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Fabrication of nanocomposite membranes from nanofibers and nanoparticles for protection against chemical warfare stimulants

S. Sundarrajan · S. Ramakrishna

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Abstract Nanoparticles of MgO were synthesized by Aero gel method. These MgO nanoparticles were then mixed with various polymer solutions (poly(vinyl chloride) (PVC), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF copolymer), polysulfone (PSU)) and then subjected to electrospinning to produce nanocomposite membranes. The hydrolysis of paraoxon, a never agent stimulant, in presence of these membranes was studied using UV. The order of the reactivity of the membranes are found to be PVC-MgO < PVDF < PSU < PVDF-MgO < PSU-MgO. After selecting PSU as the supportive candidate, relative rates of hydrolysis were compared for nanoparticles or charcoal with nanocomposite membranes. The order is as follows; Charcoal (1) < PSU-Al_2O_3 (1.5) < PSU-MgO (2.1) < Al_2O_3 nanoparticles (2.8) < MgO nanoparticles (5.4). The amount of hydrolysis of PSU-MgO composite membrane was 60% less when compared to MgO nanoparticles as such usage. The loading percentage of MgO into nanofiber is 35 %. The fabricated composite membrane (containing 5% MgO) was tested for chemical warfare agent stimulant, paraoxon, and found to be about 2 times more reactive than currently used charcoal.

Introduction

In recent years, decomposition of chemical warfare agents has become an important research topic of study all over the world. Earlier studies involved either hydrolysis by basic solutions or incinerations which are adequate and frequently used for stored chemicals. However these methods are not applicable to destroy the agents in the battlefield or contaminated equipment surfaces. These agents are present as aerosol or vapors in the battle atmosphere. Hence there is a need for protective system which can safeguard the wearer from a possible chemical or biological hazard in such type of environment. Protection against the chemical warfare agents can be achieved through the use of protective clothing and face mask.

Current protective clothing is based on either full barrier protection suits which are impermeable or permeable adsorptive protective over-garments. Functionalized activated charcoal is being used in permeable protective garments, protective CBRN respirators, and face masks. Activated charcoal (with surface area above to 1,000 m^2/g) impregnated with Cu, Ag, Zn, Mo, and triethylenediamine is being used in existing canister for face mask applications [1]. The disadvantages associated with this material are that of heavy weight and moisture retention. Moreover, most of the toxic chemicals are physisorbed (except few gases such as phosgene, hydrogen cyanide, and cyanogens chloride which are decomposed) and not decomposed thereby problem in disposal after usage.

Presently, the U.S. Army uses DS2 solution, it decontaminates nerve agent, which consist of 2% NaOH, 28% 2-methoxyethanol, and 70% diethylenetriamine [2]. After application of this solution on surfaces, one has to wait for 30 min and then cleaning with water. Apart from its low

S. Sundarrajan (✉) · S. Ramakrishna
Nanoscience and Nanotechnology Initiative, National University of Singapore, 2 Engineering Drive 3, Singapore 117576, Singapore
e-mail: nnisubra@nus.edu.sg

S. Ramakrishna
Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore

S. Ramakrishna
Division of Bioengineering, National University of Singapore, 9 Engineering Drive 1, Singapore 119260, Singapore

reactivity, this solution is quite toxic, highly corrosive, and releases toxic by-products; moreover they are not active against biological agents. Hence it is required to develop an alternative technology, which is non-hazardous to personnel while handling, costly equipment surfaces, and at the same time highly reactive. Alternative to the above DS2 solution is XE555 resin, which is presently being used by military to remove toxic agents from the contaminated surfaces [3]. However, this has few disadvantages such as sufficiently unreactive and XE 555 itself off-gassing toxins and expensive.

Various chemicals are developed recently to detoxify the chemical warfare agents such as nerve agents, blister agents, blood agents, etc. [4]. Among these chemicals, β-cylcodextrin (β-CD), *o*-iodosobenzoic acid (IBA), polyoxometalates, peroxides, oximes, chloramines [5–9] and recently reported metal oxide nanoparticles such as MgO, Al_2O_3, TiO_2, Fe_2O_3, etc are widely studied as effective catalyst against chemical warfare agents [10]. In recent years, nanomaterials are receiving continued attention in the literature for both aspects of fundamental study and industrial applications [11–15]. Recent research on nanomaterials includes nanoparticles, nanorods, nanotubes, nanowires, nanostructures, and nanocomposites, etc. [16–20]. Among these, the interest in nanoparticles stems from their unique properties, which differ considerably from those of bulk materials. Various nanoparticles such as Ag, Au, Pd, Cu, Ni, and metaloxide nanoparticles (MgO, TiO_2, CaO, Al_2O_3, Fe_2O_3, etc) are reported in the literature for various catalytic applications [21–34]. Various synthetic routes are reported for the preparation of nanoparticles. Among these methods, metal oxide nanoparticles synthesized by sol–gel process possess high catalytic efficiency when compared to other method of preparation, which is attributed not only due to their high surface area, but greater amount of highly reactive edge and corner ''defects,'' shapes, and large porosities. It has recently been reported that the application of metal oxides as gas sensor [35]. Research in the area of nanometer-sized metal oxides in general, and MgO in particular was studied for different catalytic applications. Various synthetic routes for MgO nanoparticles are reported [24, 36–37]. It is also reported that the catalytic activity in turn is dependent on the size of the nanoparticles [22].

MgO is found to be highly active and adsorb chemical warfare agents like activated charcoal but in addition to that decompose chemical warfare agents very efficiently and non-selectively; furthermore degradation products are found to be nontoxic. Decomposition of chemical warfare agents by these nanoparticles includes nerve agents, blister agents, insecticide model compounds and potential application as protective barrier skin cream [38], and also hazardous biological agents [39, 40]. However, there is difficulty in usage of these nanoparticles including reported pellet form of metaloxide nanoparticles [41] for the spillage on instrument and other surfaces effectively [42]. It is also desirable to mount these nanoparticles on supportive material to use them in other applications such as protective clothes and face masks.

Among the various materials that can be used to mount these nanoparticles, polymers are the best choice due to many merits, such as elasticity, viscosity and plasticity, that inorganic nanoparticles lack. These nanocomposites based on polymer and nanoparticles in turn can be prepared by two possible approaches. The nanoparticles can be mixed with a polymer which is the most trivial and commonly used approach. In the other one, nanoparticles can be generated during polymerization in which case nanoparticles distribute uniformly and aggregation is avoided. Nanocomposites can be synthesized by various methods including electrospinning techniques [43–45]. Electrospinning process is perhaps the most promising of all nanotechnologies, in terms of versatility and cost to produce continuous nanofibers with nanometer size and high surface area. Nanofibers find potential applications in various areas such as tissue scaffolds, blood vessel, wound dressing, battery, gas, bio- and chemical sensors, catalysis, etc [43–51].

In the present study, nanoparticle is synthesized separately and subsequently mixed with polymers and then subjected to electrospinning. The electrospun nanocomposite fibers are tested for the hydrolysis of paraoxon, a nerve agent stimulant. The decrease in absorbance intensity with time was observed in presence of nanocomposite membranes which indicates the hydrolysis of paraoxon.

Experimental section

Materials

Polysulfone (PSU), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF copolymer), and poly (vinyl chloride) (PVC) polymers used in the experiment have M_n 26,000, 110,000, 99,000, respectively and purchased from Aldrich, USA. Solvents such as tetrahydrofuran (Merck, Germany), acetone (Merck, Germany), dimethylacetamide (Merck, Germany), toluene (Merck, Germany), methanol (BDH, England), and heptane (Aldrich, USA) were used without any further purification. Paraoxon (diethyl *p*-nitrophenyl phosphate, Sigma, USA) was used as received. Dimethylformamide (Merck, Germany) of HPLC grade was stored over Molecular sieves 4.0 A° and used. SEM images were obtained from a Quanta 200 instrument from FEI (The Netherlands). Energy Dispersive Analysis of X-ray (EDX) was performed on a JOEL JSM 5600LV instrument equipped with EDX attachment. UV–Vis spectra were recorded on a Thermo Spectronic Unicam UV

300 spectrophotometer. Spectra were recorded in heptane as solvent. Surface area of the nanoparticles was measured using Brunauer-Emmett-Teller (BET) Analyzer. Commercially available nano-Al_2O_3 was purchased from Aldrich and after sieving of this material, surface area is found to be 280 m^2/g by BET method. Carbolite Type 3216 furnace (England) was used to prepare the metaloxide nanoparticles. Transmission electron microscopy (TEM) measurements were performed on JEM 2010F instrument operated at an accelerating voltage of 100 kV. XRD measurements were carried out using a Shimadzu 600 diffractometer with a scan rate of 4 °C/min.

Synthesis of MgO nanoparticles

Nanocrystalline MgO were prepared from $Mg(OH)_2$ samples by the modified procedure described by Utamapanya et al.[37]. In this method of preparation, 10% magnesium methoxide solution was prepared by stirring magnesium in methanol under nitrogen atmosphere for overnight. Then water was added with stirring to this magnesium methoxide solution taken in toluene/methanol mixture. After overnight stirring, the gel was transferred into an autoclave heated to 250 °C with 1 °C/min heating rate and kept at this temperature for 15 min. The solvent was removed by heating in the oven at 120 °C. The resulting white powder was subjected to further heat treatment by a modified procedure by us due to the non-availability of the preferred instrument such as parr reactor used by the above reference. The white powder was taken in a porcelain crucible and heated from room temperature to 220 °C at 1 °C/min and soaked at 220 °C for 5 h; and heated from 220 °C to 400 °C at 1 °C /min and soaked at this temperature for 4 h. Hence the surface area of the MgO nanoparticles synthesized is found to be 155 m^2/g by BET method which is lower than reported (400 m^2/g) [37]. TEM image of the synthesized nanoparticle is shown in Fig. 1a. The sizes of the nanoparticles are found to be 2.7–3.3 diameter and 9–14 nm length (needle shaped images were taken to calculate the size here). SEM picture (Fig. 1b) of the MgO nanoparticle appeared to be almost amorphous in nature as it is reported in the literature [37]. FTIR spectrum of the synthesized MgO is similar to the one reported (not presented here) in literature [37].

Different polymer solutions such as PVC, PVDF copolymer, and PSU having different composition of MgO nanoparticles (or Al_2O_3 nanoparticles) were prepared by mixing varying amount of MgO and polymer solution.

Fabrication of nanocomposite membranes

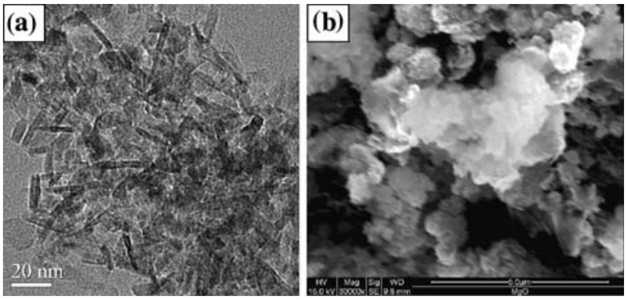


Fig. 1 (**a**) TEM image and (**b**) SEM picture of MgO nanoparticles

Solution of 20 wt% PSU (DMF), 15 wt% PVDF copolymer (acetone/dimethyl acetamide 4:6 v/v%), and 10 wt% PVC (DMF/tetrahydrofuran, 1:1 wt%) solutions were prepared in respective solvents. To these polymer solutions, MgO of different weight was added to maintain same percentage of MgO in the composite membrane after solvent evaporation. A typical procedure adopted for the preparation of PSU electrospun membrane is provided here. 1.8 g of polymer and 8.2 mL of dimethylformamide (DMF) were stirred magnetically at room temperature for overnight to dissolve the polymer. After the complete dissolution of polymer, 200 mg of MgO nanoparticles was added and stirred for 24 h at room temperature followed by sonication to disperse the nanoparticles uniformly. The resulting polymer solution was loaded into a syringe fitted to a syringe pump. The positive terminal of a high voltage DC power supply was connected to the metallic needle of the syringe. A grounded aluminum foil placed 15 cm from the tip of the needle was used as the target to collect the membranes. The syringe pump was set to deliver the solution at a rate of 4 mL/h and high voltage (11 KV) was applied. Electrospinning was carried out at room temperature in air with a relative humidity of 45–50%. The electrospun membrane was dried in a vacuum pump and tested for hydrolytic efficiency studies. The percentage of MgO in the nanocomposite membrane was found to be 10%. This was calculated on the basis of the following formula.

$$\begin{aligned}&\%\text{ of MgO in nanocomposite membrane}\\&\quad=\text{wt\% of MgO added }(0.2\,\text{g})/\text{wt\% of MgO }(0.2\text{ g})\\&\qquad+\text{polymer }(2\,\text{g}).\end{aligned}$$

Testing the hydrolysis of paraoxon

First 10 μL of paraoxon was taken in a 50 ml of heptane solution in a SMF. To 10 mL of this solution in 60 mL of heptane was added and absorbance intensity for this solution at $\lambda_{\max}$ 268 nm for paraoxon was noted. 7 mL from this stock solution was taken and to this a uniform weight of membrane was added and the decrease in absorbance intensity at $\lambda_{\max}$ 268 nm indicates the hydrolysis of paraoxon. All these membranes were heated at 120 °C for

20 min and cooled in dessicator to room temperature before doing the hydrolysis studies.

Results and discussion

Nanocomposites were prepared by mixing nanoparticles with polymer solution and then subjected to electrospinning. In order to find out the suitable polymer to support the nanoparticles, different polymers such as PVC, PVDF copolymer, and PSU were chosen. Although polymer such as poly(ethylene terephthalate) can also be chosen here, it has been reported that this polymer will be soluble and electrospinnability can be achieved by using trifluoroacetic acid as a co-solvent. This solvent binds with MgO chemically is reported in the literature.

Figure 2 show the SEM images of these electrospun nanofibers for blank and in presence of nanoparticles (10%). The Java image processing software [Image J1.29 (222 commands)] was used to measure the diameter of the fibers. The average fiber diameter of these membranes such as PVC, PVDF copolymer, and PSU were found to be 555 ± 25 nm, 450 ± 18 nm, 500 ± 25 nm, respectively. In presence of MgO nanoparticles, for PVC and PVDF the diameter were reduced to 505 ± 13 nm, 415 ± 30 nm, respectively which could possibly due to the addition of MgO whereby conductivity of the spinning solution increased thereby reduction in fiber diameter. Similar observation of reduction in fiber diameter by the addition of salts such as benzyltrialkylammonium chlorides, sodium chloride, etc is already reported in the literature [52, 53]. It is to be noted here that increase in fiber diameter is

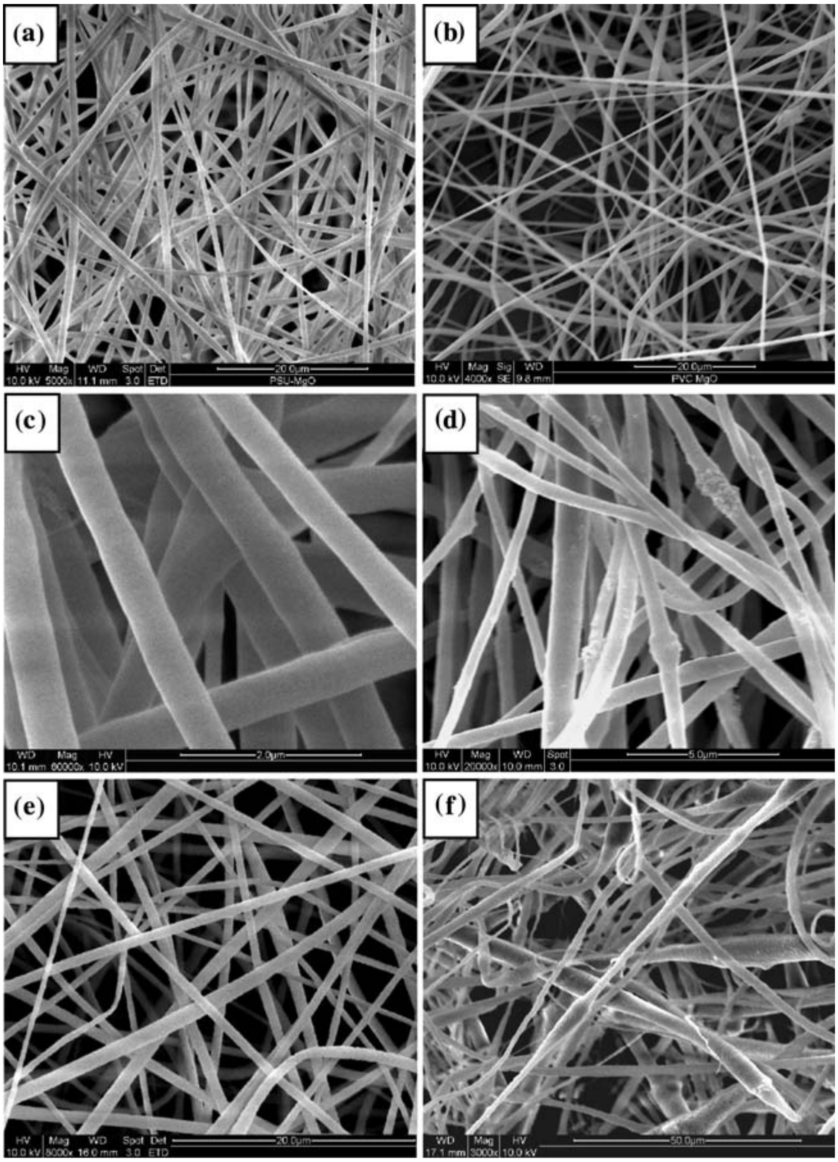


Fig. 2 SEM micrographs of electrospun PVC (**a**); PVC-MgO10% (**b**); PVDF (C) PVDF-MgO 10% (**d**); PSU (**e**); PSU-MgO 10%(**f**)

observed by the addition of MgO in the case of PSU polymer. This is unclear to us. The minimum and maximum diameter observed for PSU is found to be 400 nm and the average fiber diameter is 900 nm. Few fibers of having more than 1 micron is also observed. When electrospinning of PSU with MgO (10%) was carried out at increased voltage (15 KV), it does not produce any fiber rather dripping was observed.

These functionalized membranes were tested for the hydrolysis of nerve agent stimulant namely paraoxon in heptane. The hydrolysis was measured by using UV study (Fig. 3). The decrease in absorbance (λ_{max}) for paraoxon at 268 nm is observed here and the increased orders of the reactivity of the membranes are found to be PVC-MgO < PVDF < PSU < PVDF-MgO < PSU-MgO. The decomposition mechanism of paraoxon on MgO functionalized membranes is depicted in Fig. 4 [22].

The electrospinning was carried out for the PVC and PVDF solution after 1–2 h of mixing it with MgO. It has been observed that the PVC polymer solution turned slight bluish color and violet color with PVDF. By prolonged storage of these solutions lead to the sky blue color with PVC and intense violet color with PVDF. We believe that very low reactivity observed for PVC in presence of MgO could be due to the reaction of MgO with chlorine group in PVC polymer [53, 54].

Nanocomposite membranes were fabricated in order to find out the electrospinnability and catalytic performance of other nanoparticles towards paraoxon. In this case after the addition of Al_2O_3 (10%) to the PSU solution, electrospinning was carried out at 10 KV and there is not observed any fiber formation rather dripping taking place. Hence 0.7 g of DMF solution was added and after stirring for 3 h followed by sonication, electrospinning was achievable. However microfibers were obtained and the fibers diameter were found to be 1,660 ± 625 nm (Fig. 5a). However rare formation of few beads has also been observed. Increasing the voltage to 12.3 KV resulted in slight reduction in fiber diameter (1,300 ± 900 nm, Fig. 5b). There was also observed few fibers of around 140 nm. Attempt to prepare lower fiber diameter by playing with spinning parameter was unsuccessful.

UV–visible study was carried out for the MgO nanoparticles, Al_2O_3 nanoparticles, charcoal, and for nanocomposite membranes with time (Fig. 6) to compare the reactivity results of the present chosen materials with commercially available charcoal. The obtained results indicate that the nanocomposite membrane detoxifying the simulant without much loss in activity of MgO nanoparticles. However, it is to be noted here that approximately 50 % reduction in activity is observed for the nanocomposite membrane when compared to the MgO nanoparticles as such usage.

The decrease in absorbance value for paraoxon after 15 min of mixing with nanocomposite membranes or nanoparticles or charcoal is compared for the relative rate of hydrolysis. The order is as follows; Charcoal (1) < PSU with Al_2O_3 (1.5) < PSU with MgO (2.1) < Al_2O_3 nanoparticles (2.8) < MgO nanoparticles (5.4) and the numbers within bracket indicates the number of times increased rates of present materials towards charcoal. In MgO,

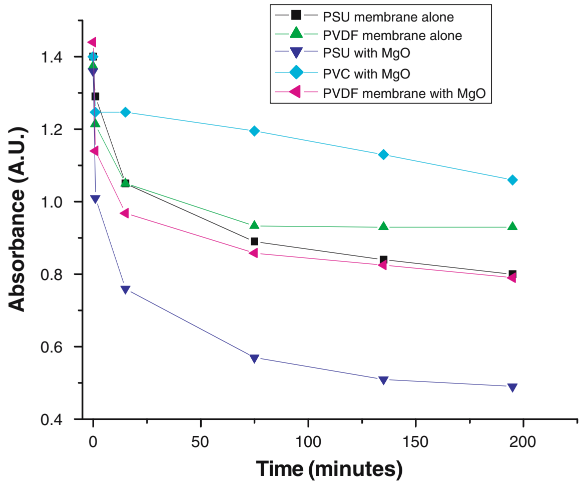


Fig. 3 Change in absorbance with time for different polymer membranes and in presence of MgO nanoparticles

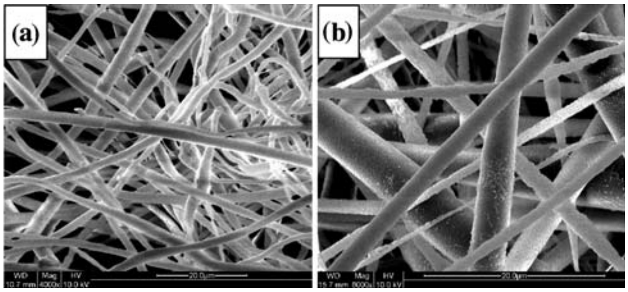
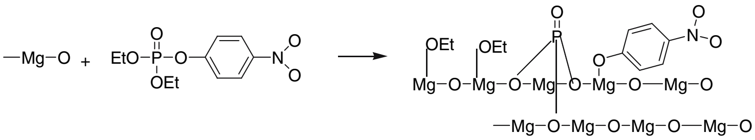


Fig. 5 SEM micrographs of electrospun PSU with Al_2O_3 at 10 KV (**a**); 12.4 KV (**b**)

Fig. 4 Decomposition mechanism of paraoxon on MgO surface



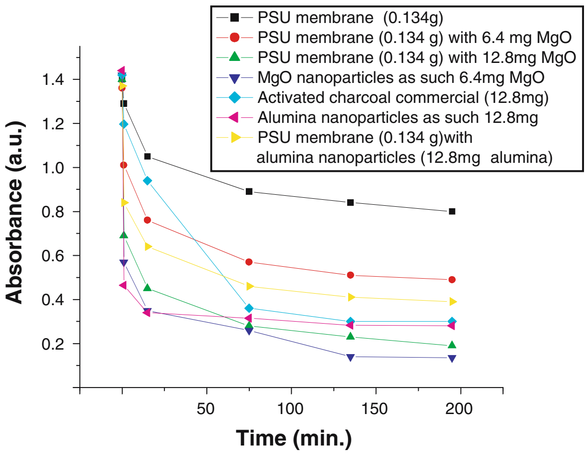
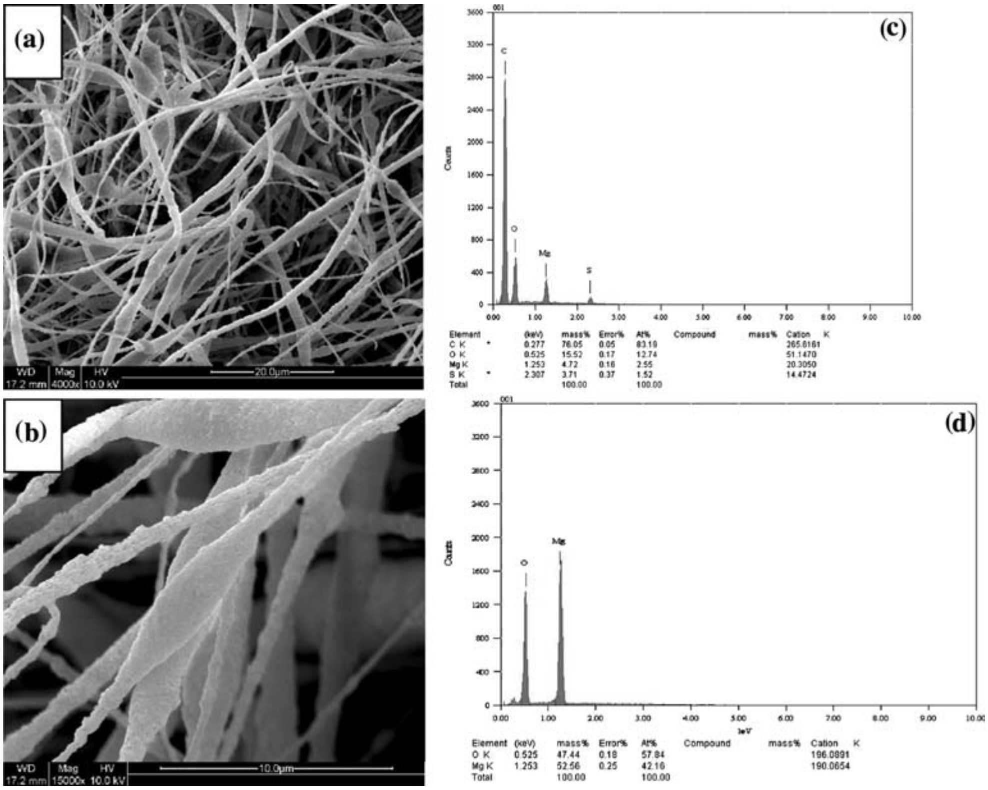


Fig. 6 Adsorption study of paraoxon on MgO, Al_2O_3, charcoal dispersed in pentane, monitored by UV/Visible spectroscopy

reduction in activity is observed when MgO is contacted with air, carbon dioxide. This problem can be overcome by coating this oxide with other coating materials, which has been well documented [55, 56]. Silyl agents, oils, cellulose, waxes, surfactants, charcoal and coating of a second metal oxide over this MgO are preferably used as coating materials in above and other references.

Further study was carried out in order to find out the maximum amount of MgO incorporation into nanofiber membrane. Instead of MgO addition to the polymer solution, first DMF (0.7 g) was added to MgO nanoparticle to wet the surface of the nanoparticles, and then to this polymer solution (1 g) was added and stirred. Figure 7 shows the SEM image and EDX of 35% MgO incorporated nanocomposite membrane. Apart from the formation of regular nanofibers (Fig. 7a), formation of few spindle like (Fig. 7b) fibers and occasionally beads were also observed in this case. The presence of MgO on the surface of the membrane was confirmed by comparing the EDX of nanocomposite membrane (Fig. 7c) with MgO nanoparticles (Fig. 7d). However the handling of resultant nanofiber due to presence of large amount of MgO is tough which resulted in breakage while peel off from the aluminum surface. To overcome this difficulty first polysulfone polymer alone was electrospun on aluminum foil for few minutes, over this 35% MgO containing polymer solution electrospinning followed by polysulfone electrospinning on this surface. Figure 8 represents the XRD spectrum recorded for the nanocomposite membrane in comparison with MgO nanoparticles). The diffraction peaks observed for both the samples at 2θ = 43 °C and 2θ = 62 °C can be assigned to MgO as reported earlier [24]. No peaks were observed for PSU membrane suggesting that it is amorphous in nature (XRD not presented here). DSC recorded for PSU also does not show any melting peak confirming

Fig. 7 SEM micrographs of electrospun PSU-MgO (35%) at 12.4 KV (**a**); spindle like structure formation (**b**); EDX data for PSU-MgO (35%) (**c**); and EDX data for MgO nanoparticles (**d**)



Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K	*	0.277	76.05	0.05	83.19			265.6161	
O K		0.525	15.52	0.17	12.74			51.1470	
Mg K		1.253	4.72	0.16	2.55			20.3050	
S K	*	2.307	3.71	0.37	1.52			14.4724	
Total			100.00		100.00				

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
O K	0.525	47.44	0.18	57.84			196.0891	
Mg K	1.253	52.56	0.25	42.16			190.0654	
Total		100.00		100.00				

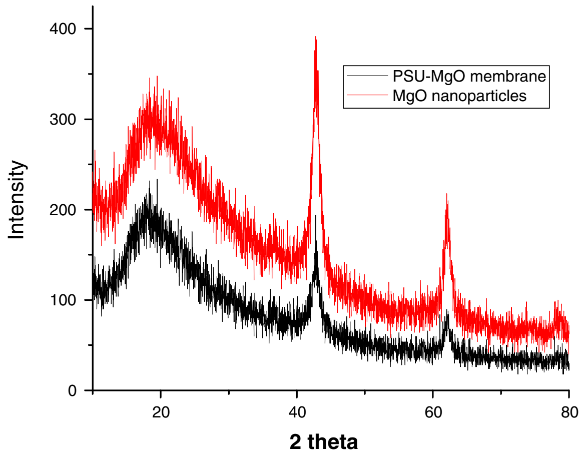


Fig. 8 XRD spectra of MgO nanoparticles and nanocomposite membranes

further pure PSU electrospun membrane is amorphous in nature (DSC thermogram is not presented here).

Conclusion

Nanocomposite membranes based on nanoparticles such as MgO and polymer were fabricated by electrospinning technique. The reactivity of the resultant membranes is found to be depends on the polymer used. This could be due to the reactivity of the nanoparticle with functional group present in the polymer chain which suggests that for the fabrication of nanocomposite membrane proper choice of polymer is also essential. The hydrolysis of paraoxon, a nerve agent stimulant was taken place in the presence of these nanocomposite membranes. The fabricated membrane based on MgO was found to be about 2 times more reactive than currently used charcoal. The maximum loading percentage of MgO that can be electrospinnable was upto 35%. The existing MgO nanoparticles as such cannot be applied where in we can use this MgO based nanocomposites as wipe on chemical and biological warfare agents spillages on buildings or sensitive instruments. IBA-β-CD complex specific to nerve agent is already developed in our group [49]. The functionalization of nanofiber with specific catalysts to degrade mustard agent and biological warfare agents is in progress. After the completion of these task different layers of these nanofibers including present study membranes will be put together along with the woven textile media for the protective clothing applications.

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References

1. Morrison W Overview of current collective protection filtration technology, Presented in 2002 NBC Defense collective protection conference, USA, 2002. Available from www.natick.army.mil [www.natick.army.mil/soldier/jocotas/ColPro_Papers/Morrison.pdf]
2. http://www.deconsolutions.com/pdf_Files/TECHNICAL%20REPORT%20MOD2003-1012 G.pdf)
3. Bergard Rohm & Hass Company, Philadelphia, Pa
4. Yang Y-C, Baker JA, Ward JR (1992) Chem Rev 92:1729
5. Moss RA, Kim KY, Swarup S (1986) J Am Chem Soc 108:788–93
6. Bunton CA, Foroudian HJ, Gillitt ND (1999) J Phys Org Chem 12:758
7. McCreery MJ (1997) US Patent No. 5607979
8. Speck JC (1959) US Patent No. 2885305
9. Yang Y-C (1999) Acc Chem Res 32:109–115
10. Klabunde KJ (2001) Nanoscale materials in chemistry. Wiley-Interscience, New York
11. Puntes VF, Krishnan KM, Alivisatos AP (2001) Science 291:2115
12. Cui Y, Wei Q, Park H, Lieber CM (2001) Science 293:1289
13. Pan ZW, Dai ZR, Wang ZL (2001) Science 291:1947
14. Poizot P, Laruelle S, Grugeon S, Dupont L, Tarascon J-M (2000) Nature 407:496
15. Sata N, Eberman K, Eberl K, Maier J (2000) Nature 408:946
16. Templin M, Franck A, Chesne AD, Leist H, Zhang Y, Ulrich R, Schadler V, Wiesner U (1997) Science 278:1795
17. Caruso F, Caruso R, Mohwald H (1998) Science 282:1111
18. Sellinger A, Weiss PM, Nguyen A, Lu Y, Assink RA, Gong W, Brinker CJ (1998) Nature 394:256
19. Boal AK, Iihan F, Derouchey JE, Thurn-Albrecht T, Russell TP, Rotello VM (2000) Nature 404:746
20. Huynh WU, Dittmer JJ, Alivisatos AP (2002) Science 295:2425
21. Wagner GW, Bartram PW, Koper O, Klabunde KJ (1999) J Phys Chem B 103:3225
22. Rajagopalan S, Koper O, Decker S, Klabunde KJ (2002) Chem Eur J 8:2602
23. Huang L, Li D-Q, Lin Y-J, Wei M, Evans DG, Duan X (2005) J Inorg Biochem 99:986
24. Makhluf S, Dror R, Nitzan Y, Abramovich Y, Jelinek R, Gedanken A (2005) Adv Funct Mater 15:1708
25. Vorontsov AV, Panchenko AA, Savinov EN, Lion C, Smirniotis PG (2002) Environ Sci Technol 36:5261
26. Kozlov DV, Vorontsov AV, Smirniotis PG, Savinov EN (2001) Appl Catal B Env 32:11
27. Vorontsov AV, Davydov L, Reddy EP, Lion C, Savinov EN, Samirniotis PG (2002) New J Chem 26:732
28. Koper OB, Lagadic I, Volodin A, Klabunde KJ (1997) Chem Mater 9:2468
29. Wagner GW, Koper OB, Lucas E, Decker S, Klabunde KJ (2000) J Phys Chem B 104:5118
30. Wagner GW, Procell LR, O'Conner RJ, Munavalli S, Carnes CL, Kapoor PN, Klabunde KJ (2001) J Am Chem Soc 123:1636
31. Templeton MK, Weinberg WH (1985) J Am Chem Soc 107:97
32. Mitchell MB, Sheinker VN, Mintz EA (1997) J Phys Chem B 101:11192
33. Carnes CL, Stipp J, Klabunde KJ, Bonevich J (2002) Langmuir 18:1352
34. Carnes CL, Kapoor PN, Klabunde KJ, Bonevich J (2002) Chem Mater 14:2922
35. Epifani M, Diaz R, Arbiol J, Comini E, Sergent N, Pagnier T, Siciliano P, Faglia G, Morante JR (2006) Adv Funct Mater 16:1488

36. Štengl V, Bakardjieva S, Maříková M, Bezdička P, Šubrt J (2003) Mater Lett 57:3998
37. Utamapanya S, Klabunde KJ, Schlup JR (1991) Chem Mater 3:175
38. Koper O, Lucas E, Klabunde KJ (1999) J Appl Toxicol 19:S59
39. Stoimenov PK, Klinger RL, Marchin GL, Klabunde KJ (2002) Langmuir 18:6679
40. Koper OB, Klabunde JS, Marchin GL, Klabunde KJ, Stoimenov P, Bohra L (2002) Curr Microbiol 44:49
41. Koper O, Klabunde KJ, PCT WO 01/78506
42. Fitch JP, Raber E, Imbro DR (2003) Science 302:1350
43. Huang Z-M, Zhang Y-Z, Kotaki M, Ramakrishna S (2003) Comp Sci Tech 63:2223
44. Li D, Xia Y (2004) Adv Mater 16:1151
45. Ramakrishna S, Fujihara K, Teo W-E, Lim T-C, Ma Z (2005) An introduction to electrospinning and nanofibers. World Scientific Publisher, Singapore
46. Subbiah T, Bhat GS, Tock RW, Parameswaran S, Ramkumar SS (2005) J Appl Polym Sci 96:557
47. Gibson HLS, Truong Q, Walker JE, Owens JR, Wander JD, Jones WE Jr. (2003) MRS Bulletin 574
48. Nanotechnology Innovation for Chemical, Biological, Radiological, and Explosives (CBRE): Detection and Protection, The AVS Science and Technology Society 2002, www.wtec.org/nanoreports/cbre/CBRE_Detection_11_1_02_hires.pdf
49. Ramakrishnan R, Sundarrajan S, Yingjun L, Barhate RS, Lala NL, Ramakrishna S (2006) Nanotechnology 17:2947
50. Choi SS, Lee SG, Joo CW, Im SS, Kim SH (2009) J Mater Sci 39:1511
51. Choi SS, Lee SG, Im SS, Joo YL (2003) J Mater Sci Lett 22:891
52. Yang QB, Li DM, Hong YL, Li ZY, Wang C, Qiu SL, Wei Y (2003) Synth Metals 137:973
53. Zhou Q, Tang C, Wang Y-Z, Zheng LI (2004) Fuel 83:1727
54. Horikawa S, Takai Y, Ukei H, Azuma N, Ueno A (1999) J Anal Appl Pyrol 51:167
55. Rajagopalan S, Koper OB, Klabunde KJ, Malchesky PS, Winecki S (2005) U.S. Pat. No. 6860924
56. Bediol AF, Sigel MJ, Koper OB, Melgunov MS, Klabunde KJ (2002) J Mater Chem 12:3599