

Preparation of Electrically Conducting Self-Organized Micro-Hybrid Structures*

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We used a self-organized polymer microhoneycomb structure as a template to form polyaniline structures that contain hexagonal voids. The polyaniline was synthesized in situ and adsorbed spontaneously on a polymer honeycomb structure that was immersed in the solution. Successive adsorption cycles led to thicker polyaniline coating. The characteristic honeycomb structure could be preserved during the process. Electrical measurements showed that the film resistance is the sum of contact and sheet resistance. [DOI: 10.1380/ejsnt.2015.19]

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I. INTRODUCTION

Honeycomb films were reported by Francois *et al.* in 1994 [1] and since then have been the topic of intense research in various fields and for various applications [2]. The outstanding features of the honeycomb films are the regularity of their porous structure, the ease of fabrication [3], the control of the pore parameters (diameter and rim width) [4], and the wide range of applicable materials [5]. Applications range from improved photocatalyst activity [6] to cell culturing [7].

Polyaniline (PANI) is a now widely known semiconducting polymer that has first been reported by Letheby in 1830 [8]. At that time, its potential for sensing devices was completely unknown. With the birth of the molecular sensor concept in 1960 [9], however, PANI returned into the spotlight when McDiarmid investigated the pH dependence of PANI conductivity [10] and subsequently various devices that use PANI have been reported [11].

Here we report on the fabrication of PANI-coated honeycomb structures and their electrical conductivity. Those structures may be useful as chemical sensors. The highly porous structure increases the active surface area of the sensing material, PANI, while the mesh structure of the honeycomb provides robustness of the device - even if parts of the honeycomb structure are damaged, electricity can flow 'around' the damages areas.

II. EXPERIMENTAL

Honeycomb films are prepared by casting a polymer solution under high humidity. The organic solvent should have a low boiling point (i.e. should evaporate easily)

and the polymer solution needs to have a miscibility gap with water. A common combination is polystyrene and ethyl acetate. In order to stabilize the condensed water droplets, an amphiphilic polymer is added, in our case a poly ion complex made of poly(styrene sulfonate) and N, N-dioctadecyl-N, N-dimethyl ammonium [12]. A 10:1 mixture of those two polymers (5 mg of polystyrene-co-maleic anhydride and 0.5 mg of the polyion complex in 1 ml of ethyl acetate) was cast on a glass substrate and allowed to evaporate at around 80% relative humidity. The strongly light scattering white films were characterized by optical and electron microscopy.

Polyaniline was prepared by oxidative polymerization of aniline in acidic aqueous solution that contained an emulsifier, dodecylbenzene sulfonate (DBSA), that was added to stabilize the polyaniline suspension [13]. Aniline (0.045 mL), DBSA (0.45 g), and conc. HCl (1.5 mL) were added to 50 mL of deionized water in a 100 mL standard glass beaker and stirred for 20 minutes. Ammonium persulfate (0.1 g) was added and a honeycomb-coated glass slide was vertically immersed in the mixture and stirred for another 60 minutes during which the solution turned green.

III. RESULTS AND DISCUSSIONS

Polyaniline exists in different oxidation states that show different degree of conductivity. Leucoemeraldine is the completely reduced form that shows low conductivity. The semi-oxidized emeraldine base is conductive when doped with acid. The completely oxidized pernigraniline, again, exhibits low conductivity [10]. The green color indicates the half-oxidized emeraldine. When the honeycomb template is removed and washed with deionized water, it is very slightly colored green. The photograph of this film and the corresponding electron microscopy image are shown in Fig. 1B. After drying, the same honeycomb film was again immersed in freshly prepared solutions, as described in the previous paragraph.

Figure 1 shows the photographs and electron micrographs of honeycomb films before and after PANI adsorp-

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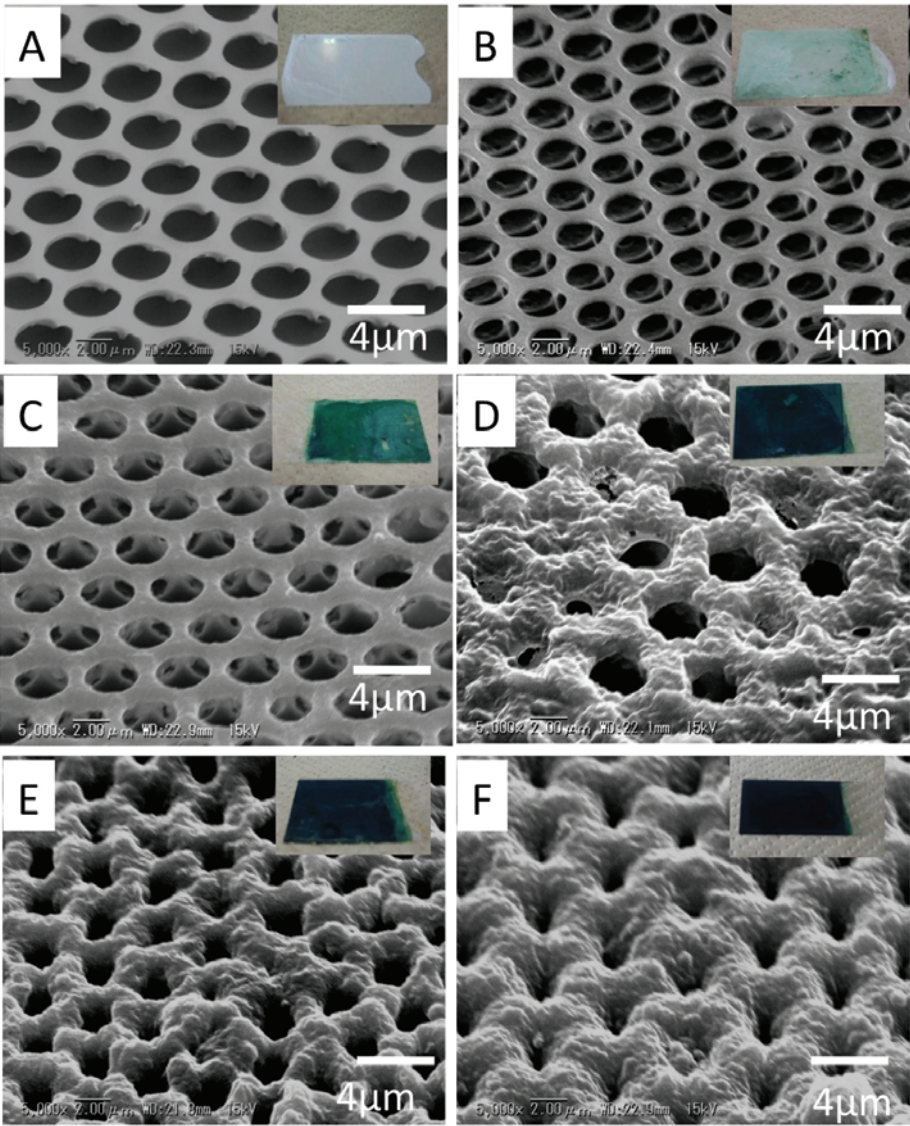


FIG. 1. Scanning electron microscope images of honeycomb films after different numbers of PANI adsorption cycles. The insets are photographs of the films on a 20 mm × 50 mm glass slide. A: pristine honeycomb film. B-F: Films after 1, 2, 3, 4, and 5 adsorption cycles, respectively.

tion. The pristine honeycomb film (Fig. 1A) shows a characteristic uniform diameter of the air holes and a smooth polymer surface between the holes. After one PANI adsorption step, the optical photograph shows a very slight green color. A slight roughening of the honeycomb top layer can be seen in the electron micrograph. After two adsorption cycles, both the overall color and the microscopic surface roughening becomes more prominent. Both features become much more pronounced after three adsorption cycles, indicating a nonlinear PANI adsorption characteristics for subsequent steps. It seems that a thin priming layer is formed in the first PANI adsorption aides the adsorption of further PANI layers. Also, with increasing adsorption cycles, the air-hole diameter shrinks. That means that PANI nanoaggregates are formed in solution and attach in a diffusion-controlled manner freely from various angles onto the honeycomb film. Figure 2 shows the cross-sectional view of the hobeyscomb film, illustrating that the polymer of the honeycomb film is surrounded

TABLE I. Resistance of PANI-modified honeycomb films

Electrode distance(mm)	No. of PANI layers	$\Omega_{\text{tot}}(\Omega)$
5	2	3200
10	2	5050
15	2	6300
20	2	7800
5	3	2600
10	3	2800
20	3	3300
5	4	3000
10	4	4500
20	4	6400

by PANI.

Figure 2 clearly shows that the PANI is homogeneously adsorbed onto the honeycomb polymer. The triangular features (A) in the top layer of the honeycomb film is

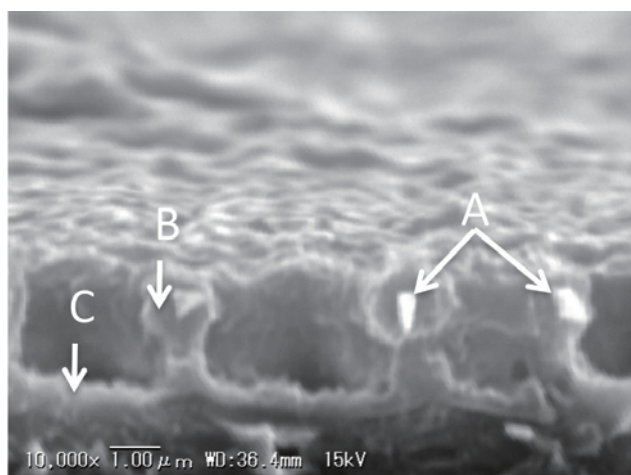


FIG. 2. Cross sectional SEM view of a honeycomb film after four adsorption cycles. A is the polystyrene honeycomb template, B is the PANI layer adsorbed to the honeycomb structure, and C is the PANI layer adsorbed to the polystyrene base film.

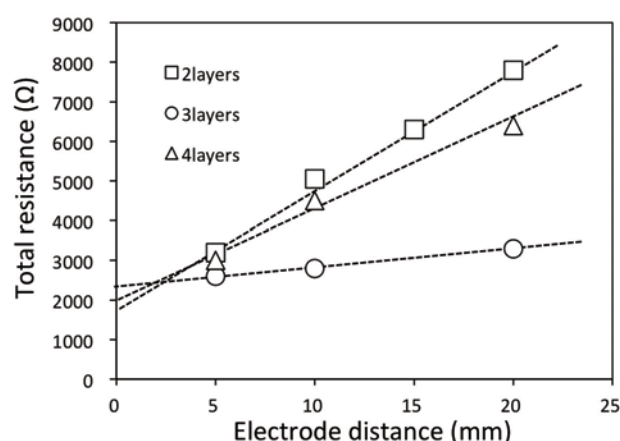


FIG. 3. Plot of the resistance of three different PANI honeycomb films at various electrode distances. The dotted lines are guides to the eye.

the polystyrene, which is surrounded by an approximately 200 nm thick PANI layer (B). The bottom layer of the honeycomb is also covered with a thin PANI layer (C).

Gold electrodes were deposited onto the samples through a mask with two voids that were 5 mm wide and 10 mm long. The electrodes had distances of 5, 10, 15 and 20 mm, respectively. The rectangular measurement area was separated from the rest of the honeycomb film by a

frame of insulating polymer. From the voltage/current curve obtained by a source meter (Keithley Digital Multimeter 2000) we could estimate the sheet resistance of the film. The total resistance Ω_{tot} of the film is the sum of the sheet resistance Ω_s and the contact resistance Ω_c . By measuring the Ω_{tot} at various electrode distances, we can deconvolute Ω_s and Ω_c . Table I shows the data for Ω_{tot} of PANI honeycomb films after two, three and four cycles of PANI adsorption. As expected, Ω_{tot} increases with electrode distance for a given number of PANI layers, because Ω_s increases while Ω_c should be constant. On the other hand, Ω_{tot} does not change in a predictable way when comparing the data for the same electrode distance and different number of PANI layers. That means that the films show a certain range of electric conductivity that depends on the preparation conditions of the films. The most likely candidate for such a variation of conductivity is proton-doping, which is difficult to control during film deposition.

Figure 3 is a graphical representation of the obtained conductivity data. The dotted lines are guides to the eye. The intersection with the y -axis shows Ω_c and the slope of the lines indicate Ω_s . Table II summarizes the calculated values for Ω_s and Ω_c from Fig. 3. Even though the data shows some scatter, the linear regression has a mean root square error of >0.98 , which is a sufficiently high value to conclude the validity of the data. Even though Ω_s shows some variation, the sheet resistance value of 0.5–3 k Ω /cm is a typical value for PANI. Also the value of 2 k Ω for the contact resistance Ω_c is reasonable.

IV. CONCLUSIONS

We prepared so-called honeycomb films by a bottom-up self-organization method that relies on the formation of breath figures by condensation of water droplets on an evaporating polymer solution. These honeycomb films were used as templates for the deposition of in-situ prepared polyaniline. Optical and electron microscopy imaging showed that PANI was homogeneously adsorbed onto the honeycomb template. The thickness of the PANI coating can be controlled by the number of adsorption cycles. The sheet conductivity of the pristine films is in the k Ω /cm range and they thus might be used as pH sensors.

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TABLE II. Calculated Ω_c and Ω_s for different numbers of PANI adsorption cycles

No. of PANI layers	Ω_c (Ω /cm)	Ω_s (Ω)	R^2
2	3010	1825	0.994
3	470	2350	0.997
4	2214	2050	0.985

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