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Novel hybrid multifunctional magnetoelectric porous composite films

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ABSTRACT

Novel multifunctional porous films have been developed by the integration of magnetic $CoFe_2O_4$ (CFO) nanoparticles into poly(vinylidene fluoride)-Trifuoroethylene (P(VDF-TrFE)), taking advantage of the synergies of the magnetostrictive filler and the piezoelectric polymer. The porous films show a piezoelectric response with an effective d_{33} coefficient of -22 pC/N^{-1}, a maximum magnetization of 12 emu g^{-1} and a maximum magnetoelectric coefficient of 9 mV cm^{-1} Oe^{-1}. In this way, a multifunctional membrane has been developed suitable for advanced applications ranging from biomedical to water treatment.

1. Introduction

Porous films and membranes are playing an increasingly important role in various fields such as energy, environment, chemical and medical industries, being regarded as one of the most promising functional materials [1–3]. They are attracting increasing attentions both at a research and application levels and experiencing strong development in novel theories, technologies and applications [1,4,5].

Porous films can be prepared from (organic) polymers, inorganic materials, liquids (immobilized liquid composite membranes) and from self-assembled smaller molecules (in analogy to biological membranes). Polymer films and dominate a very broad range of industrial applications due to the large variety of polymeric materials commercially available that can be prepared by versatile and industrially scalable methods with tailored microstructure and properties. Further, polymer based membranes can be produced in large areas and with various membrane shapes (flat sheet, tubular, hollow-fiber, capillary, capsule) and formats including modules with high packing densities [1].

Among polymeric porous films, the ones based on poly(vinylidene fluoride) (PVDF) and its copolymers are emerging as one of the most promising membranes due to their good mechanical and thermal properties and chemical stability [6,7]. Compared to its PVDF homo-polymer, PVDF-Trifuoroethylene P(VDF-TrFE) displays further advantages such as high dipole moment, high dielectric constant, and possibility of controlling porosity at room temperature [7]. Furthermore, P(VDF-TrFE), for TrFE contents between 50% and 80%, crystallizes in the piezoelectric phase independently of the processing method, allowing the preparation of piezoelectric porous films with improved flux and fouling in the case of filtration and separation membranes [8,9], improved sensing properties for biomedical monitoring [10] and with the possibility of environmental energy storage and harvesting [11].

The incorporation of magnetic nanoparticles in porous structures is still very recent [12] and the use of such nanoparticles in multifunctional porous films is essentially unexplored. Nevertheless, the addition of magnetic nanoparticles can take a step forward these materials concerning the development of multifunctional porous films able to separate components with distinct magnetic properties (e.g. oxygen is paramagnetic while nitrogen is diamagnetic) [13], generate heat [14], large and controlled deflections [15] or in-situ pore size switching [16]. If the magnetic particles are also magnetostrictive, other innovative applications such as magnetostrictive ultrasonic thrombolysis membranes [17] or magnetic sensor membranes[18] can be also developed. Additionally, the inclusion of magnetostrictive nanoparticles in a piezoelectric porous structure can allow the preparation of magnetoelectric (ME) membranes [19].

The magnetoelectric (ME) effect, defined as the variation of the electrical polarization (ΔP) of a material in the presence of an applied magnetic field (ΔH) (Eq. (1)), or as the variation of the magnetization in the presence of an applied electric field can be seen as the interrelation between the electric and magnetic properties of matter and is quantified by the ME coefficient (α) [19–21].

$$\Delta P=\alpha\Delta H \tag{1}$$

The ME effect within porous structures will allow novel applications in areas – Fig. 1 – such as sensors, actuators, transformers and microwave devices [19,20], in technological applications such as separation membranes, water treatment, drug release, cell culture or medical devices [16,22,23]. In this way, ME porous structures represent an innovative concept to be added to the increasingly large variety of applications of porous structures [6,24,25].

Despite this promising and interesting potential, just few reports have vaguely addressed the concept of ME porous structures [26,27].

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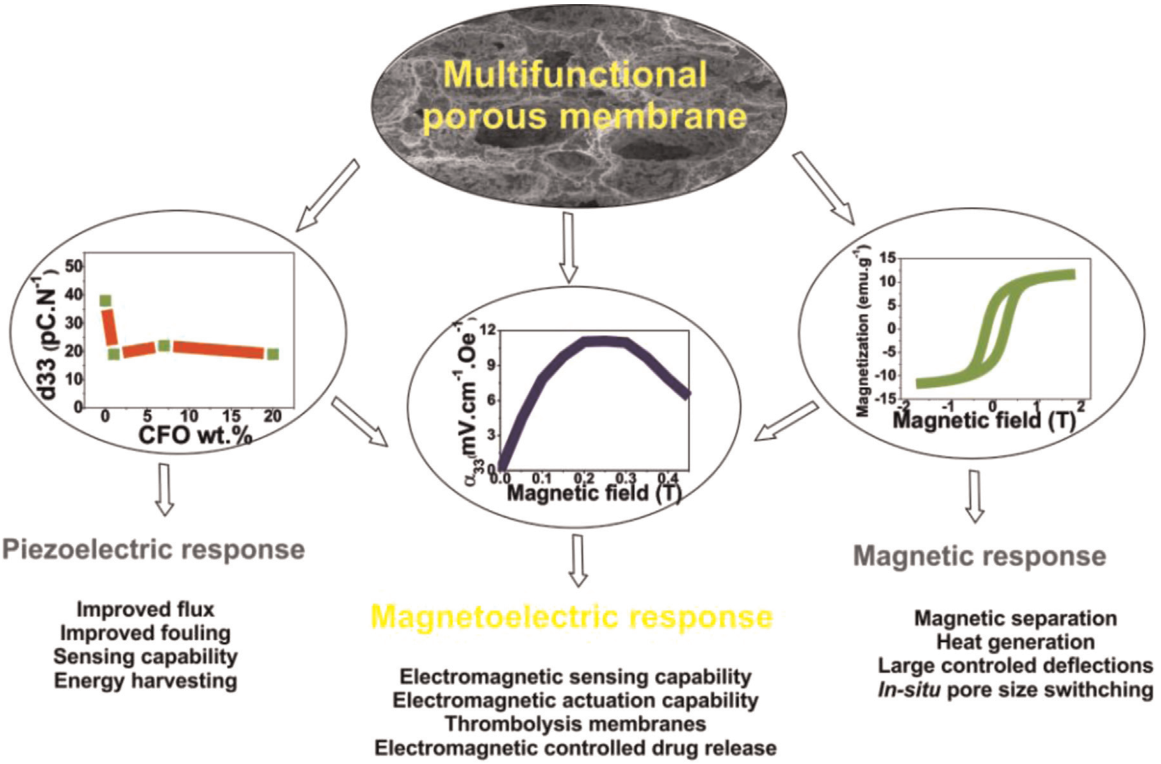

Fig. 1. Porous ME composite structure, its main responses and possible applications.

This work reports on the development of ME porous films that pave the way for improved applications in the areas of membrane technology and ME materials.

$CoFe_2O_4$(CFO)/Poly(vinylidene fluoride-Trifluoroethylene) (P(VDF-TrFE)) porous piezoelectric, magnetic, magnetostrictive and magnetoelectric films have been developed.

P(VDF-TrFE) was chosen as piezoelectric material since it exhibits one of the highest piezoelectric responses among polymer materials over a wide range of temperature depending on its composition [28] and CFO nanoparticles were chosen as magnetic/magnetostrictive phase due to the large magnetostrictive coefficients and high Curie temperatures [29].

2. Experimental

All chemicals and nanoparticles were used as received from the suppliers: CFO nanoparticles were purchased from Nanoamor with dimensions between 35 and 55 nm [30]. N,N-Dimethylformamide (DMF, pure grade) was supplied by Fluka and P(VDF-TrFE) was supplied by Solvay Solexis.

Composite porous films of CFO/P(VDF-TrFE) with 1, 7 and 20 nanoparticle weight percent (wt.%) were prepared by solvent casting and crystallization at room temperature, with thickness of ranging from 200 to 400 μm. Higher contents of ferrite nanoparticles were not used to avoid damaging the porous structure and the agglomeration of ferrite nanoparticles in the porous surface as demonstrated in other nanoparticles [31]. Previously, the CFO nanoparticles were added to 8 mL of N,N-dimethyl formamide (DMF) and placed in an ultrasound bath during 8 h to ensure a good dispersion of the nanoparticles in the solution and also to avoid loose aggregates. After that, 2 g of P(VDF-TrFE) were added to this suspension, achieving a polymer/solvent ratio of 20:80, and mixed with a Teflon^{TM} mechanical stirrer until complete dissolution of polymer. Finally, the material was placed on a dried glass substrate at room temperature to ensure the complete evaporation of the solvent.

The structure of the ME porous films was investigated using a Quanta 650 FEG (FEI) Environmental Scanning Electron Microscope with an acceleration voltage of 5 kV.

Poling of the films was achieved, after an optimization procedure, by corona poling at 10 kV during 120 min at 120 °C in a home-made chamber and cooling down to room temperature under applied field. The piezoelectric response (d_{33}) of the samples was analyzed with a wide range d_{33}-meter (model 8000, APC Int. Ltd.).

Magnetic hysteresis loops at room temperature were measured using an ADE 3473-70 Technologies vibrating sample magnetometer.

In order to obtain the out-of-plane ME coefficient α_{33}, the first index indicating the collinear ferroelectric poling and electrical measurement directions, and the second indicating the applied magnetic field direction, a DC and AC magnetic field were applied along the direction of the electric polarization of the P(VDF-TrFE), i.e., perpendicular to the composite membrane surface.

An AC driving magnetic field of 1 Oe amplitude at 7 kHz (resonance of the composite) was provided by a pair of Helmholtz coils. A DC field with a maximum value of 0.5 T was applied by an electromagnet. The induced ME voltage was measured with a Standford Research Lock-in amplifier (SR530).

3. Results and discussion

The typical microstructure of pure copolymer film samples and composites is presented in Fig. 2.

It can be observed that the porous structure characteristic of neat P(VDF-TrFE) polymer is maintained, however the typical spherical shape [6,7] of these pores is replaced by an ellipse shaped structure. The origin of this change can be explained by the high weight of CFO nanoparticles during the slow polymer crystallization by solvent casting method. Further, it is observed that