Pressure and microwave sensors/actuators based on smart hydrogel/conductive polymer nanocomposite

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ABSTRACT

A nanocomposite is fabricated by formation of a conductive polymer, using in situ oxidative polymerization, inside a thermosensitive crosslinked hydrogel. FE-SEM micrographs show the nanometric domains of the conductive material (polyaniline, PANI) dispersed in the hydrogel matrix based on cross linked poly(N-isopropylacrylamide) (PNIPAm). The thermosensitive properties of PNIPAm and copolymers with 2-acrylamido-2-methyl propane sulfonic acid (AMPS) are not affected by the presence of conductive polymer nanoparticles. The incorporation of PANI improves the mechanical properties of the hydrogel allowing it to swell up to 30,000% without breaking. Since the conductive polymer absorbs strongly microwave radiation at pH < 4 and heats up, the nanocomposite containing PANI suffer phase transition upon microwave irradiation. At pH > 4, PANI is not conductive and the nanocomposite becomes insensitive to microwaves. However, using a pH insensitive conductive polymer (polypyrrole, PPy) in the nanocomposite makes it sensitive to microwaves at all pH values. The nanocomposite is used in a chemomechanical actuator where drug release is driven remotely by microwave irradiation. Since the PNIPAm-co-2%AMPS/PANI nanocomposite is soft and electronically conductive, could be used as pressure/force sensor. It is shown that a compressive force applied on a cylinder of that nanocomposite increases the conductivity of material. Additionally a switch is built which turns off upon microwave irradiation. Therefore, the nanocomposites are potential candidates for different technological applications, such as: a force/pressure electrical sensor, a drug delivery device driven remotely by microwaves, pH or temperature electrical switches and an electric switch driven by microwaves.

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1. Introduction

Hydrogels sensitive to external parameters (pH, temperature, ionic force, electric field, etc.) constitute the so-called "smart" hydrogels which could react actively to changes in the environment [1,2]. Crosslinked acrylamide based thermosensitive hydrogels are interesting candidates for biomedical or pharmaceutical applications, such as drug release [3] because they change volume and expel a significant amount of its inner solution when a transition is induced by external action. These kind of materials based on smart hydrogels could also be used in chemical [4] or mechanical [5] actuators as well as environment sensors [6] for technological applications.

However, it would be most interesting to induce the volume change at distance using electromagnetic radiation of low energy. In fact, smart nanocomposite hydrogels containing gold nanoparticles and driven by absorption of near infrared radiation-NIR has been proposed [7–10]. It is well known that conductive polymers strongly absorb electromagnetic radiation, specifically in the microwave range, with heating up of the polymer [11].

In addition, we have shown previously that macroporous hydrogels loaded with conductive nanoparticles (including polyaniline nanospheres and nanofibers) could be driven to volume collapse by microwave or laser light (near infrared range) irradiation [12]. At the same time, behavior of semi-interpenetrated system of PANI inside thermosensitive hydrogel showed that properties of both materials were not alters, significantly. That is to say, each component of material could respond by itself.

It is noteworthy that even though the incorporation of conducting polymers to hydrogel network has been described before [13], it have been usually assumed that the conducting polymer form an interpenetrating [14] or semi-interpenetrating networks [15–17]. However, we think this would be the case when a water soluble polymer is made inside a hydrogel network [18].

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It is well known that polyaniline is insoluble in the aqueous polymerization solution and precipitates from the solution during polymerization. For that in the present communication we show how a nanocomposite could be easily fabricated by formation of conductive polymer (hydrophobic) inside a nanoporous matrixbased on PNIPAm hydrogels. The formation occurs by oxidative polymerization of the appropriate monomer (aniline-ANI or pyrrole-Py), previously loaded inside the hydrogel matrix. Semi-interpenetration of linear polyaniline inside a hydrogel network should involve the formation of isolated PANI chains which have not been detected in water. It is more likely that aggregates of PANI chains, in form of PANI nanoparticles which have been detected in water, also are formed in the water filled pores of the hydrogel. Accordingly, in contrast with previous assumptions, we show clear evidence on the formation of separate nanoscopic domains of PANI incorporated to PNIPAm and copolymers with 2-acrylamido-2-methyl propane sulfonic acid (AMPS). The distinction is quite relevant because the semi-interpenetration of one polymer in a crosslinked matrix alters the physicochemical properties of the gel (e.g. transition temperature) while in a nanocomposite the physicochemical properties are the linear addition of the components properties. The nanocompositing of the conducting polymer and the hydrogel provide novel properties to materials which arise from the synergic combination of each component properties. Using those properties, different sensors and actuators can be built.

The incorporation of a relatively rigid conducting polymer in a soft matrix based on superabsorbent hydrogel enhances the mechanical properties of material. Accordingly, the superabsorbent nanocomposite could swell up to 30,000% without breaking. The conducting polymer absorbs microwaves and heats up, driving the thermal phase transition of the hydrogel. The thermal phase transition is shown as a volume change and the release of the inner solution. Therefore, a drug delivery actuator driven remotely by microwave irradiation is demonstrated.

Besides that, the presence of the conducting polymer makes the nanocomposite electronically conductive while the hydrogel matrix makes the material elastic. In that way, the nanocomposite deforms under pressure and the resistance changes, allowing us to build an electronic pressure/force sensor.

Finally, the volume change upon microwave irradiation combined with the electronic conductivity of the nanocomposite is used to build a microwave actuated electrical switch.

While we built all the actuators as macroscopic devices, the underlying properties are molecular in nature. Therefore, it is likely that the devices can be miniaturized up to nanometric size with success.

2. Experimental

2.1. Synthesis of nanocomposites

PNIPAm hydrogels were prepared by free radical polymerization dissolving in distilled water 0.5 M N-isopropylacrylamide (NIPAm-Scientific Polymer Products) and 10 mM N,N′-methylenebisacrylamide (BIS-Scientific Polymer Products) as crosslinker agent, using ammonium persulfate (APS-Cicarelli) (0.001 g/ml) and N,N,N′,N′-tetramethylethylenediamine (TEMED-Aldrich) (10 μl/ml) as redox initiator and activator, respectively. In other cases, 2-acrylamido-2-methyl propane sulfonic acid (AMPS-Scientific Polymer Products) (2 or 20% moles of NIPAm monomers) was added to NIPAm to synthesize the co-monomer.

The experimental steps of nanocomposite formation are described in Scheme 1. Small discs of dry hydrogels were immersed into a solution with 0.1 M ANI (Fluka)/1 M HCl, until the solution was absorbed. A known amount of APS (equimolar to ANI) was then added as oxidant to produce PANI inside of gel. The experience was
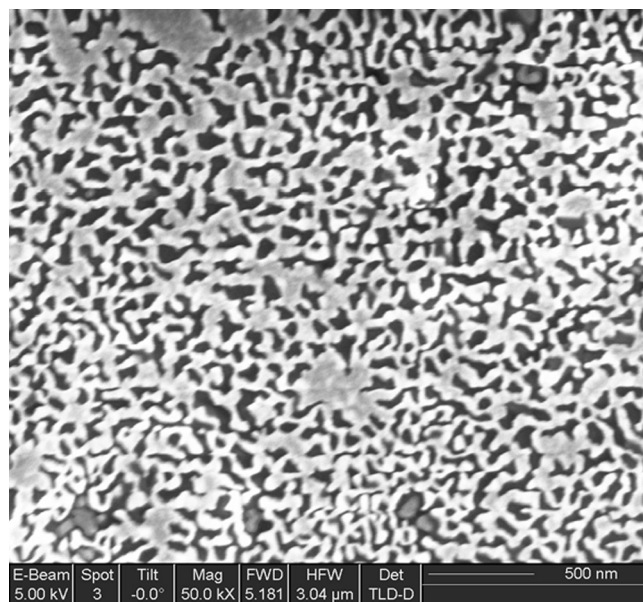

Fig. 1. SEM micrographs of PANI incorporated into a PNIPAm hydrogel.

carried out at room temperature. A similar process was carried out to impregnate hydrogels with polypyrrole (PPy).

2.2. Scanning electron microscopy (SEM)

Scanning electron micrographs (Fig. 1) were taken at low vacuum and low field in a LEO 1450VP Variable Field Emission SEM. The images of porous hydrogels were analyzed using "ImageJ 1.45s" software to ascertain the pore size and distribution. The FE-SEM micrographs were obtained in a dual beam workstation (FEI Helios Nanolab 600) equipped with a field emission gun scanning electron microscope (FE-SEM). The elemental measurements were performed by energy dispersive spectroscopy (EDX) with an accelerating voltage of 20 kV using EDAX instruments detector and EDAX Genesis® Software (Table 2).

2.3. Swelling dynamic experience

Previously weighted dry hydrogels samples were immersed in solutions. At certain time intervals, the sample was removed from solution and was weighed. The swelling percent can be calculated as a function of time, according to:

$$\% S_w = \frac{W_s - W_d}{W_d} \times 100$$

where W_s represents the weight of the swollen state of the sample at a given time and Wd is the weight of dry sample. Graphic of $\% S_w$ vs time were built to analyze the swelling kinetic (Fig. 2a). Every data of $\% S_w$ obtained were averaged of five measurement with absolute error around ±150. The experiments were carried out in buffer solution at pH 7 and room temperature. Photography of nanocomposite was taken before and after of equilibrium swelling state to show the extraordinary increase of volume (Fig. 2b).

2.4. Differential scanning calorimeter (DSC)

DSC measurements were performed to determine the phase transition temperature (T_{PT}) of hydrogels and nanocomposites swollen in water (Table 1). The sealed pan with a water swollen hydrogel piece was quickly frozen inside the DSC chamber until −25 °C. This temperature is reached by an aqueous Cl_2Ca solution