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In-situ nanofabrication via electrohydrodynamic jetting of countercharged nozzles

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Summary

Methods to *in-situ* construct nanostructures are the key tools of nanotechnology. Herein, for the enforced combination of two nanomaterials, an *in-situ* combination technique, ‘electrohydrodynamic jetting of countercharged nozzles (EJC)’, was explored. EJC used an attraction force between negative and positive surface charges generated by electrohydrodynamic spinning and spraying. The obtained nanostructures were dependent on the types of materials and jetting conditions. Poly(methyl methacrylate) nano- or micro-fibers were uniformly combined with polystyrene nano- or microparticles. When lipoic acid (an antioxidant drug) was used instead of polystyrene, composite structures of fibers and surface nanodots resulted. The method could also enforce gold nanoparticles stick onto the surface of fibers. EJC is an efficient technique to fabricate composite nanostructures using materials with a wide range of properties.

Introduction

Since 1930s [1], electrospinning [2, 3] has been a subject of intensive research for generating one-dimensional nanofibers from a variety of materials including polymers [4, 5], composites [6], and ceramics [7]. Applications for the technique include tissue scaffolds [8], drug delivery [9], waveguides [10], filtration [11], chemical sensors [12], etc.

The nanofibers prepared by electrospinning could be modified by different methods to improve and/or functionalize their properties. For example, it is well known that a broad range of applications benefits from exploitation of biological species, e.g. enzymes, proteins, viruses and bacteria. These applications require the biological objects immobilized in specific carriers, and the immobilization has been achieved via physical adsorption [13, 14]. To improve the poor cell-adhesive characteristics of scaffolds, Park *et al* used plasma and hydrochloric acid treatment for altering the hydrophobic surfaces of electrospun nanofibers into hydrophilic ones [15]. Drew *et al* have shown that the surfaces of electrospun fibers could be coated with metal oxide nanoparticles via electrostatic interactions by immersing in a liquid medium [16]. To fabricate superhydrophobic membranes, nanofibers could be coated by a water-based layer-by-layer adsorption process after chemical vapor deposition [17, 18]. Co-axial electrospinning can produce hybrid biomaterial structures for drug delivery [19, 20]. All the above methods are subjected to certain limitations, such as severe processing conditions, multi-step processing, chemical/physical pretreatments, etc. Herein, we present a simple *in-situ* method for the modification of surfaces and immobilization of functional materials. It based on the neutralization phenomenon between electrospun nanofibers and electrosprayed droplets. The surfaces of the fibers and the droplets have opposite charges supplied by their electrohydrodynamic spinning/spraying nozzles. The similar neutralization technique has been developed to stabilize aerosols [21] and to decrease the charge of electrospray-generated ions [22]. Borra *et al* have developed a microreactor using the electrospraying method of neutralization [23, 24]. The oppositely charged droplets of two different reagents attracted each other, and chemically reacted after their coagulation. This neutralization method has advanced in our study to modify nanofibers, referred to as ‘electrohydrodynamic jetting of countercharged nozzles (EJC)’.

Experimental

Poly(methyl methacrylate) (PMMA, Mw=360,000 g/mol), polystyrene (PS, M_w=350,000 g/mol and 13,000 g/mol), and NaF were purchased from Sigma-Aldrich, USA. Alpha-lipoic acid (ALA, 206.33 g/mol) was received from Tokyo Chemical Industry, Japan. All of the materials were used without further purification. All the jetting solutions were prepared by the dissolution of components in dimethylformamide (DMF, Sigma-Aldrich, USA). NaF nanosuspension in DMF was prepared by a wet ball milling technology [25]. ALA-derivatized gold clusters (ca. 20 nm) were prepared in water by the two-phase reduction of aqueous $HAuCl_4$ by the toluene-water method [26].

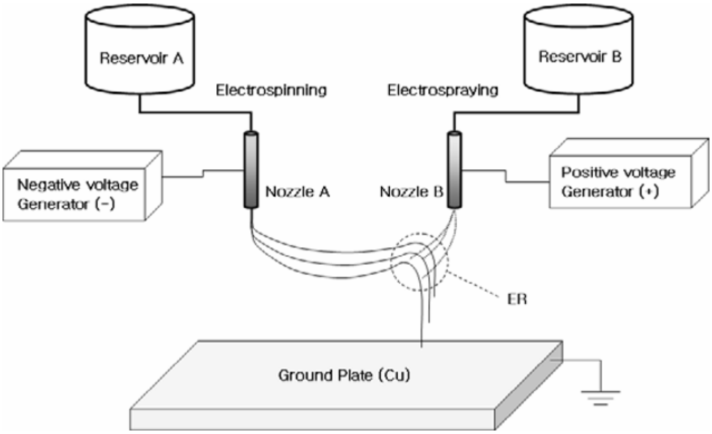


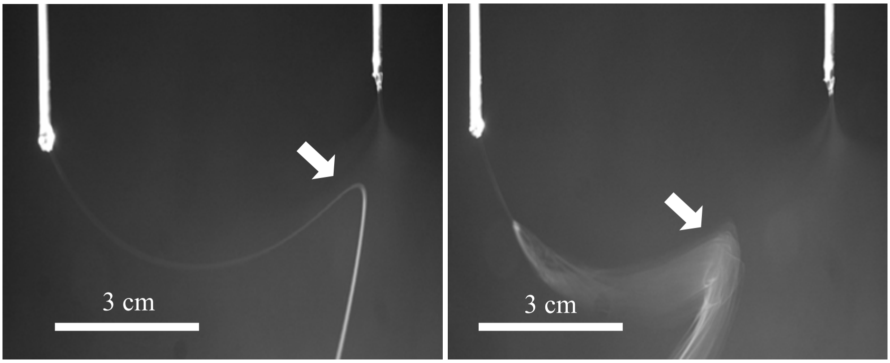
Figure 1. Schematic configuration of EJC. The encountering region (ER) is the area where the fiber stream changes its direction because of neutralization.

Two identical nozzles of countercharges were facing each other over a ground plate as shown in Fig. 1. The nozzle-to-nozzle and the nozzle-to-ground distance were 7 and 10 cm, respectively. The ground was a cupper plate (40 × 40 cm^2). The positive and negative DC voltage supplies were purchased from Convertech (South Korea, SHV model) and NanoNC (South Korea, H.V. model), respectively. A stainless steel nozzle of 19 gauge (I.D.: 0.69 mm, O.D.: 1.07 mm) was used for both electrospinning and electrospraying. The jetting solutions were stored in a 5 ml syringe (Becton, Dickinson and Company, USA). The flow rate of 1 ml·h^{-1} was controlled by a syringe pump (KDS100, KD Scientific, USA) with a control step size of 10 μl·h^{-1}. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) images were obtained using S-4800 (Hitachi, Japan). SEM samples were examined after carbon coating (3 nm).

Results and discussion

Countercharged electrospraying-to-electrospraying and electrospinning-to-electrospraying were tried in our early development for *in-situ* nanofabrication. In electrospraying-to-electrospraying, as-sprayed nanoparticles were successfully formed, but encountering phenomena between the countercharged particles were hardly observed. Instead, the as-sprayed nanoparticles tended to spray towards the surfaces of countercharged nozzles. However, encountering between charged fibers and countercharged particles dominantly happened in electrospinning-to-electrospraying. Thus, the neutralization phenomenon and *in-situ* nanofabrication of electrospinning-to-electrospraying systems were investigated in here.

It was observed that the stream of electrospinning changed its direction upon neutralization. The encountering region (ER in Fig. 1), where most neutralization occurs, can be found in Fig. 2. When PMMA and PS solutions were simultaneously electrospun and electrosprayed respectively from two identical but countercharged nozzles, the PMMA fibers changed their moving directions after encountering with the oppositely charged PS droplets due to changes in electrostatic forces.



a) b)

Figure 2. EJC stream photographs at different voltages: a) 0 (left nozzle) to +8 kV (right nozzle), b) -4 to +4 kV. The PMMA solution was electrospun from the left nozzle, and the PS solution was electrosprayed into particles from the right nozzle. The arrows indicate encountering region.

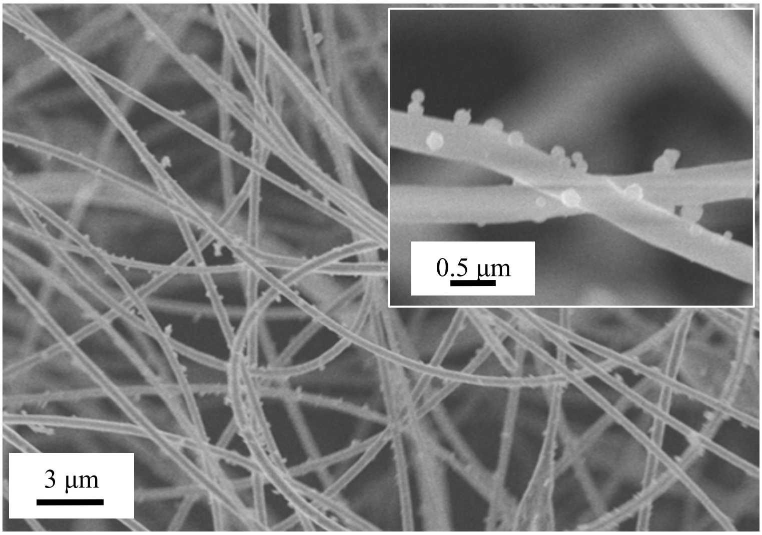
Since this method uses the surface electrostatic charges generated by electrical energy inputs, various materials can be processed only if they can be electrospun or electrosprayed. The neutralization phenomenon can be used any time before the relaxation of surface electrostatic charge significantly occurs. It was reported in a certain case that the surface charge of electrospun fibers can remain up to 3 months [27].

A 5 wt% PS (13,000 g/mol) solution was stably electrosprayed with a positive voltage between +4 and +8 kV, without supplying a negative voltage to the other nozzle. Due to electrostatic induction (Fig. 2a), a 13 wt% PMMA solution was electrospun at 0 kV when a PS solution was electrosprayed at a voltage greater than +6 kV. As the negative voltage of the spinning nozzle increased, the ER moved to the middle area among the two nozzles and the ground (Fig. 2b). The electrostatic attraction between the left nozzle and the ground plate may lead to the change of ER position.

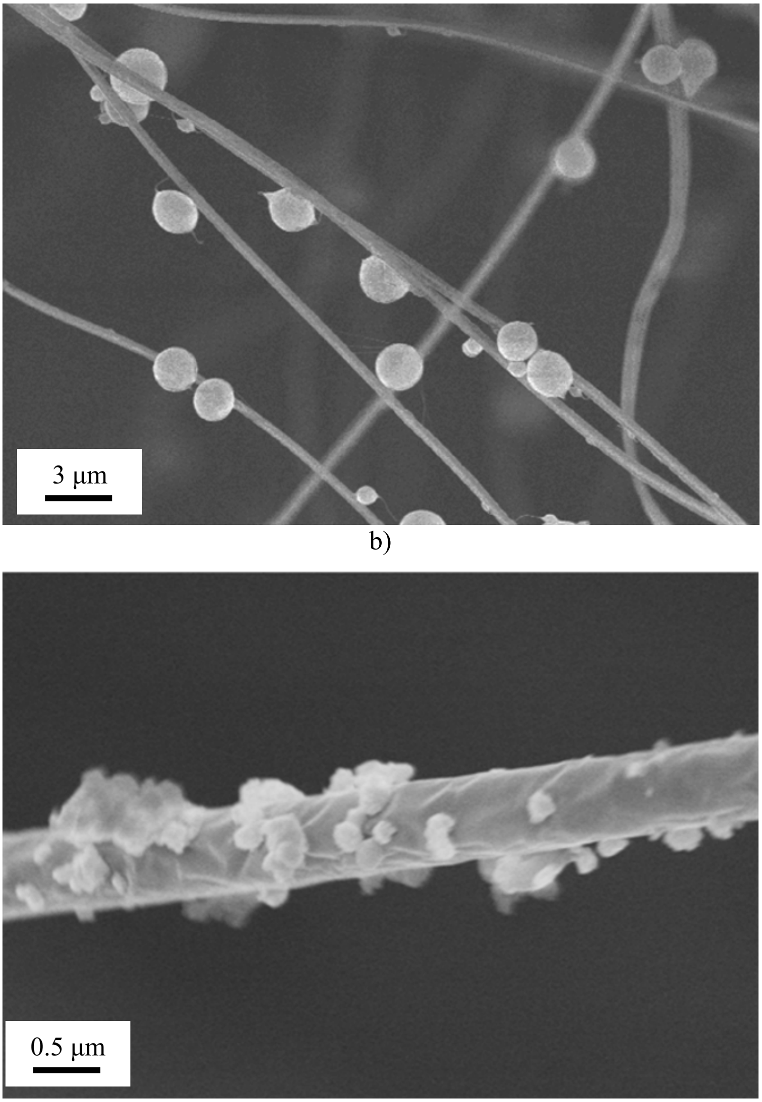
Figures 3a and 3b show the SEM micrographs of the composite structures of PS particles on PMMA fibers. PS particles of 100 – 200 nm were uniformly attached to the surfaces of PMMA fibers in Fig. 3a. It is possible that the PS particles are well dispersed and the attachment does not significantly depend on the direction of spraying or spinning due to the nature of electrostatic attractions and repulsions.

Increasing the molecular weight of PS can change the structures of composites. Figure 3b shows the structures formed by a higher molecular weight PS (Mw = 350 kg/mol) with the same EJC configuration and voltage. The increase of molecular weight caused an increase in PS particle size without significant change in the diameter or morphology of the PMMA fibers. As the entanglement density and viscosity of the spraying solution increased, its spinning tendency increased. Indeed, a few PS fibers are discernable in Fig. 3b. Thus, the molecular weight of the polymer can be used as a parameter for controlling particle size.

Instead of a polymer solution, NaF nanosuspension (volume-averaged particle size = 100 nm) in DMF was used in Figure 3c. NaF hybrid nanofibers can provide increased physical properties to dental materials [28] and prevent the demineralization of teeth through F release [29]. The crystalline particles are attached to the surface of PMMA fibers. Aggregation to a certain degree can also be found, which indicates that electrohydrodynamic force may not be enough to break up aggregates during EJC.



a)



b)

c)

Figure 3. SEM micrographs of PMMA fibers *in-situ* combined with droplets of different solutions: a) PS (Mw = 13 kg/mol, 3 wt%), b) PS (Mw = 350 kg/mol, 3 wt%), c) NaF (7 wt%) [PMMA 13 wt%, –4 to +4 kV].

When both PS and NaF solutions were sprayed under positive electrostatic potential using a multi-nozzle having two parallel subnozzles, both PS and NaF particles similar to Fig. 3b and 3c independently formed on the surface of PMMA fibers (data not given). In the experiment, both 7 wt% PS (13 kg/mol) solution and 7 wt% NaF nanosuspensions were simultaneously electrosprayed at + 8 kV, and the PMMA solution was electrospun by – 4 kV in the same EJC configuration.

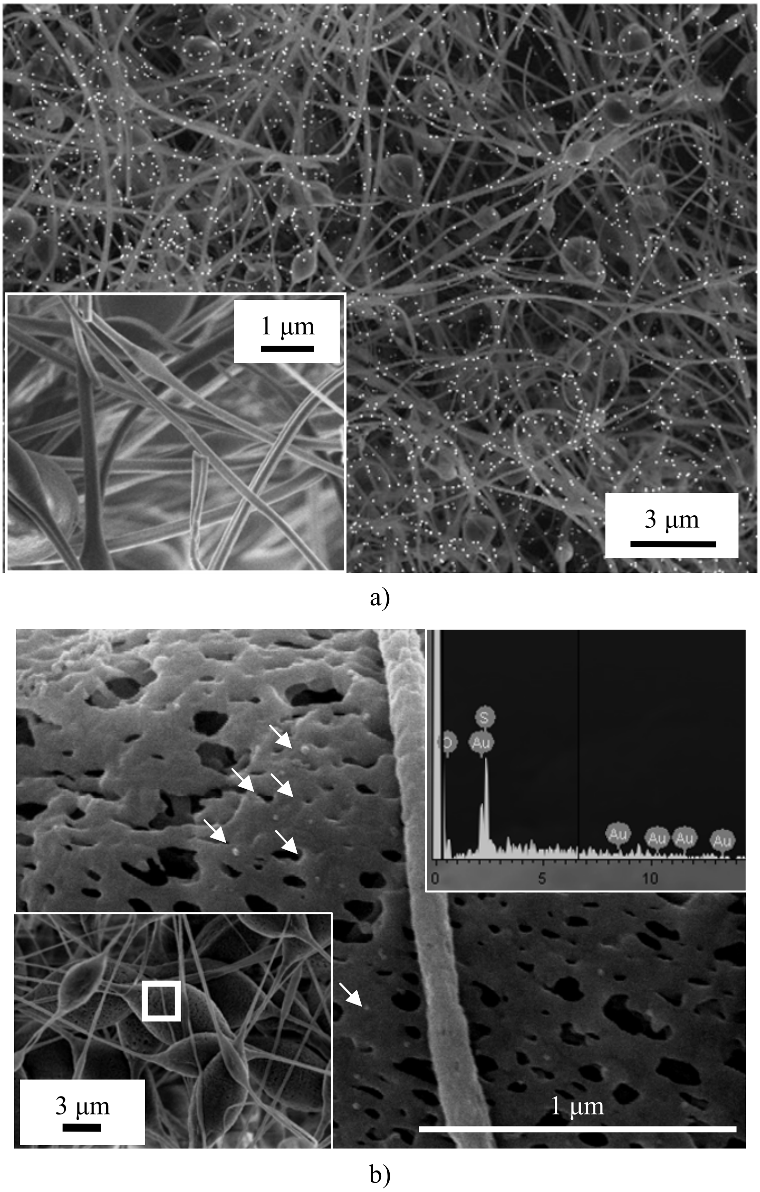


Figure 4. SEM micrographs: a) PMMA beads-on-string structures *in-situ* coated with ALA. The white dots in the EDX mapping image show the existence of sulfur of ALA and the inset shows no particle formation on the surface of fibers, b) PS beads-on-string fibers coated with gold nanoparticles. The image is enlarged from the left lower inset, and the arrows indicate gold nanoparticles. The right upper inset shows an EDX result. [10 wt% PMMA, 10 wt% PS, 10 wt% ALA DMF solutions, and 1 wt% gold nanoparticle aq. dispersion, -4 to +4 kV]

Organic molecules of small molecular weights are used to modify the surface properties of nanofibers, which has commonly been done by two-step processes [15, 17, 18]. EJC method can electrospin nanofibers and simultaneously modify its surface with countercharged molecules. Herein, the surface of PMMA fibers is coated with ALA as shown in Fig. 4a. The existence of ALA on surface was confirmed by energy dispersive X-ray analysis (EDX): EDX mapping of the sulfur K orbital in the image shows that ALA forms not spherical particles like PS in Fig. 3 but 2D domains on the surface of fibers.

Gold nanoparticles are widely used as convenient substrates for the specific immobilization of functional molecules. To further explore the potential applications of EJC, Au-colloidal solution was electrosprayed instead of PS and ALA. Fig. 4b shows that gold nanoparticles (ca. 20 nm) were successfully attached on the surface of fibrous structures, which was confirmed by EDX. The PS and PMMA fibers of beads-on-string structures used in the experiments of ALA and gold nanoparticles (Fig. 4) can be replaced by the same fibers used in Fig. 3. The porous surface structure of Fig. 4b is not a characteristic of EJC.

Surface modification has become an important process for various materials, especially the biological materials made for biosensors, biochips, biocompatible thin coatings for medical application, biodegradable scaffolds, and filter systems [30-34]. The EJC technique is useful to uniformly modify a surface, which appears to be distinctly different from simple dipping process or plasma coating. It can successfully immobilize various functional materials on the surface of as-spun polymer fibers. The composite structures appear to be relatively stable, since no significant detachment of coating materials were noticed after preparation.

Conclusions

Electrohydrodynamic jetting of countercharged nozzles (EJC) technique is able to *in-situ* fabricate various nanostructures using electrostatic attraction forces between two electrohydrodynamic jetting streams. Composite materials, such as fibrous structures combined with various as-sprayed materials, such as polymers, low molecular weight organic molecules, or metal nanoparticles, were conveniently obtained. While small molecular weight organic molecules formed 2D dots, a polymer solution produced spherical particles on the surface of fibers. As the molecular weight of polymer increased, larger polymer particles were formed on the surface of fibers. This in-situ combination technology has unique potential for the enforced *in-situ* nanofabrication of various bio-, electrical, and electronic materials.

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References

1. Formhals A (1934) US Patent No. 1:975, 504.
2. Li D, Xia YN (2004) Adv Mater 16(14):1151-1170.
3. Greiner A,Wendorff JH (2007) Ang Chemie-International Ed 46(30):5670-5703.
4. Lyons J, Li C, Ko F (2004) Polymer 45(22):7597-7603.
5. Sanches NB, Dias ML, Pacheco E (2005) Polym Testing 24(6):688-693.
6. Kedem S, Schmidt J, Paz Y, Cohen Y (2005) Langmuir 21(12):5600-5604.
7. Li D, Herricks T, Xia YN (2003) Appl Phys Letters 83(22):4586-4588.
8. Wang YK, Yung T, Ramakrishna S (2005) Aust. J. Chem. 85:704.

9. Jing Z, Xu XY, Chen XS, Liang QZ, Bian XC, Yang LX, Jing XB (2003) J Control Release 92(3):227-231.
10. Liu HQ, Edel JB, Bellan LM, Craighead HG (2006) Small 2(4):495-499.
11. Barhate RS,Ramakrishna S (2007) J Mem Sci 296(1-2):1-8.
12. Sawicka KM, Prasad AK, Gouma PI (2005) Sensor Lett 3(1):31-35.
13. Jia H, Zhu G, Vugrinovich B, Kataphinan W, Reneker DH, Wang P (2002) Biotechnol Prog 18(5):1027-1032.
14. Herricks TE, Kim SH, Kim J, Li D, Kwak JH, Grate JW, Kim SH, Xia YN (2005) J Mater Chem 15(31):3241-3245.
15. Park K, Ju YM, Son JS, Ahn KD, Han DK (2007) J Biomat Sci-Polym Ed 18(4):369-382.
16. Drew C, Liu X, Ziegler D, Wang XY, Bruno FF, Whitten J, Samuelson LA, Kumar J (2003) Nano Lett 3(2):143-147.
17. Zhai L, Cebeci FC, Cohen RE, Rubner MF (2004) Nano Lett. 4(7):1349-1353.
18. Ma ML, Mao Y, Gupta M, Gleason KK, Rutledge GC (2005) Macromolecules 38(23):9742-9748.
19. Li D,Xia YN (2004) Nano Lett 4(5):933-938.
20. Huang ZM, He CL, Yang AZ, Zhang YZ, Hang XJ, Yin JL, Wu QS (2006) J Biomed Mater Res Part A 77A(1):169-179.
21. Xie JW, Lim LK, Phua YY, Hua JS, Wang CH (2006) J Colloid Interface Sci 302(1):103-112.
22. Ebeling DD, Westphall MS, Scalf M, Smith LM (2000) Anal Chem 72(21):5158-5161.
23. Borra JP, Camelot D, marijnissen JCM, Scarlett B (1996) J Aerosol Sci 27:181-182.
24. Borra JP, Camelot D, Chou KL, Kooyman PJ, Marijnissen JCM, Scarlett B (1999) J Aerosol Sci 30:945-958.
25. Pang P, Li W, Liu Y (2007) Rare Metals 26(2):118-123.
26. Abad JM, Mertens SFL, Pita M, Fernandez VM, Schiffrin DJ (2005) J Am Chem Soc 127(15):5689-5694.
27. Schreuder-Gibson HL,Gibson P (2004) Inter Nonwoven J winter:39-45.
28. Drummond JL,Bapna MS (2003) Dental Mater19(3):226-231.
29. Nakabo S, Torii Y, Itota T, Ishikawa K, Suzuki K (2002) Dental Mate 18(1):81-87.
30. Gibson P, Schreuder-Gibson H, Rivin D (2001) Colloid Surf A-Physicochem Eng Asp 187:469-481.
31. Li WJ, Laurencin CT, Caterson EJ, Tuan RS, Ko FK (2002) J Biomed Mater Res 60(4):613-621.
32. Matsumoto H, Mizukoshi T, Nitta K, Minagawa M, Tanioka A, Yamagata Y (2005) J Colloid Interface Sci 286(1):414-416.
33. Okuda H,Kelly AJ (1996) Phys Plasmas 3(5):2191-2196.
34. Hull PJ, Hutchison JL, Salata OV, Dobson PJ (1997) Adv Mater 9(5):413-417.