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Highly Adapted Polymer Templates Formed By Phase Inversion Technique for Electrodeposition of Platinum Dots

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Platinum dots were fabricated by using procedure that combines a phase separation step to form a porous polymer template followed by an electrochemical deposition step to produce Pt dots. First, the phase separation technique was used to form a thin porous polymer film of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) on a gold substrate using a solution that contained a volatile solvent, a less volatile non-solvent and a polymer. After the polymer template was formed on the substrate, electrochemical deposition through the polymer template was performed to fill the porous film with platinum. This was followed by the removal of the template by dissolution in acetone or N-methyl-pyrrolidone (NMP) to produce Pt dots.

Keywords: Pt-Dots, Phase inversion, phase separation technique, electrodeposition

1. INTRODUCTION

The ability to fabricate structures on the micron and submicron scales has revolutionized science. By placing these microstructures into bulk materials, we can capitalize on their unique properties to generate functional materials for a wide range of applications.[1-2] The platinum group metals, (e.g., palladium and platinum) have high surface stability and are employed in a wide range of applications, such as electrodes and catalysts in electrochemistry and surface sciences. Because of their superior surface qualities, the structure of these materials has recently attracted much attention.[3-5] Several methods have been employed to produce various sizes and shapes of platinum particles on substrates. These include lithographic techniques [6-8] and methods that use porous alumina or poly(styrene) sphere templates. [9-10] Template-deposition techniques have been widely used to fabricate nanostructured materials at a very low cost. First, the template is assembled from a self-organizing material such as polystyrene spheres which become widely used to assemble these templates because they are commercially available in a wide range of sizes with a narrow size distribution. [10] Several concepts, such as gravity sedimentation [11-13] and capillary forces at the meniscus between a substrate and the spheres' colloidal solution[14-18] were initially considered when the idea of assembling spheres into templates was first explored. After the formation of the templates, the interstitial spaces are then impregnated with the desired precursors. Finally, the template is removed, resulting in arrays of anti-dot porous films that reflect the inverted structure of the template. Various anti-dot porous films have been prepared by several groups via infiltration of the spaces between the template by metals[19-20] and metal oxides.[21-22]

In an attempt to prepare nanodots of metals, Bartlett *et al.[*23] used a double templated electrodeposition technique for the fabrication of supported thin arrays of nanodots. This was achieved by electrochemical deposition of the metal inside the cavities of macroporous poly(pyrrole) templates, which were themselves prepared by templated electrodeposition using self-assembled poly(styrene) spheres on evaporated Au substrates as the primary template arrays. The size and the distance between the metal dots in the arrays were manipulated by changing the deposition charge or the diameter of the poly(styrene) spheres used to form the primary template. The electrochemical deposition has a number of significant advantages such as produces a high density deposit and no shrinkage of the material takes place when the template is removed. Additionally, it can be used to prepare a wide range of materials and allows for fine control over the thickness of the resulting film through control of the total charge passed during depositing the film. Xu *et al.[*24] reported two methods for the fabrication of arrays of nanospheres of gold and thermoelectric alloys by electrochemical deposition through a poorly conductive nickel oxide mesh or by infiltration of molten metals into a carbon matrix at high temperature and pressure.[25] All of the above mentioned procedures suffer from long preparation steps, along with the difficulties of scaling up the template to cover larger surface areas.

In this paper, we demonstrate a simple scheme that combines a phase separation step to form a polymer template, with an electrochemical deposition step, to produce Pt dots. First, the phase separation technique was used to form a thin porous polymer film of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) on a gold substrate. The thin polymer film was formed by the dip coating method using a solution that contained a volatile solvent, a less volatile non-solvent and a polymer. The preferential loss of solvent will generate meta- or unstable composition, and phase separation will be induced at this point. The phase separation was achieved by diffusion of the non-solvent into the polymer film to produce a polymer membrane containing spherical cavities. Once the template was formed on the substrate, electrochemical deposition through the polymer template was performed to fill the porous film with Pt. This was followed by the removal of the template by dissolution in acetone or N-methyl-pyrrolidone (NMP) to produce Pt macrodots. The ability to fabricate these dots plays an extremely important role in elucidating the catalytic, optical and magnetic properties of these materials and their diverse applications. Pt particles can be used in a range of applications in electronics, sensor technology and electrochemical reactions in fuel cells.[26-27] Additionally, the impeding of the Pt particles into the porous polymer film could enhance the mechanical strength as well as thermal and conductivity of the film and open the door for its use in wide applications. [28] Also typical metals include gold, silver, platinum, and palladium when linked to or embedded within polymeric drug carriers, metal particles can be used as thermal release triggers when irradiated with infrared light or excited by an alternating magnetic field. [29] The advantages of producing templates by phase separation are low cost, short production time, and significant potential for industrial scale-up.

2. EXPERIMENTAL

All solvents and chemicals were of reagent quality and were used without further purification. PVDF-HFP (MW 400,000 g mol^{-1}), hexachloroplatinic acid, H_2PtCl_6 (purity 99.99%), isopropanol, N-methyl-pyrrolidone (NMP) and acetone were obtained from Aldrich. All solutions were freshly prepared using reagent-grade water (18 MΩ cm), Integral System from Millipore.

Beforehand, the gold substrates were prepared by evaporating 10 nm of a chromium adhesion-promoting layer, followed by 200 nm of gold onto 1 mm thick glass microscope slides. The gold substrates were thoroughly cleaned before use. First, they were sonicated in deionized water for 30 min, followed by sonication in isopropanol for 1.5 h. The substrates were then rinsed with deionized water and dried under a pure and gentle argon stream.

The porous polymer templates were formed by the phase separation technique from a solution containing a poly(vinylidene fluoride-co-hexafluoropropylene(PVDF-HFP) powder in both acetone and water. Acetone was selected; because it is a solvent for the PVDF-HFP and is readily volatile. Water was selected; because it is a non-solvent for the PVDF-HFP and less volatile than acetone. First, the required weight of the PVDF-HFP powder was added to acetone while stirring, until a clear polymer solution was obtained. Then, water was added to this solution while stirring. The water was added to the polymer solution in a controllable manner to obtain the required weight ratio of acetone to water. Adding water to the polymer solution increased the viscosity of the mixture, and if the weight ratio of acetone to water exceeded 1:1, the polymer began to precipitate.

A thin layer of polymer film was formed on a gold substrate by the dip coating technique at a controlled speed of 0.2 cm/min. Coating thickness generally increases with faster withdrawal speed. The thickness is determined by the balance of forces at the stagnation point on the liquid surface. A faster withdrawal speed pulls more fluid up onto the surface of the substrate before it has time to flow back down into the solution. The thickness is primarily affected by the viscosity of the polymer solution. Thick polymer film was obtained from a solution containing 2wt.% PVDF-HFP with a ratio of 1:1 of acetone to water. The pore size of the polymer template was tuned by controlling the weight ratio of acetone to water. Polymer templates of submicron sized pores were obtained from a 1 wt.% PVDF-HFP with a weight ratio of 1:1, acetone to water. The substrate was then left to dry in ambient conditions. The acetone is much more volatile than water and started to evaporate first and the evaporation of the acetone led to instantaneous mutual diffusion between the solvent and non-solvent, creating a highly porous polymer matrix.

Electrochemical deposition was performed in a conventional three-electrode configuration thermostated cell at 25°C that was controlled by a potentiostat/galvanostat (VSP-Biologic Science Instruments). The template-coated gold substrate was the working electrode, with a large area platinum gauze counter electrode and a saturated calomel reference electrode (SCE). Pt films were deposited from an aqueous solution containing 50 mM of hexachloroplatinic acid under potentiostatic conditions at 0.05 V versus SCE. This potential was chosen because it produced a smooth Pt film inside the pores of the polymer film. The thickness of the Pt film was adjusted by controlling the total charge passed during the electrodeposition of the metal. After deposition, the samples were soaked in acetone or methylpyrrolidone (NMP) for 1 hour to remove the PVDF-HFP template, to produce Pt dots.

An environmental scanning electron microscope FEI Nova 200 dual-beam scanning electron microscope was employed to study the morphologies and structures of both the polymer templates and metal films of the Pt macro-dots.

3. RESULTS AND DISCUSSION

Platinum dots were fabricated by using a simple procedure shown in Figure 1 that combines a phase separation step, to form a polymer template and an electrochemical deposition step to produce Pt macrodots. PVDF-HFP is a copolymer consisting of crystalline vinylidene fluoride (VDF) and amorphous hexafluoropropylene (HFP) units. When the polymer is subjected to the phase separation conditions, it yields a great number of pores with a wide range of pore sizes. Many examples of phase separation of PVDF-HFP were reported for various applications. [30-32] In this paper, the porous polymer template composed of PVDF-HFP was prepared by phase separation using a solution containing a volatile solvent, e.g., acetone, and a less volatile non-solvent, e.g., water. First, the polymer powder was dissolved into acetone to form a clear solution. Then, water was added to the polymer solution. A thin layer of the polymer /acetone / water mixture was formed on the substrate. Then, the substrate was left to dry in ambient conditions. The evaporation of the acetone leads to an instantaneous occurrence of mutual diffusion between the solvent and the non-solvent, thus creating a highly oriented porous structure in the polymer matrix. The opposing diffusion causes the solvent to evaporate from the thin polymer film, while the non-solvent will penetrate the film. When the PVDF-HFP polymer is subjected to these two types of diffusion, it can undergo microphase separation to form a diverse array of periodic nanostructures.[33]

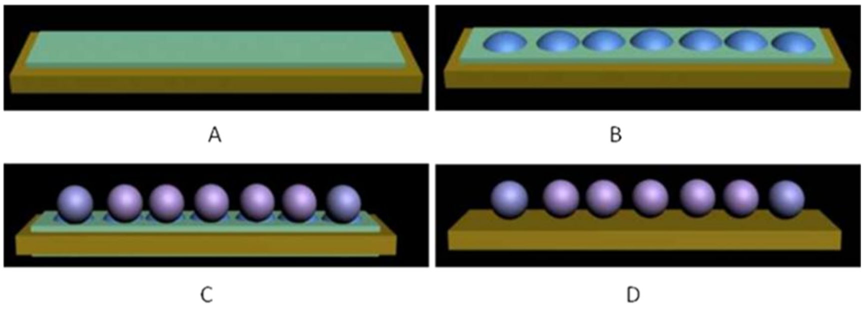

Figure 1. Schematic illustration of the procedure involved in the formation of the Pt macro-dots using the phase separation and electrodeposition techniques: A) Dip coating formation of a thin film from polymer/solvent/non-solvent mixture. B) Evaporation of solvent to form a template of a porous polymer film. C) Electrochemical deposition of Pt through the template. D) Dissolving the template to form Pt macro-dots.

Figures 2A-D show SEM images of the PVDF-HFP thin films formed on top of the gold substrates. The polymer films have various morphologies and different pore sizes according to the formation conditions. Figure 2A, shows an SEM image of a thin polymer film, obtained from a 2 weight % PVDF-HFP polymer in acetone. Water was not added to this solution and when acetone evaporated, no phase separation occurred, so a compact polymer film formed on top of the gold substrate. High magnification SEM images show the existence of a small number of microporous due to the evaporation of acetone. In Figure 2B, the SEM image shows the morphology of the polymer film obtained by phase separation from a 2 weight % PVDF-HFP polymer in acetone. Water was added to this solution at a weight ratio of 1:1 of acetone to water. As the acetone evaporated, the phase separation occurred and the mutual diffusion between solvent and non-solvent formed a diverse range of periodic macrostructures.

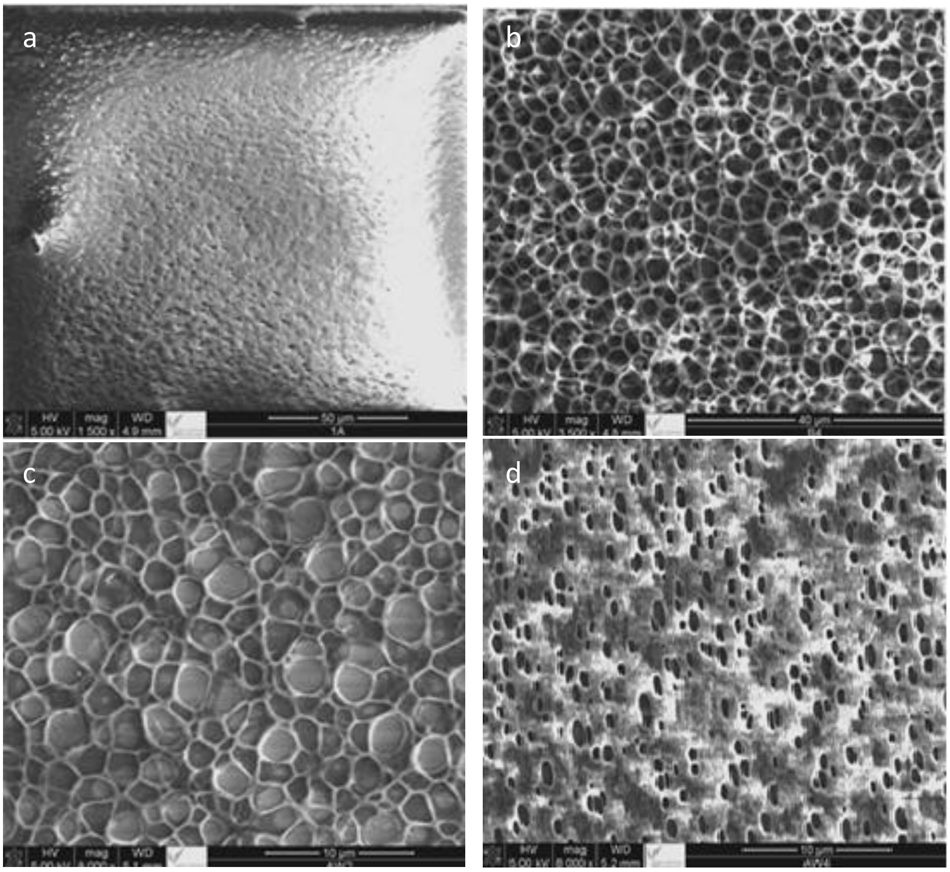

Figure 2. SEM images of the polymer films produced by phase separation techniques on the top of a gold substrate. A) non-porous polymer film obtained from a 2.0 wt. % of PVDF-HFP polymer in acetone. B) Multiple layers of porous template obtained from a 2.0 wt. % of PVDF-HFP polymer in acetone. Water was added to this solution, with a weight ratio of 1:1 of acetone to water. C) A thin layer of a porous template obtained from a 1.0 wt % of PVDF-HFP polymer in acetone. Water was added to the solution with a weight ratio of 10:1 of acetone to water respectively. D) A thin layer of a porous template produced from a 1.0wt. % of PVDF-HFP polymer in acetone. Water was added to the solution with a weight ratio 1:1 of acetone to water.

The pores that were created have irregular sizes and diameters in the range of a few micrometers. Additionally, the polymer film was relatively thick and consisted of multiple layers of misaligned and connected spherical macrocavities.

In an attempt to control the thickness of the polymer film and consequently the number of layers of macrocavities, a polymer/acetone/water solution of different compositions have been used. Figure 2C shows the SEM image of a porous polymer film created by phase separation using a 1.0 weight % PVDF-HFP polymer in acetone. Water was added to the solution at a weight ratio of 10:1 of acetone to water. Lowering both the concentration of the polymer and the water content produced a less viscous solution. Dip coating of this less viscous polymer solution produced a very thin porous film, seemingly composed of a single monolayer of these macrocavities on the gold substrate. The ability to produce templates of controlled thickness and porosity will facilitate the diffusion of ions, thus providing efficient access to the conducting substrates during the electrochemical deposition step. Additionally, to control the film thickness, the possibility of tuning the pore size of the polymer template has been investigated. To achieve this, the amount of water in the polymer/acetone/water mixture has been increased. Figure 2D shows an SEM image of the polymer template obtained from a 1 weight % PVDF-HFP polymer in acetone. Water was added to the solution at a weight ratio of 1:1 of acetone to water. The image clearly indicates that the pore size decreases as the amount of water in the polymer solution increases. The pore diameter changed from a few microns (figure 2B) to submicron (figure 2D) as the acetone to water ratio varied from 10:1 to 1:1. Moreover, the pores became increasingly separated in the case of adding more water to the polymer film.

The electrochemical deposition of platinum from an aqueous solution of *hexachloroplatinic acid*(HCPA) has been studied.[34-35] Pt films with a controlled thickness were electrochemically deposited from aqueous solutions through the pre-assembled porous polymer templates. Figure 3 shows the current versus time curve for the electrodeposition of the Pt film through a porous polymer templateunder potentiostatic conditions. As the platinum film grows in the template, the active electrode surface area increases continuously and the current also increase. If the film thickness grows more than the thickness of the template, the platinum macro-dots will touch each other to form a continuous film.. The thickness of the electrodeposited film could be precisely controlled by varying the charge passed during electrodeposition.

Figure 4A shows an SEM image of a two-dimensional film of Pt macrodots prepared using the PVDF-HFP polymer template. The porous polymer template was prepared using the same conditions that has been used to prepare the film shown in the Figure 2C. The deposition charge was calculated at 0.21 mAh/cm^2. The image indicates that the deposition of the metal only occurred inside the spherical macro-voids, starting at the bottom of the film on the circular exposed regions of the gold substrate and the Pt macrodots have a uniform hemispherical shape.

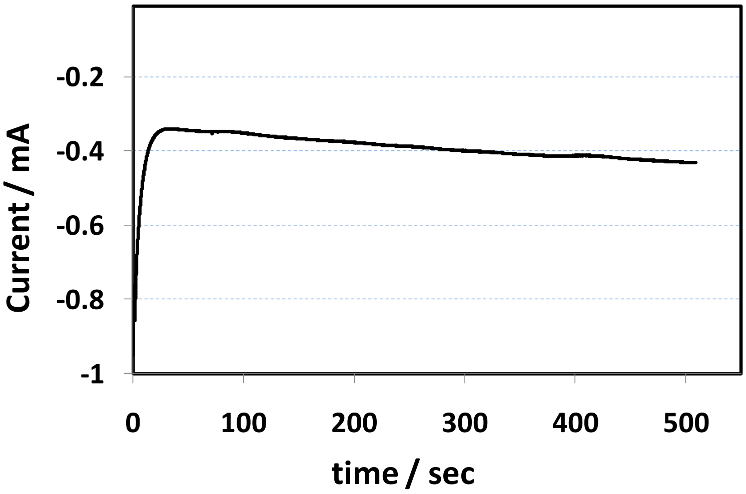

Figure 3. Current versus time curve for the electrodeposition of Pt in a porous polymer template. Pt films were deposited from an aqueous solution containing 50 mM of hexachloroplatinic acid under potentiostatic conditions at 0.05 V versus SCE using a conventional three-electrode cell.

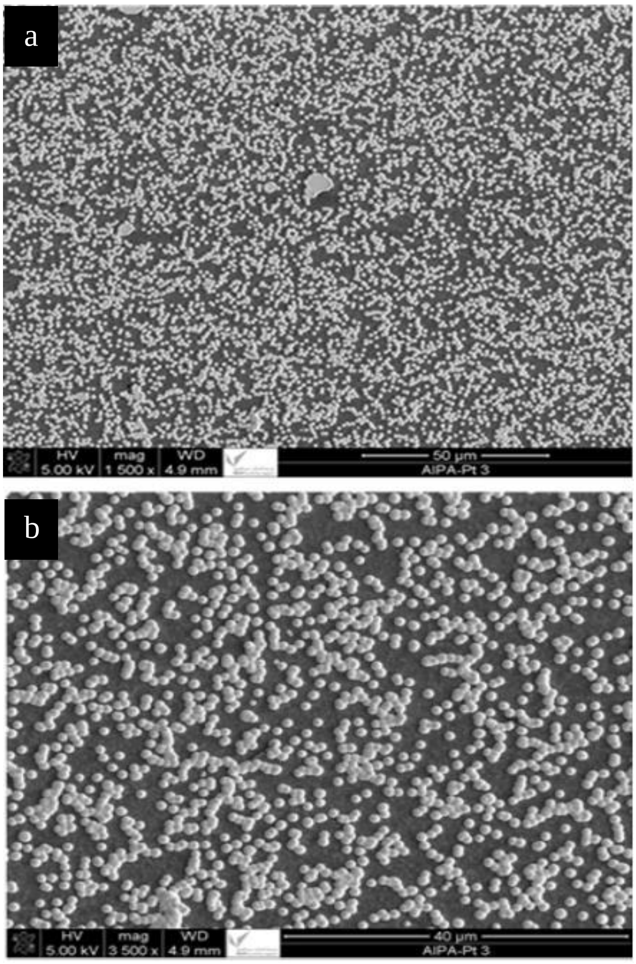

Figure 4. SEM image of Pt macro-dots produced by the electrodeposition through a PVDF-HFP template (a). and the Pt macro-spheres after removing of the PVDF-HFP templates by dissolving in acetone solution (b).

When the height of the electrodeposited Pt film increased the Pt macrodots started to come into contact with each other. Removing the polymer template by dissolving it in acetone leaves a film Pt dots on top of gold substrate. We found no evidence suggesting significant shrinkage or expansion of the structure during the electrodeposition process or after the template was removed, as shown in figure 4B-C. Consequently, the resulting Pt macrodots is a true cast of the template structure.

4. CONCLUSIONS

In conclusion, the combination of the phase separation and electrochemical deposition provides a simple scheme that can be used to fabricate Pt macrodots. The thin polymer film was formed by the dip coating method using a solution containing acetone as a volatile solvent, water as a less volatile non-solvent and a polymer. As the acetone evaporates, the phase separation takes place, and the mutual diffusion between the solvent and the non-solvent forms a diverse range of periodic macrostructures. The thickness of the polymer template can be changed by changing the viscosity of the polymer/acetone/water mixture. Moreover, the pore size of the polymer template can be tuned by controlling the weight ratio of acetone to water. Electrodeposition through the pores of the template produces Pt macrodots. The ability to easily fabricate a large variety of such photonic metallic structures at a low cost will secure applicability in many diverse areas which range from biotechnology to optoelectronics.

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References

1. C. B. Murray, C. R. Kagan and M. G. Bawendi, *Science*, 270 (1995) 1335.
2. M. Zhao, L. Sun and R. M. Crooks, *J. Am. Chem. Soc.*, 120 (1998) 4877.
3. M. E. Abdelsalam, S. Mahajan, P. N. Bartlett, J. J. Baumberg , and A. E. Russell, *J. Am. Chem. Soc.*, 129 (2007) 7399.
4. R. Gómez, J. Solla-Gullón, J. M. Pérez and A. Aldaz, *J. Raman Spectrosc.*, 36 (2005) 613.
5. R. Gómez, J. M. Pérez, J. Solla-Gullón, V. Montiel and A. Aldaz, *J. Phys. Chem. B*, 108 (2004) 9943.
6. O. Dial, C. C. Cheng and A. Scherer, *J. Vac. Sci. Technol. B*, 16 (1998) 3887.
7. E. F. Wassermann, M. Thielen, S. Kirsch, A. Pollmann, H. Weinforth and A. Carl, *J. Appl. Phys.*, 83 (1998) 1753.
8. M. Farhoud, M. Hwang, H. I. Smith, M. L. Schattenburg, J. M. Bae, K. Youcef-Toumi and C. A. Ross, *IEEE Trans. Magn.*, (1998) 34.
9. R. Zhu, Y. T. Pang, Y. S. Feng, G. H. Fu, Y. Li and L. D. Zhang, *Chem. Phys. Lett.*, 368 (2003) 696.
10. M. S. Sander and L. Tan, *Adv. Funct. Mater.*, 13 (2003) 393.
11. M. Himmelhaus and H. Takei, *Phys. Chem. Chem. Phys.*, 4 (2002) 496.
12. P. Pieranski, *Contemp. Phys.*, 24 (1983) 25.

13. K. E. Davis, W. B. Russel and W. J. Glantschnig, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 411.
14. H. Miguez, F. Meseguer, C. Lopez, A. Blanco, J. S. Moya, J. Requena, A. Mifsud and V. Fornes, *Adv. Mater.*, 10 (1998) 480.
15. N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura and K. Nagayama, *Nature*, 361 (1993) 26.
16. O. D. Velev, P. M. Tessier, A. M. Lenhoff and E. W. Kaler, *Nature*, 401 (1999) 548.
17. K. Nagayama, *Colloids Surf.*, 109 (1996) 363.
18. P. Jiang, J. F. Bertone, K. S. Hwang and V. L. Colvin, *Chem. Mater.*, 11 (1999) 2132.
19. Y. A. Vlasov, X. Z. Bo, J. C. Sturm and D. J. Norris, *Nature*, 414 (2001) 289.
20. P. N. Bartlett, J. J. Baumberg, P. R. Birkin, M. A. Ghanem and M. C. Netti, *Chem. Mater.*, 14 (2002) 2199.
21. P. N. Bartlett, J. J. Baumberg, S. Coyle and M. E. Abdelsalam, *Farad. Discuss.*, 125 (2004) 117.
22. B. T. Holland, C. F. Blanford, T. Do and A. Stein, *Science*, 281 (1998) 538.
23. M. A. Ghanem, P. N. Bartlett, P. De-Groot and A. Zhukov, *Electrochem. Commun.*, 6 (2004) 447.
24. L. Xu, W. Zhou, M. E. Kozlov, I. I. Khayrullin, I. Udod, A. A. Zakhidov, R. H. Baughman and J. B. Wiley, *J. Am. Chem. Soc.*, 123 (2001) 763.
25. N. Eradat, J. D. Huang, Z. V. Vardeny, A. A. Zakhidov, I. I. Khayrullin, I. Udod and R. H. Baughman, *Synth. Met.*, (2001) 116.
26. M. Wirtz, C .R. Martin, *Adv. Mater.*, 15 (2003) 455.
27. S. Cheong, J. D. Watt and R. D. Tilley, *Nanoscale*, 2 (2010) 2045.
28. L. Estevez, A. Kelarakis, Q. Gong, E. H. Daas and E. P. Gianelis, JACS, 133 (2011) 6122.
29. G. A. Hughes, Nanomedicine: Nanotechnology, Biology, and Medicine, 1 (2005) 22.
30. K. M. Kim, N. G. Park, K. S. Ryu andS. H. Chang, *Electrochim. Acta*, 51 (2006) 5636.
31. Y. Cao, B. You and L. Wu, *Langmuir*, 26 (9) (2010) 6115.
32. L. Estevez, A. Kelarakis, Q. Gong, E. H, Da'as, and E. P. Giannelis, *J. Am. Chem. Soc.*, 133 (2011) 6122.
33. D. J. Lin, C. L. Chang, F. M. Haung and L. P. Cheng, *Polymer*, 44 (2003) 413.
34. J. Lin-Cai and D. Pletcher, *J. Electroanal. Chem.*, 149 (1983) 237.
35. N. Georgolios, D. Jannakoudakis and P. Karabinas, *J. Electroanal. Chem.*, 264 (1989) 235.