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Preparation of thermo-sensitive poly(N-isopropylacrylamide) film using KHz alternating current Dielectric barrier discharge

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Abstract. Plasma, a quasi-neutral gas, is referred to as the forth state of matter. Plasma surface treatment consists of plasma surface modification, plasma polymerization and plasma surface grafting. Dielectric barrier discharge (DBD) is an effective way of producing homogeneous plasma. DBD consists of infinite micro-discharges, which distribute irregularly the whole discharge space both in time and in space. The self-made equipment of atmospheric pressure plasma vapor deposition of poly(N-isopropylacrylamide) (PNIPAm) was used in the environment of argon. PNIPAm is a new type of smart thermo-sensitive macromolecule material that is characterized by a sudden precipitation on heating, switching from a hydrophilic to a hydrophobic state. The samples were characterized by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and Fourier Transform infrared spectroscopy (FTIR). It was revealed from the results of SEM analysis that the PNIPAm films were formed on the surface of the smooth glass slides, according to XPS and FTIR, it was found that there exists PNIPAm.

Introduction

Plasma consists of a collection of electrons and ions as well as neutrals, atomic and molecular species that exhibit a collective behavior in the presence of an electromagnetic field [1]. Much attention has paid on tailoring a polymer with properties different on its surface from its bulk in the past decades [2-4]. In the past, plasma polymerization is usually carried out in vacuum plasma systems, but recently there has been a growing trend towards plasma-chemical reactions at atmospheric pressure [5]. Plasma surface treatment is a convenient, energy-saving and dry process and it is an environment-friendly technology. It can give the material surface new features without altering the bulk properties at the same time. Therefore, the material surface engineering has been widely used in automotive, microelectronics, biotechnology and chemical industries [6-9], and plasma polymerized film on the surface has many excellent physical properties such as a good shape, sterile, surface complete and good biocompatibility.

Temperature-sensitive polymer materials refer to macromolecule materials that have stimulus to temperatures and they are intelligent materials such as poly (N-isopropylacylamide) (PNIPAm). Poly (isopropylacylamide), has been the most frequently studied thermo-sensitive polymer because of its lower critical solution temperature (LCST) of 32.0℃ [10, 11]. PNIPAm shows a LCST around 32.0℃ in an aqueous environment because the well-hydrateted polymer chains below the LCST have a random coil configuration. Above the LCST, the polymer chains take on a much more compact configuration by sudden dehydration and increased hydrophobic interaction between the polymer chains. Plasma deposition of PNIPAm film has been investigated for different applications like retinal function and cartilage- engineered [12-16].

Self-made plasma equipment

A general electrical system for generating DBD plasma is adopted, which is shown in Fig. 1. Two electrodes are parallel electrodes with dielectric barrier, using argon as working gas, and the HV supply is able to output a signal ranging from 1 ~ 20KHz. The discharge gap between the electrodes can be varied from 1 to 4 mm. The discharge current is measured through a current probe.
Glass slides were washed by deionized water and anhydrous alcohol, and then dried. Glass slides were carried out in a continuous plasma treatment. The discharge voltage used for the generation of plasma was 15kV. In this article we control the argon velocity constant at 1.0 l/min.

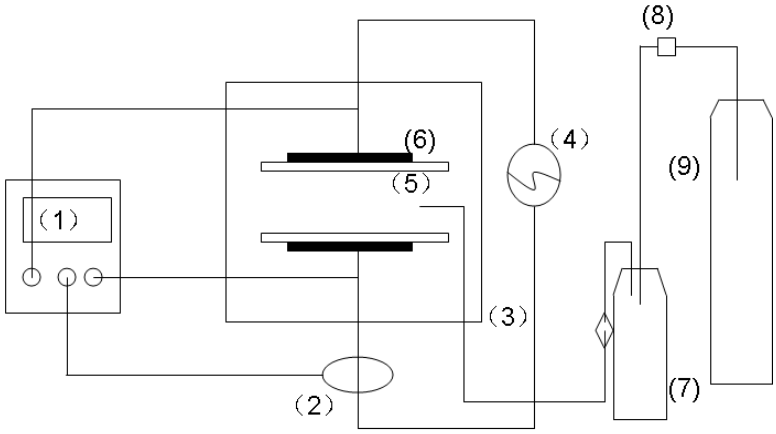

Fig.1 Schematic of the DBD experimental setup.

1-oscillograph; 2-current probe; 3-galss shield; 4-plasma generator; 5-quartz glasses; 6-upper electrode; 7-solution bottle; 8-flowmeter; 9-argon gas bottle

Scanning electron microscopy (SEM)

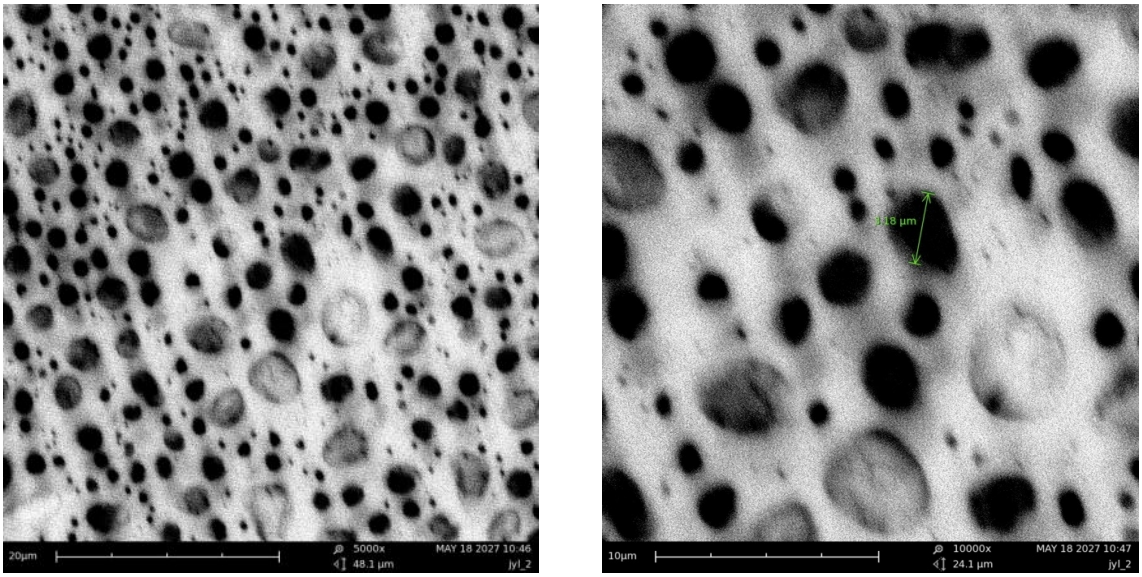

Fig.2 SEM images of PNIPAm films. 5000X (left), and 10000X (right).

Fig.2 shows the SEM images of plasma polymerization of aqueous solution of NIPAm as a function of polymerization times 600s. It can be found that the surface of the treated sample becomes rough, with there are accumulates polymer on the surfaces. The observation by using SEM with magnification of 5000 times, it has shown that the formed pinhole is not uniform. With the magnified picture of 10000 times, it can be seen the aperture of the pinhole is about 3.18µm.

X-ray photoelectron spectra (XPS)

XPS scans were used to verify the presence of PNIPAm films on the surface of the glass slide. Fig.3 shows the XPS of the samples. The surface layer of untreated glass slide exhibits oxygen, carbon and silicon elements while the surface layer of treated sample shows not only the oxygen, carbon and silicon elements and it also contains nitrogen element. Comparing the XPS of the untreated and treated samples, we can speculate that there exhibit nitrogen, monomer, polymer and its middle product on the surface of treated glass slide. These results showed that PNIPAm were successfully deposited on the surface of the glass slide.

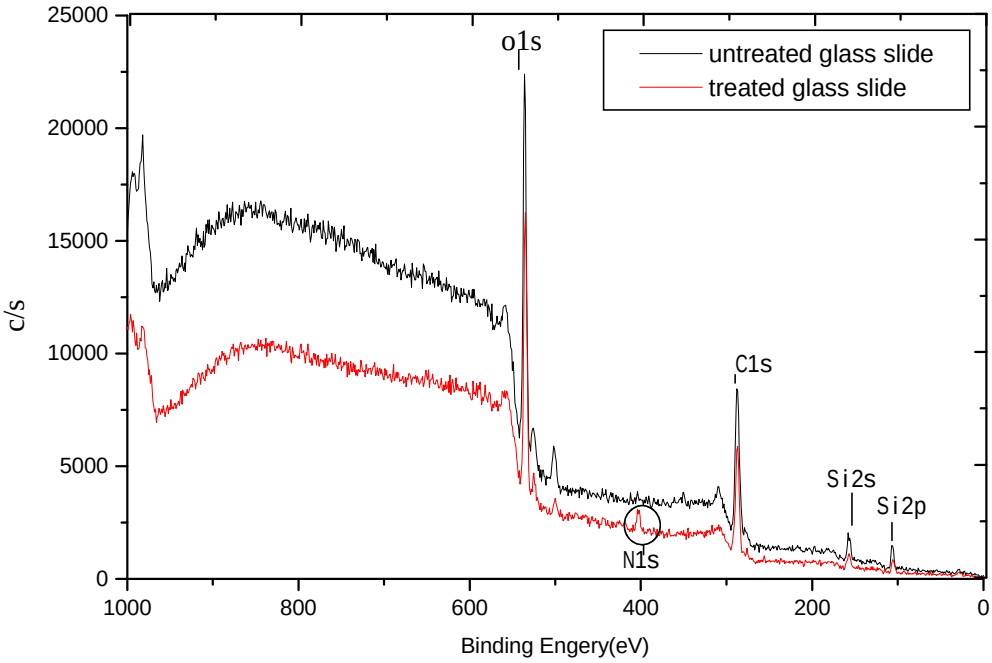

Fig.3 XPS data taken from the untreated and treated glass slide.

Fourier Transform infrared spectroscopy (FTIR)

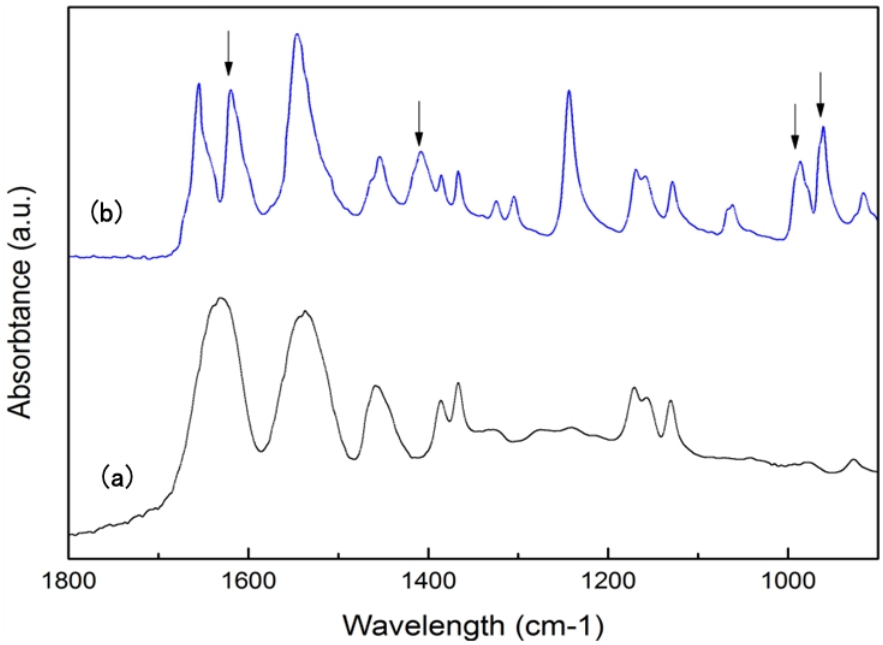

Fig.4 FTIR spectra of PNIPAm films (a) and NIPAm monomer (b).

Fig.4 shows the FTIR spectra for both PNIPAm films (a) synthesized by polymerization initiated by atmospheric plasma and NIPAm monomer (b). FTIR spectrum of solid NIPAm monomer (Fig.4,

curve b) shows typical peaks corresponding to amide I (1657cm^{-1}), amide II (1550cm^{-1}), amide III (1245cm^{-1}), methyl (1387, and 1368cm^{-1}) and methylene groups (1458cm^{-1}). The FTIR spectrum of NIPAm monomer also exhibited the characteristic peaks at 1622, 1410, 993, 966, and 918cm^{-1} associated with the vinyl groups (C=C and CH_2= stretching peaks). During plasma polymerization of NIPAm (Fig.4, curve a), the characteristic peaks of vinyl groups (C=C, CH_2= Stretching peaks) disappeared. This result implies that NIPAm polymerization takes place, most probably by a radical polymerization mechanism through the path of vinyl bonds (C=C) cleavage. The presence of two IR peaks of almost equal intensity at 1366 and 1386cm^{-1} confirms high retention of specific chemical composition of NIPAm monomer. In addition, no new peaks appeared indicating that no formation of new molecular chemical bonds or structures has occurred. However, the reappearance of the characteristic peaks of NIPAm monomer (vinyl groups, i.e., C=C, CH_2= stretching peaks) could indicate that some quantities of non-reacted NIPAm monomer and eventually PNIPAm homopolymer probably coexist when the NIPAm was plasma polymerized from more concentrated solutions.

Conclusions

Plasma polymerization of (PNIPAm) was effectively carried out to the glass slide. Deposition of the plasma polymer on the surface of glass slide was evidenced by the SEM images. It was found that there have PNIPAm films on the sample surface, as shown by XPS and FTIR. The preparation method of pure PNIPAm without polymer crosslinker will be extremely valuable for further application to thermo-sensitive smart materials.

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