Plasma Etching Technology for Surface and Chemical Modifications of Aluminium and Poly Methyl Meth Acrylate Nanocomposites

Narendra Kumar Agrawal[1, *], Ravi Agarwal[2], Y. K. Vijay[3], and K. C. Swami[1]

[1] *Department of Physics, Malaviya National Institute of Technology, Jaipur, Rajasthan 302017, India*
[2] *Center for Converging Technologies, University of Rajasthan, Jaipur, Rajasthan 302004, India*
[3] *Department of Physics, University of Rajasthan, Jaipur, Rajasthan 302004, India*

Systematic study was carried out to characterize the effects of helium (He) ion plasma on nano composite polymer membrane. Nanoparticles of Aluminium (Al) were synthesized by biological root. 25 micron nanocomposite polymeric membranes were prepared using solution casting method. Helium ion plasma treatment was done for these membranes. These membranes were characterized before and after plasma treatment to make comparative study by different technique such as optical microscopy, SEM-Scanning electron microscope and Fourier transform infrared spectroscopy to identified surface and chemical modifications.

Keywords: Inert Gas Plasma, Aluminum NPs, Plant Mediated Synthesis, Plasma Etching, Nanoparticles (NPs), Nanocomposites (NCs).

1. INTRODUCTION

Metallic nanoparticles traditionally synthesized by wet chemical synthesis, used chemicals were often toxic. Since metallic nanoparticles are widely used in biological applications. So, there is a growing need to develop environmentally friendly processes for nanoparticle synthesis that do not left toxic by-products. Biological methods of nanoparticle synthesis using micro-organisms, plants including algae, fungi, bryophyte, pteridophyta etc. have been suggested as possible ecofriendly alternatives to chemical and physical methods.[1] Among the various metallic nanoparticles, Aluminium (Al) nanoparticles have recently received substantial attention for various reasons-like high refractive index, high electrical conductivity, chemical catalysis and antimicrobial activities.[2]

Polymers have become very important materials in modern manufacturing processes due to wide varieties of chemical properties, but it is well known that permanent bonding,[3] printing,[4] coating,[5, 6] etc. are difficult on many polymers without surface pre-treatment.[7–9] Therefore, surface treated polymers have significant advantages in

specific requirements of surface properties while retaining bulk properties unchanged. Physical and chemical modifications of polymeric materials are of great interest in artificial skin development.[10–12]

Complex nature of plasma due to presence of ions, neutrals and radiation in discharge makes low-temperature plasmas widely useable in growing number of materials fabrication processes including etching of complex patterns and surface modifications of polymeric membranes.[13] Plasma surface treatment usually refers to plasma reaction that either results in modification of molecular structure of the surface or atomic substitution.[14] The accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in membrane structure and to form macromolecule radicals, which subsequently initiate graft copolymerization.[15] Plasma treatment can be done by either regular plasma treatment, or plasma graft copolymerization (PGC).[16, 17]

Various plasma components such as electrons, ions, radical etc. are involved in this process.[18, 19] These components react or exposed surfaces. Since some parts of the surface are exposed to energies higher than characteristic bond energy of polymers,[20] these parts undergo scission reactions and form new bonding configurations

---
*Author to whom correspondence should be addressed.

on surface.[22] Plasma treatment of polymer surface causes not only a modification during the plasma exposure,[23] but also leaves active sites on the surfaces which are subjected to post-reaction.[24–26] Glow-discharge plasma technique is particularly useful for functionalization of surfaces as it is possible to modify outermost surface layer by this technique. These factors improve the adhesion properties of the surface.[27]

In this paper we have synthesized polymer nanocomposites using Al NPs and Poly Methyl Meth Acrylate (PMMA). These nancomposites materials were exposed with He plasma, and modification in surface and chemical properties was investigated.

2. MATERIALS AND METHODS

In the present study Al NPs were synthesized using Mentha arvensis (pudina) plant extract. The plant washed with sterile distilled water. The plant extract was prepared by taking 25 g of thoroughly washed plant material in a 250 mL Erlenmeyer flask with 100 mL of distilled water, and then boiling the mixture for 10 min in a water bath. The leaf broth was cooled and filtered through Whatman No. 1 filter paper (pore size 25 μm). For preparation of Al nanoparticles, 10 mL of the prepared plant extract was added to 90 ml of 1 mM aluminium nitrate solution and incubated in a rotary shaker for 2 h. The color of the solution changed from light yellow to black indicating the formation of Al nanoparticles.[20, 28]

PMMA granules were obtained as commercial grade from Loxim Polymers, Jaipur) and used to prepare flat sheet membranes by solution cast method. PMMA granules are weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution. The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution at room temperature for around 5 hours. 4% Al nanoparticles (of PMMA) were dispersed in the solvent dichloromethane using ultra-sonicator. This dispersed solution was added to the PMMA solution and stirred for around 30 minutes. The solution was put into flat-bottomed petri-dishes floating on mercury to ensure a uniform structure of membranes. Solvent was allowed to evaporate slowly over a period of 10–12 hours. The films so obtained were peeled off using forceps.[30, 31]

Plasma treatment set-up consists of a source chamber with complete power supply, connected to a vacuum system. A magnet is positioned to get a magnetic field (0.5 K. Gauss) inside the source chamber.[32, 33] Argon gas used for generate plasma is admitted into source chamber using a flow controller and applying DC power between two electrodes. The confined plasma in the chamber is used for surface modification. Applying a high voltage between two electrodes with magnetic field generates the DC glow discharge. The current in the upper and lower electrodes is maintained at few 10 mA and 4.5 KeV.

In this study we have used He plasma. The plasma is almost homogenous in a low-pressure glow discharge. The reaction chamber is evacuated and then refilled with low-pressure He gas to create glow discharge plasma. Plasma is energized by direct current.[34] Other energetic species in plasma include radicals, electrons and meta-stable photons in short-wave UV range.

UV-Vis spectrum of NPs was taken using UV-Vis spectrophotometer SHIMADZU 1800. FTIR Analysis was done using FTIR spectrophotometer (IR Affinity-1 Shimadzu) in the range of 4000–400 cm^{-1} for knowing the possible functional groups present with synthesized Al NPs. Scanning Electron Microscopic (SEM) analysis was done using Hitachi S-4500 SEM machine. Morphology and particle size of Al NPs are also determined using transmission electron microscopy (TEM) Technika TEM instrument operating at 200 kV.

3. RESULTS AND DISCUSSION

UV-Visible absorption spectrum shows characteristic surface plasmon resonance (SPR) peak of Al NPs at 396 nm (Fig. 1), indicating reduction of aluminium nitrate and formation of Al nanoparticles.

Absorption bands obtained using FTIR are classified as (A) stretching vibration of Al NPs at 761 cm^{-1}, (B) C=C unsaturated at 1286 cm^{-1}, (C) C=O stretching vibration at 1720 cm^{-1}, (D) CH_3 stretching vibration at 3128 cm^{-1} and (E) C—H stretching vibration 3685 cm^{-1} of aromatic compounds (Fig. 2).

Al NPs were dispersed in acetone by ultra-sonication and used for particle size analysis (Fig. 3). Image clearly shows spherical shape NPs with particle size ranging from 3–6 nm. Grain boundaries can be easily identified from TEM images showing no aggregations in No NPs,
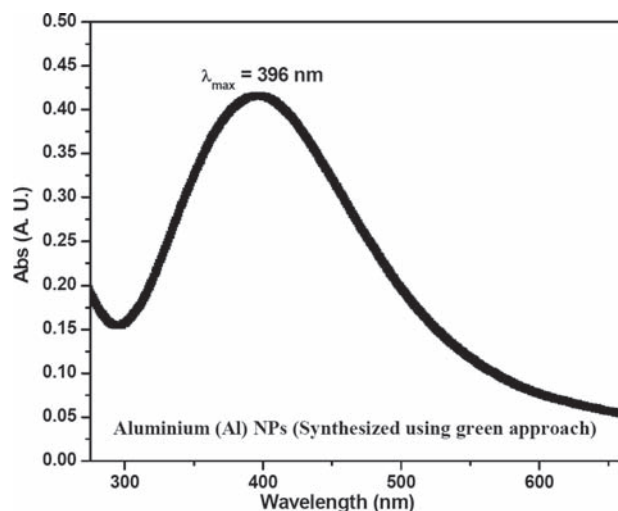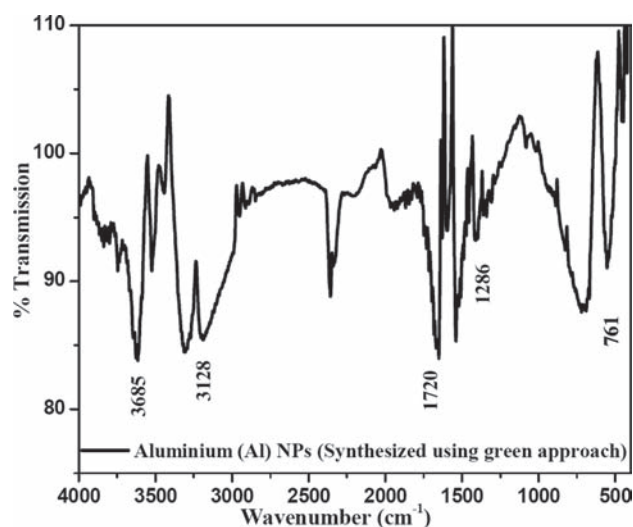

Figure 1. UV-Vis absorption spectrum of Al NPs.

Figure 2. FTIR spectra of vacuum dried Al NPs.

Figure 4. SEM image of Al NPs.

especially particle size and grain boundaries can more clearly identified form dark field image of NPs (Fig. 3(d)). Here for present study, TEM image is best indicator of particle size. But to determine aggregation present in NPs at higher sample amounts, we have also recorded SEM images of synthesized Al NPs (Fig. 4). As individual Al NPs can easily be identified form image, showing no aggregation in NPs even at higher sample amount. These Al NPs are used for synthesis of Nanocomposite Polymer Membranes, He plasma treatment was done and characterized using different techniques.[15]

LABOMED optical microscope was used for recording optical images. Micrographs were stored in computer through CCD camera which is attached to the computer with standard Pixel View software. Images shows that pristine membrane have very smooth surface but plasma treatment increase its porosity and roughness. Nanocomposite membrane is comparatively having high porosity but plasma treatment again increases its porosity and roughness (Fig. 5).
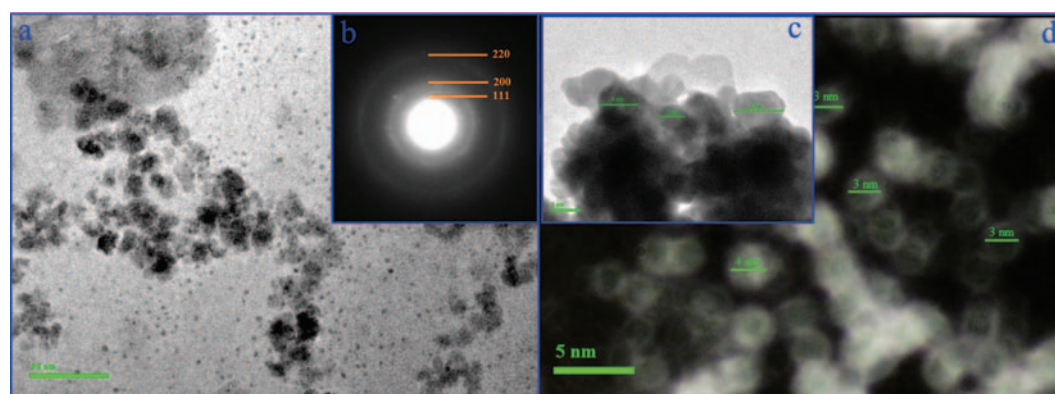
FTIR spectra are obtained on FTIR spectrometer. FTIR is used to gather information about chemical structure of a compound and chemical modification after plasma treatment. The FTIR images of the pristine and doped (untreated and plasma treated) membranes are as shown in the Figure 6. We notice certain characteristic differences in peaks at certain wavelengths. These wavelengths are indicators of change in chemical bonding and structure of samples due to plasma treatment.

Peaks at around $3000–2750$ cm^{-1} are characteristic of –CH$_3$ bonds. The similar peaks in the FTIR spectra of treated and untreated samples show that there is no change in the basic structure of nanocomposite membranes. The increments in the absorption bands of C—O at 1030 cm^{-1} and C=O at 1770 cm^{-1} has been attributed to the creation of unsaturated –C=C– bonds at 1645 cm^{-1} after plasma treatment. It is also observed from FTIR spectra that C—C and C—H bands have been decreased after plasma treatment. It indicates that cross linking phenomenon enhanced during plasma treatment. While Al NPs are showing its characteristic peak in 761 cm^{-1} for nanocomposite membrane.

Figure 3. TEM and diffraction pattern of Al NPs (a) Al NPs at 50 nm scale, (b) diffraction pattern, (c) Al NPs at 5 nm scale and (d) Dark field image of Al NPs at 5 nm scale.
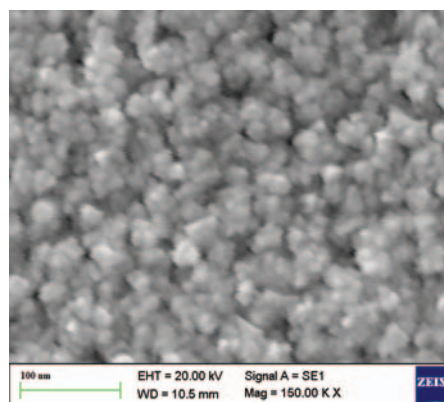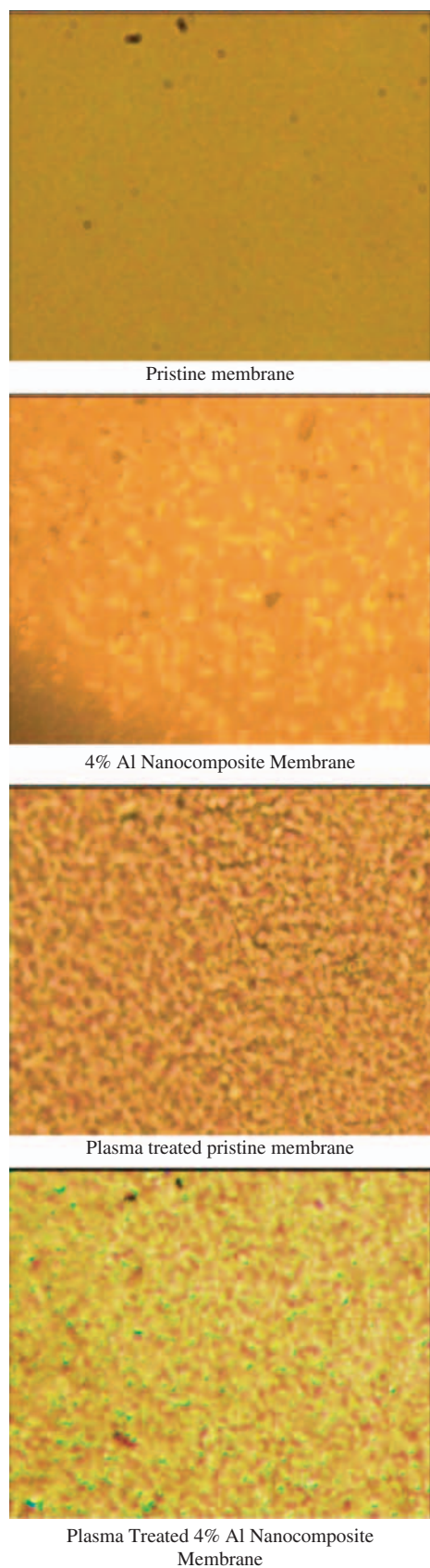
Pristine membrane

4% Al Nanocomposite Membrane

Plasma treated pristine membrane

Plasma Treated 4% Al Nanocomposite Membrane

Figure 5. Optical microscope images of pristine and Al nanocomposite membrane both plasma treated and untreated.

Pristine membrane

4% Al Nanocomposite Membrane

Plasma treatment pristine membrane
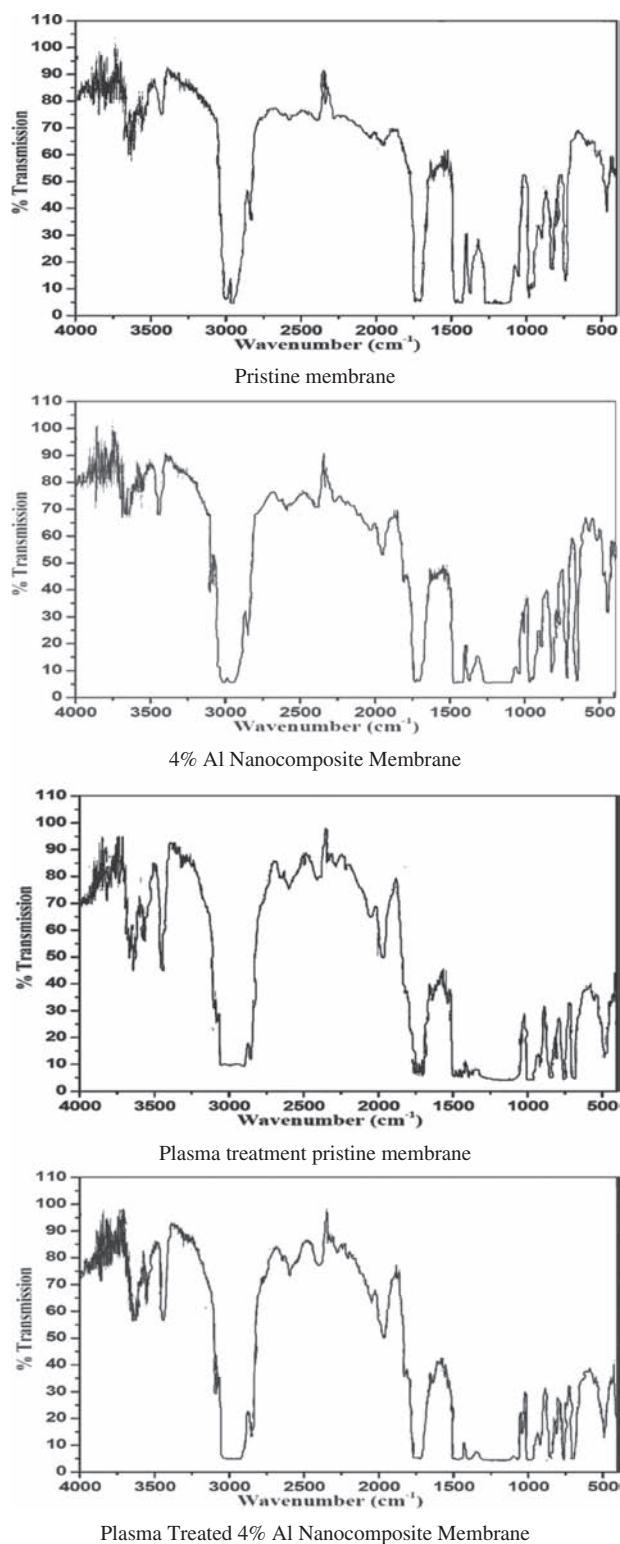
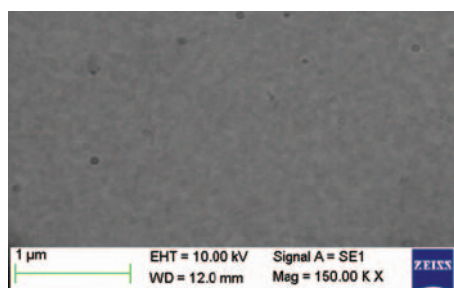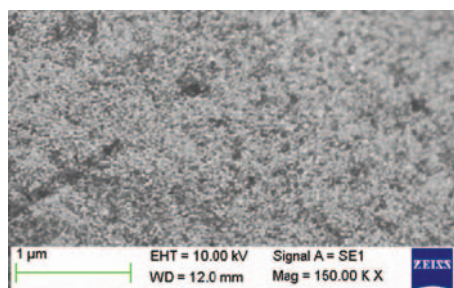Plasma Treated 4% Al Nanocomposite Membrane

Figure 6. FTIR spectra of pristine and Al nanocomposite membrane before and after plasma treatment.
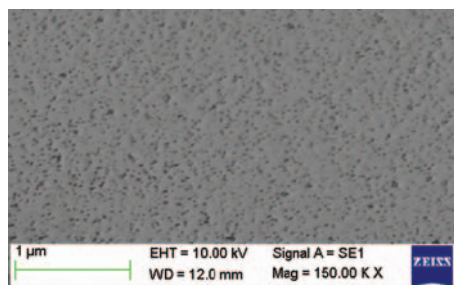
We investigated surface morphologies of these nanocomposite membrane using SEM. The SEM images of nanocomposite membrane are shown in Figure 7. Scanning Electron Microscopic (SEM) analysis was done
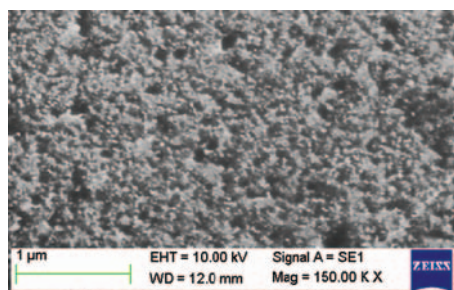
Pristine membrane

4% Al Nanocomposite Membrane

Plasma treated pristine membrane

Plasma Treated 4% Al Nanocomposite Membrane

Figure 7. SEM images of pristine and Al nanocomposite membrane both plasma treated and untreated.

using Hitachi S-4500 SEM machine. Plasma treated nanocomposite membrane can be compared with untreated one which shows improve in porosity and roughness.

4. CONCLUSIONS

Color of solution changes from yellow to black as plant extract was mixed in aqueous solution of aluminium ion complex, this gives primary indication of formation of aluminium nanoparticles, which is further confirmed by

analyzing of these NPs by different technique like UV-Vis spectrophotometer, FTIR, TEM and SEM.

UV-Visible spectrum obtained in visible range of 300 nm to 800 nm. A typical absorbance SPR peak at 396 nm of aluminium nanoparticles was obtained due to surface Plasmon vibrations of aluminium nanoparticles. Particle size of biosynthesized aliminium nanoparticles were further confirmed by TEM and SEM measurements which comes around 3–5 nm. FTIR measurement carried out to identify the possible interaction between biomolecule and Al NPs. The FTIR measurements of biosynthesized aluminium nanoparticles show absorption bands at around 761 cm^{-1}, 1286 cm^{-1}, 1720 cm^{-1}, 3128 cm^{-1} and 3685 cm^{-1}.

Pristine PMMA membranes and Al nanocomposite membrane (4 weight%) were prepared by solution cast method. Helium Plasma treatment technique applied here has shown considerable improvement in chemical and surface properties of membranes. Plasma treatment has helped in increasing flux whereas doping has modified the surface properties. Optical microscope images and SEM images shows high porosity and roughness after plasma treatment. As nanocomposite membranes are prepared without help of any support, it can be concluded that PMMA has considerable strength as compared to other polymeric materials like polyamide which cannot be prepared without the help of support. The increments in the absorption bands of C—O at 1030 cm^{-1} and C=O at 1770 cm^{-1} has been attributed to the creation of unsaturated –C=C– bonds at 1645 cm^{-1} after plasma treatment, While decrease in intensity of C—C and C—H bands indicates that cross linking phenomenon enhanced after during plasma treatment.

References and Notes

1. Y. Sanchuan, L. Xuesong, L. Jingqun, W. Dihua, L. Meihong, and G. Congjie, *Separation and Purification Technol.* 76, 283 (**2011**).
2. H. S. Nalwa (ed.), Encyclopedia of Nanoscience and Nanotechnology, American Scientific Publishers, Los Angeles (**2004/2011**), Vols. 1–25.
3. H. S. Nalwa and S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, India (**1996**), Vols. 1–2.
4. H. S. Nalwa, Polymer Optical Fibers, American Scientific Publishers, Los Angeles (**2004**).
5. H. S. Nalwa, Polymeric Nanostructures and Their Applications, American Scientific Publishers, Los Angeles (**2004**), Vols. 1–2.
6. H. S. Nalwa, Handbook of Organic Conductive Molecules and Polymers, John Wiley & Sons, USA (**1997**), Vols. 1–4.
7. J. Singh, W. M. Saied, R. Kaur, and I. Badea, *Rev. Nanosci. Nanotechnol.* 2, 275 (**2013**).

8. B. Bagra, P. Pimpliskar, and N. K. Agrawal, *Proceedings of 58th DAE-Solid State Physics Symposium, AIP Proceedings*, Patiala, Punjab, India, December (**2013**).

9. P. Pimpliskar, B. Bagra, A. Sharma, S. Khandwal, and N. K. Agrawal, *Proceedings of 58th DAE-Solid State Physics Symposium, AIP Proceedings*, Patiala, Punjab, India, December (**2013**).

10. N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *J. Mat. Sci. Sur. Eng.* 1, 32 (**2013**).

11. H. Ji, J. Choi, G. Lim, B. Parida, K. Kim, J. H. Jo, and H. S. Kim, *J. Nanosci. Nanotechnol.* 13, 7806 (**2013**).

12. S. Y. Jang and S. H. Han, *J. Nanosci. Nanotechnol.* 13, 7820 (**2013**).

13. N. K. Agrawal, N. A. Kumar, M. Singh, Y. K. Vijay, and K. C. Swami, *Proceedings of 58th DAE-Solid State Physics Symposium, AIP Proceedings*, Patiala, Punjab, India, December (**2013**).

14. S. J. Lee, D. H. Kim, J. K. Kang, D. Y. Kim, H. M. Kim, and Y. S. Han, *J. Nanosci. Nanotechnol.* 13, 7839 (**2013**).

15. A. Goyal, V. Sharma, A. Sharma, R. Agarwal, K. B. Sharma, and S. L. Kothari, *J. Nano-Electronic Physics* 3, 254 (**2011**).

16. L. J. Ghil, T. Y. Youn, N. R. Park, and H. W. Rhee, *J. Nanosci. Nanotechnol.* 13, 7912 (**2013**).

17. P. Agarwal, R. Agarwal, and N. K. Agrawal, *Proceedings of 58th DAE-Solid State Physics Symposium, AIP Proceedings*, Patiala, Punjab, India, December (**2013**).

18. N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *J. Mat. Sci. Sur. Eng.* 1, 4 (**2013**).

19. W. M. King, P. A. Cantor, L. W. Schoellenback, and C. R. Cannon, High-retention reverse-osmosis desalination membranes from cellulose acetate, Membranes from Cellulose Derivatives, Interscience Publisher, New York (**2001**), Vol. 1.

20. N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *J. Mat. Sci. Sur. Eng.* 1, 23 (**2013**).

21. A. Sveshnikov, I. Klicmanová, P. Demo, and Z. Kožíšek, *Adv. Sci. Eng. Med.* 5, 569 (**2013**).

22. S. U. Maheshwari, S. V. Kumar, and N. Nagiah, *Adv. Sci. Eng. Med.* 5, 1305 (**2013**).

23. P. Agarwal, A. Mehta, S. Kachhwaha, and S. L. Kothari, *Adv. Sci. Eng. Med.* 5, 709 (**2013**).

24. M. Hatami, K. V. Rao, M. Ahmadipour, and V. Rajendar, *Adv. Sci. Eng. Med.* 5, 1039 (**2013**).

25. J. K. Beasley, The Evaluation and Selection of Polymeric Materials for Reverse Osmosis Membranes, Interscience Publisher, New York (**1997**), Vol. 1.

26. S. Vijay, J. K. Vijayavargiya, A. Sharma, and Y. K. Vijay, *Adv. Sci. Eng. Med.* 5, 1058 (**2013**).

27. N. K. Agrawal, K. Awasthi, Y. K. Vijay, and K. C. Swami, *J. Adv. Electrochemistry* 2, 31 (**2013**).

28. S. Goel and S. K. Mathew, *Solar Phys.* 289, 1413 (**2014**).

29. N. K. Agrawal, M. Singh, Y. K. Vijay, and K. C. Swami, *Adv. Sci. Eng. Med.*, Accepted for publication.

30. Y. Haldorai, S. Chitra, and J. J. Shim, *Adv. Sci. Eng. Med.* 5, 1044 (**2013**).

31. R. Agarwal, N. K. Agrawal, and R. Singh, *Adv. Sci. Eng. Med.* 6, 203 (**2014**).

32. M. R. Anwar, K. Vattipalli, E. Myrah, R. Asmatulu, and S. Prasad, *Adv. Sci. Eng. Med.* 5, 633 (**2013**).

33. K. Hyun and K. S. Soo, *J. Mem. Sci.* 286, 193 (**2009**).

34. R. Kolenák and M. Martinkovic, *Adv. Sci. Eng. Med.* 5, 527 (**2013**).