparticles, which allows obtention of colloids with just one hemisphere coated with CNTs.

Experimental Section

Poly(diallyldimethylammonium chloride) (PDDA), $M_w < 500\,000$ Da, and poly(sodium 4-styrenesulfonate) (PSS), M_w 70 000 Da, were purchased from Aldrich. Sodium chloride was obtained from Merck. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system with a resistivity higher than 18.2 $M\Omega$ cm. Multiwall carbon nanotubes (MWNTs) synthesized using plasma-enhanced chemical vapor deposition (PECVD)[29] were kindly provided by Nanolab (Boston, MA) as a powder. Polystyrene and melamine colloidal particles were purchased from Microparticles GmbH, Berlin. SiO_2 nanoparticles (200 and 450 nm average diameters) were synthesized following the well-known Stöber method,[30] and concentrated by centrifugation.

Carbon nanotubes were oxidized by means of the following procedure.[31] A 10-mg aliquot of MWNTs was sonicated for 2 h in 10 mL of a mixture of H_2SO_4/HNO_3 (3:1). Then the sample was washed with a dilute NaOH aqueous solution and then washed 3× with water by centrifugation/redispersion cycles. Finally, the MWNTs were dispersed in water, obtaining a stable dispersion of oxidized MWNTs with carboxylic groups on the walls, providing a negative surface charge. Previous works have shown by X-ray photoelectron spectroscopy (XPS) analysis that the oxygen content for oxidized single-wall carbon nanotubes is between 9 and 14 atom %.[32]

Polyelectrolyte-coated PS particles were prepared by diluting 50 μL of a suspension of PS spheres (3 wt %) with water up to 1 mL, adding 1 mL of PDDA solution (1 mg/mL, containing 0.5 M NaCl), waiting for 20 min to allow PDDA adsorption, and then removing

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(11) Krstic, V.; Duesberg, G. S.; Muster, J.; Burghard, M.; Roth, S. *Chem. Mater.* **1998**, *10*, 2338. Sano, M.; Kamino, A.; Okamura, J.; Shinkai, S. *Langmuir* **2001**, *17*, 5125.

(12) Nakashima, N.; Kobae, H.; Sagara, T.; Murakami, H. *Chem. Phys. Chem.* **2002**, *3*, 456. Gao, B.; Yue, G. Z.; Qui, Q.; Cheng, Y.; Shimoda, H.; Fleming, L.; Zhou, O. *Adv. Mater.* **2001**, *13*, 1770.

(13) Guo, Y.; Minami, N.; Kazaoui, S.; Peng, J.; Yoshida, M.; Miyashita, T. *Physica B* **2002**, *323*, 235. Kim, Y.; Minami, N.; Zhu, W.; Zazaoui, S.; Azumi, R.; Matsumoto, M. *J. Appl. Phys.* **2003**, *42*, 7629.

(14) Shimoda, H.; Oh, S. J.; Geng, H. Z.; Walker, R. J.; Zhang, X. B.; Mcneil, L. E.; Zhou, O. *Adv. Mater.* **2002**, *14*, 899. Wu, B.; Zhang, J.; Wei, Z.; Cai, S.; Liu, Z. *J. Phys. Chem. B* **2001**, *105*, 5075. Liu, Z.; Shen, Z.; Zhu, T.; Hou, S.; Ying, L. *Langmuir* **2000**, *16*, 3569.

(15) Mamedov, A. A.; Kotov, N. A.; Prato, M.; Guldi, D. M.; Wicksted, J. P.; Hirsch, A. *Nat. Mater.* **2002**, *1*, 190. Olek, M.; Ostrander, J.; Jurga, S.; Möhwald, H.; Kotov, N.; Kempa, K.; Giersig, M. *Nano Lett.* **2004**, 1889.

(16) Decher, G.; Eckle, M.; Schmitt, J.; Struth, B. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 32−39.

(17) Decher, G. *Science* **1997**, *277*, 1232. Kotov, N. A.; Dekany, I.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 13065.

(18) Lvov, Y.; Decher, G.; Sukhorukov, G. *Macromolecules* **1993**, *26*, 5396.

(19) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6117.

(20) Radtchenko, I. L.; Sukhorukov, G. B.; Leporatti, S.; Khomutov, G. B.; Donath, E.; Mohwald, H. *J. Colloid Interface Sci.* **2000**, *230*, 272.

(21) Caruso, F.; Lichtenfeld, H.; Donath, E.; Mohwald, H. *Macromolecules* **1999**, *32*, 2317. Tedeschi, C.; Caruso, F.; Mohwald, H.; Kirstein, S. *J. Am. Chem. Soc.* **2000**, *122*, 5841.

(22) Caruso, F. *Adv. Mater.* **2001**, *13*, 11. Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111.

(23) Lvov, Y.; Haas, H.; Decher, G.; Mohwald, H.; Mikhailov, A.; Mtchedlishvily, B.; Morgunova, E.; Vainshtein, B. *Langmuir* **1994**, *10*, 4232.

(24) Keller, S. W.; Johnson, S. A.; Brigham, E. S.; Yonemoto, E. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1995**, *117*, 12879. Chen, T.; Somasundaran, P. *J. Am. Ceram. Soc.* **1998**, *81*, 140. Caruso, F.; Lichtenfeld, H.; Möhwald, H.; Giersig, M. *J. Am. Chem. Soc.* **1998**, *120*, 8523. Caruso, F.; Möhwald, H. *Langmuir* **1999**, *15*, 8276. Caruso, F.; Susha, A. S.; Giersig, M.; Möhwald, H. *Adv. Mater.* **1999**, *11*, 950. Salgueiriño-Maceira, V.; Caruso, F.; Liz-Marzán, L. M. *J. Phys. Chem. B* **2003**, *107*, 10990. Correa-Duarte, M. A.; Sobal, N.; Giersig, M.; Liz-Marzán, L. M. *Adv. Mater.* **2004**, *16*, 2179.

(25) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2201. Caruso, F.; Schüler, C.; Kurth, D. G. *Chem. Mater.* **1999**, *11*, 3394. Caruso, F.; Caruso, R. A.; Möhwald, H. *Chem. Mater.* **1999**, *11*, 3309. Caruso, F.; Trau, D.; Möhwald, H.; Renneberg, R. *Langmuir* **2000**, *16*, 1485. Caruso, F.; Yang, W.; Trau, D.; Renneberg, R. *Langmuir* **2000**, *16*, 8932. Gittins, D. I.; Caruso, F. *Adv. Mater.* **2000**, *12*, 1947. Caruso, F.; Spasova, M.; Salgueiriño-Maceira, V.; Liz-Marzán, L. M. *Adv. Mater.* **2001**, *13*, 1090.

(26) Caruso, F. *Chem. Eur. J.* **2000**, *6*, 413.

(27) Lavalle, P.; Gergely, C.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C.; Picart, C. *Macromolecules* **2002**, *35*, 4458. Picart, C.; Lavalle, P.; Hubert, P.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C. *Langmuir* **2001**, *17*, 7414. Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12531.

(28) Advincula, R.; Aust, E.; Meyer, W.; Knoll, W. *Langmuir* **1996**, *12*, 3536−3540. Xie, A. F.; Granick, S. *Macromolecules* **2002**, *35*, 1805.

(29) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, *282*, 1105.

(30) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(31) Yu, R.; Chen, L.; Liu, Q.; Lin, J.; Tan, K.-L.; Ng, S. C.; Chan, H. S. O.; Xu, G.-Q.; Hor, T. S. A. *Chem. Mater.* **1998**, *10*, 718.

(32) Zhao, W.; Chulho, S.; Pehrsson, P. E. *J. Am. Chem. Soc.* **2002**, *124*, 12418.

excess PDDA by three repeated centrifugation/wash cycles. The centrifugation speed was dependent on the particle size and was 2500 g/10 min for 1-μm diameter spheres. PSS (1 mg/mL containing 0.5 M NaCl) was then deposited onto the coated PS particles in a similar fashion and using the same conditions, followed by an additional layer of PDDA, which forms the outermost layer.

CNT/PDDA multilayer coatings were deposited on the PS spheres as follows: 15 μL of the (PDDA/PSS/PDDA)-coated PS particles (2 wt %) were dispersed in 4 mL of a 0.2 M NaCl solution, and then 4 mL of CNT dispersion (0.5 mg/mL) was added. An adsorption time of 30 min was then allowed, and excess CNTs were removed by five repeated centrifugation (800*g*, 10 min)/wash cycles. PDDA (1 mg/mL solution containing 0.5 M NaCl, adsorption time of 30 min) was subsequently deposited and the excess was removed from the supernatant after centrifugation (1200*g*, 10 min). Additional CNT/PDDA multilayers were deposited as described above.

The same procedure was used for deposition on SiO_2 particles ((PDDA/PSS/PDDA)-coated SiO_2) and also for MF particles ((PSS/PDDA)-coated MF) but avoiding the first PDDA polymer layer since MF particles have positive surface charge.

Hollow capsules were prepared by exposing 0.5 mL of MF spheres coated with 3 (PDDA/CNT) bilayers to 1 mL of HCl solution (1 mL, pH 1) for 20 min. To ensure complete core removal, this process of acid exposure/washing was repeated 2×. The hollow capsules were then washed 3× by centrifugation at 12 000*g* for 10 min and redispersed in pure water.

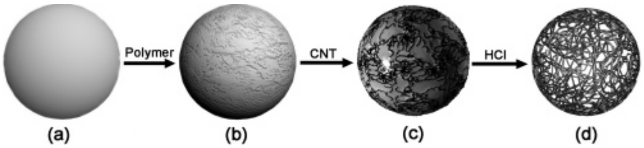
For preparing 0.5×1 cm^2 monolayers of hexagonally ordered PS spheres, silicon substrates were cleaned in a solution of 7% NH_4OH/30% H_2O_2/water (1:1:5) for 60 min at 80 °C, rinsed with milli-Q water, and dried under an argon stream. PS spheres (980 nm) were used as received (10% aqueous dispersion). The particle suspension was diluted by mixing with an equal volume of ethanol. The ethanol/water PS solution was slowly deposited on the surface of clean water inside a 15 cm ϕ Petri dish, using a glass pipet, so that a particle monolayer was formed. Part of the surface was left uncovered to avoid formation of cracks in the lattice during the following steps of the preparation. Finally, the monolayer was deposited on a substrate by slow water evaporation.

The obtained templates (0.5×1 cm^2 monolayer of hexagonally ordered PS spheres) were coated with MWNTs following basically the same procedure described above. The monolayer substrate was first introduced into a solution of PDDA (1 wt %, 0.5 M NaCl) during 2 h, and after 5 washing cycles with pure water for 20 min, PSS (1 mg/mL, 0.5 M NaCl) was deposited using the same conditions, followed by an additional layer of PDDA. Then the substrate was introduced into a MWNT dispersion (0.5 mg/mL, 0.1 M NaCl) during 4 h, and finally the substrate was washed with pure water 5× (10 min each).

Results and Discussion

The method used for assembly of MWNTs on spherical colloids is based on the formation of polyelectrolyte multilayers by sequential adsorption of oppositely charged polymers, and thus relies on the mutual electrostatic attraction between the charged species. The starting negatively (PS, SiO_2) or positively (MF) charged spherical colloids were coated respectively with a positively or negatively charged polyelectrolyte (PDDA or PSS) in order to obtain a uniform distribution of charges on the surface.[22] Carbon nanotubes synthesized by the plasma-enhanced chemical vapor deposition (PECVD) method[29] do not carry a surface charge, and therefore must be modified prior to the assembly. In this work, charging was performed by chemical oxidation using sulfuric and nitric acid, which led to the formation of carboxylic groups at both the tips and sidewalls,[31,33] which are responsible for the presence of the necessary negative charges on the carbon nanotube surface to obtain a stable dispersion of individual carbon nanotubes in water and to assemble on positively charged surfaces. The production of hollow polyelectrolyte/CNT capsules from the obtained core−shell particles can be performed by dissolution and removal of the cores with an appropriate solvent (dilute HCl solution for MF, tetrahydrofurane for PS, or HF for silica). The various steps followed in this procedure are summarized in Scheme 1.

Scheme 1. Summary of the Various Steps during CNT Assembly: (a) Spherical Colloidal Particle; (b) Polyelectrolyte Coating; (c) Adsorption of Carbon Nanotubes; and (d) Removal of the Core



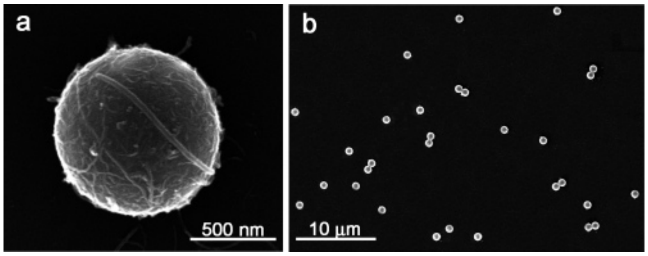


Figure 1. SEM images of 980- nm polystyrene particles coated with one layer of MWNTs.

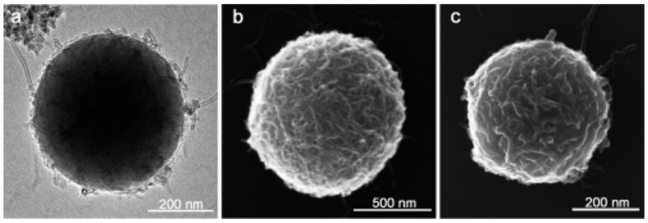


Figure 2. Electron micrographs showing various colloidal spheres coated with MWNTs: (a) TEM of a silica particle (450 nm) coated with one layer of MWNTs; (b) SEM picture of a polystyrene particle (980 nm) coated with 2 layers of MWNTs; and (c) SEM image of a melamine particle (350 nm) coated with 3 layers of MWNTs and covered with an external layer of PDDA.

Figure 1shows representative SEM images of the resulting nanocomposite particles upon adsorption of nanotubes on PS (in this particular case) spheres. Irrespective of the sizes and thickness of the nanotubes, homogeneous wrapping of the surface by the CNTs was obtained and the particles were stable without further treatment.

This assembly process can be generalized to the assembly of CNTs with different diameter and length onto spherical particles of various size and nature as templates. Examples are shown in Figure 2 of composite colloids formed by assembly of one or more monolayers of carbon nanotubes

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(33) Jiang, K.; Eitan, A.; Schadler, L. S.; Ajayan, P. M.; Siegel, R. W.; Grobert, N.; Mayne, M.; Reyes-Reyes, M.; Terrones, H.; Terrones, M. *Nano Lett.* **2003**, *3*, 275.

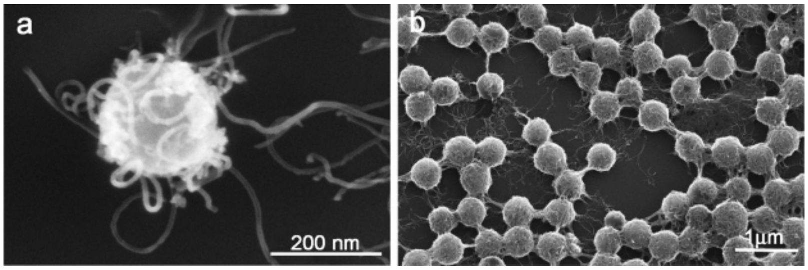

Figure 3. (a) TEM micrograph of 3−5-μm-long CNTs assembled on 200-nm-diameter silica spheres. (b) SEM micrograph of 20−50-μm-long CNTs assembled on 400-nm-diameter polystyrene spheres.

with different lengths on melamine, polystyrene, and silica spheres. In all cases, compact and uniform packing was achieved, allowing a good control on the thickness of the nanocomposites through the number of layers deposited. The appearance is slightly different in Figure 2c, since the 350-nm melamine spheres were coated with three monolayers of carbon nanotubes and finally covered with an additional polyelectrolyte layer, which assists in preserving the structure of the composite in aqueous solution.

The versatility in the size and nature of the colloids and the CNTs allows design of a variety of structures, ranging from the pure core−shell morphologies shown in Figure 2, for CNTs which are short compared to the size of the template, to interconnected networks when the CNTs are long compared to the diameter of the spheres. Examples are shown in Figure 3. In Figure 3a, one silica particle (200-nm diameter) is shown on which 3−5 μm long carbon nanotubes were assembled. It is clear that the CNTs do not wrap the sphere completely and therefore stick out of the surface at various sites, so that such a hairy morphology can lead to “connections” between particles. It is remarkable that a large degree of flexibility is observed for these carbon nanotubes, which can be related to some loss of rigidity during the oxidation process. Even larger size differences can be achieved, as shown in Figure 3b, for 400-nm diameter PS spheres on which 20−50 μm long CNTs were assembled. In this image one can clearly see that the partially desorbed carbon nanotubes can function as anchoring bridges for creating connections between particles. This feature can be exploited to link colloidal spheres to other structures or to enhance the attachment to various substrates.

Hollow shells made of interconnected CNTs can be successfully prepared after PDDA/PSS/PDDA/CNT layers have been deposited onto decomposable colloidal template particles, such as weakly cross-linked MF particles. When the coated particles are exposed three times to hydrochloric acid at pH 1 for 10 min, decomposition of the MF particles into their constituent oligomers occurs. The oligomers have a cross section of approximately 1 nm and are readily expelled from the core by permeating the polyelectrolyte/CNT layers forming the shells. When the obtained hollow capsules are characterized by SEM (Figure 4a and b), it looks like the diameter of the dried shells (ca. 900 nm) is slightly larger than that of the core−shell precursors (600−650 nm), indicating that spreading occurs upon drying on the substrate, an effect that is often observed for capsules made of flexible materials.[34] This flattening of the shells upon drying has been confirmed by tilting the sample within the SEM (Figure 4c).

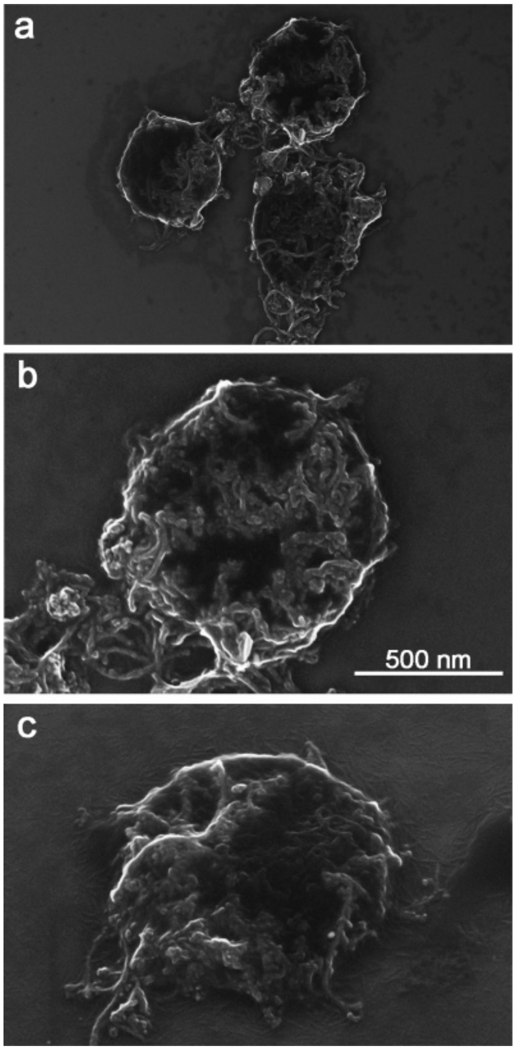

Figure 4. SEM micrographs of a collapsed shell made of three layers of polyelectrolyte followed by three CNT/polyelectrolyte bilayers: (a and b) top view; (c) tilted (10°) view.

This method opens up the opportunity to build new 3D hollow structures based on the assembly of CNT-coated colloidal spheres as building blocks and subsequent template removal.

A first demonstration of the potential of this method to build nanostructured materials was performed by using a 2D hexagonally ordered assembly of polystyrene spheres as a substrate for CNT assembly. A 0.5 × 1 cm^2 monolayer of hexagonally ordered PS spheres (1710 nm) was obtained by

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(34) Pastoriza Santos, I.; Schöler, B.; Caruso, F. *Adv. Funct. Mater.* **2001**, *11*, 122. Sukhorukov, G. B.; Brumen, M.; Donath, E.; Möhwald, H. *J. Phys. Chem. B* **1999**, *103*, 6434.

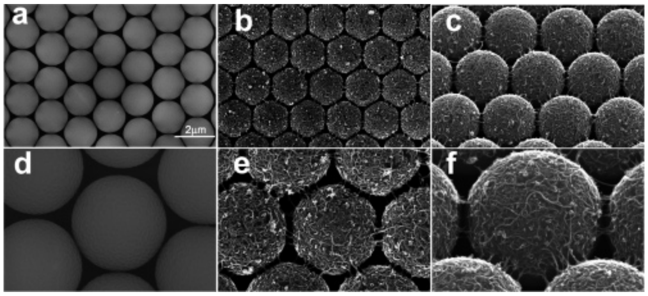

Figure 5. SEM images of polystyrene particles with hexagonal order before (a and d) and after (b,c,e,f) assembly of carbon nanotubes. All images correspond to the same sample but images c and f have been obtained with a tilting angle of 10°. Scale corresponds to a.

a recently published technique[35] (see Experimental Section for details). Assembly of PDDA and CNTs on this nanostructured solid substrate can be carried out using the standard LBL procedure,[17] whereby the CNTs are deposited following the morphology of the sphere monolayer and maintaining the 2D ordered structure. SEM images of the formed nanostructures show that some carbon nanotubes serve as connecting points between neighboring spheres within the resulting composite monolayer (Figure 5). Such CNT connections can ensure that electrical conductivity is maintained in the film, even with a minimum load of CNTs. Resistivity values between 650 and 750 kOhm were measured for dry samples.

The presence of such connections between particles suggests that CNT deposition takes place selectively on the upper surface, with no infiltration within the interstices. This hypothesis can be tested by sonication of the modified substrates in water, so that the links between particles are broken while the CNT coating remains intact. Examination of the resulting aqueous colloid (see Figure 6) clearly indicates that the PS particles are functionalized with carbon nanotubes exclusively in one hemisphere, which can be further exploited for nanostructure build-up based on asymmetric interactions.

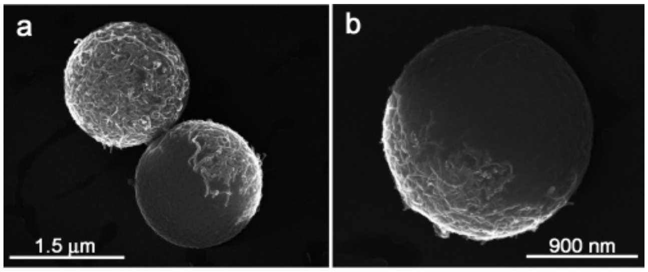

Figure 6. SEM images of polystyrene particles functionalized with CNTs on a single hemisphere. Note that some structure is observed on the bare PS surface (see also Figure 5d), but the contrast is much more intense for CNTs due to charging.

Conclusions

In summary, we have demonstrated that by using the LBL assembly technique stable and well-defined mono- and multilayers of CNTs can be deposited on various spherical colloids. The resulting CNT structures are excellent candidates to be used as building blocks for the fabrication of novel nanocomposite materials with a regular and ordered distribution of carbon nanotubes. Also, this fabrication technique should allow realization of optically homogeneous CNT thin films with a controlled thickness and regular nanostructures which are needed for the fabrication of many useful devices such as chemical sensors, pressure sensors, switches, linear and nonlinear optical devices, and nanoelectronic devices. We have also been able to prepare Janus particles through assembly on monolayers, which constitutes a relevant development in colloid synthesis and processing.

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(35) Kosiorek, A.; Kandulski, W.; Chudzinski, P.; Kempa, K.; Giersig, M. *Nano Lett.* **2004**, 4, 1359.