Applied Surface Science 307 (2014) 589–592

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Electrochemical synthesis of highly ordered polypyrrole on copper modified aluminium substrates

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ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 5 April 2014
Accepted 6 April 2014
Available online 18 April 2014

Keywords:
Electrodeposition
Ordered polypyrrole
X-ray diffraction
Infrared spectroscopy
Copper films
Aluminium alloy surface

ABSTRACT

Fabrication of highly ordered conducting polymers on metal surfaces has received a significant interest owing to their potential applications in organic electronic devices. In this context, we have developed a simple method for the synthesis of highly ordered polypyrrole (PPy) on copper modified aluminium surfaces via electrochemical polymerization process. A series of characteristic peaks of PPy evidenced on the infrared spectra of these surfaces confirm the formation of PPy. The X-ray diffraction (XRD) pattern of PPy deposited on copper modified aluminium surfaces also confirmed the deposition of PPy as a sharp and intense peak at 2θ angle of 23° attributable to PPy is observed while this peak is absent on PPy deposited on as-received aluminium surfaces. An atomic model of the interface of PPy/Cu has been presented based on the inter-atomic distance of copper–copper of (1 0 0) plane and the inter-monomer distance of PPy, to describe the ordering of PPy on Cu modified Al surfaces.

1. Introduction

Conducting polymers are being widely studied across scientific and engineering disciplines owing to their unusual and tunable electrical and optical properties [1]. Among the conducting polymers, PPy based materials have been one of the most widely studied polymers due to their potential applications in fuel cells, electrochromic displays, biosensors, actuator components in microsurgical tools, nerve repair conduits and corrosion protection properties [2]. Further, PPy has been of particular interest for its use in practical devices due to the long term stability of its electrical conductivity [2].

Commercially available metals including titanium, aluminium, zinc, nickel, copper, platinum, etc. have been employed as substrates for electrochemical deposition of PPy [3–8]. Additionally, copper modified poly(tetrafluoroethylene) films have also been used as substrates for the deposition of PPy [9,10]. However, there are no reports so far on the growth of ordered PPy on metal surfaces. It is widely accepted that the electrical and optical properties of conjugated polymers in thin films are closely related with ordered molecular packing, crystallinity and interchain distance of π-conjugated segments [11]. Studies on orientation and molecular ordering/crystallinity of conjugated polymers such as (poly(3-hexylthiophene) [11], poly(phenylene vinylene) [12], poly(p-phenylene)s [13], bis(3-hydroxypropyl)-sexithiophene [14], etc. have been previously reported, however, the crystallinity of ordered PPy deposited on metal surfaces has not been investigated in-depth in these reports [8]. Therefore, preparation of high quality and well ordered PPy on metal surfaces via commercially viable methods becomes of great interest.

In this paper, we have developed a unique approach for the preparation of highly ordered PPy on copper modified aluminium substrates via electro-deposition technique. The observations suggest that the PPy growth on copper modified aluminium surface leads to a greater degree of self-organization of the polymer chains and results in the formation of a highly ordered structure.

2. Experimental

Pyrrole was distilled under reduced pressure prior to use. All other chemicals used were of analytical grade and used without further purification. The cleaned as-received aluminium substrates of AA6061 alloy were modified with copper films using a method described in our previous publication [15]. After modification with copper, the samples were rinsed with de-ionized water, and immediately immersed into a solution containing 0.05 mol/L pyrrole and 0.5 mol/L oxalic acid. The electro polymerization of pyrrole

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http://dx.doi.org/10.1016/j.apsusc.2014.04.077
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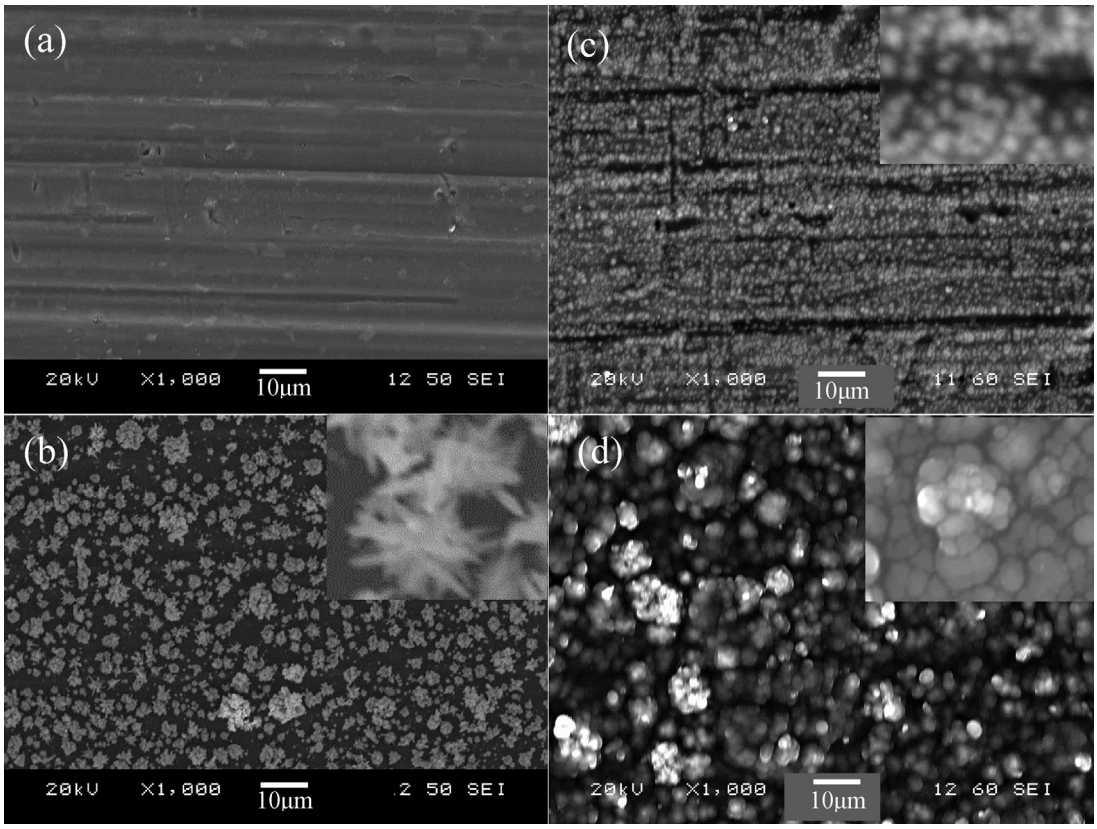

Fig. 1. SEM images of (a) as-received aluminium substrate, (b) copper modified aluminium substrate, (c) PPy deposited on aluminium substrate and (d) PPy deposited on copper modified aluminium substrate. Insets of Fig. 1(b–d) show the respective high magnification images and the scale bar is 5 μm.

was then performed at a potential of 1.7 V [9,10] for a period of 15 min, using a two electrode system separated by a distance of 15 mm. The PPy deposited copper modified aluminium surfaces were rinsed with distilled water followed by rinsing in ethanol and then dried overnight at 70 °C on a hot-plate. The morphological analyses of the PPy deposited surfaces were performed using a JEOL JSM-6480 LV scanning electron microscopy (SEM). Nicolet 6700 Infrared reflection absorption spectrometer (IRRAS) was employed to characterize the chemical structure of the PPy films. X-ray diffraction (XRD) analyses of the samples were carried out using a Bruker D8 Discover system to investigate their crystalline nature.

3. Results and discussion

SEM images of as-received aluminium and copper modified aluminium surfaces are shown in Fig. 1(a) and (b), respectively.

SEM image of as-received aluminium surface shows the presence of stripes arising from the rolling process during the fabrication of aluminium alloys plates while the copper modified aluminium surfaces show the presence of micro-islands of copper made of micro-rods of copper (inset of Fig. 1b). The SEM image of PPy deposited on as-received aluminium surface shows a dense particles-shaped morphology (Fig. 1(c)). However, PPy deposited on copper modified aluminium surfaces (Fig. 1(d)) revealed cauliflower like micro-nanostructures similar to that described in the literature where the PPy deposited on noble metals was presented [16].

The infrared reflection absorption (IRRAS) spectrum of PPy deposited on copper modified aluminium substrate is shown in Fig. 2(a1). The spectrum shows the presence of a series of characteristic peaks of PPy. The peaks at 960 cm^{-1} and around 784 and 682 cm^{-1} are attributed to the C=C in-plane bending of pyrrole ring and C—H out-of-plane bending in PPy, respectively. The peak at 1094 cm^{-1} is attributed for $N^{+}H_2$ in-plane vibration. The peak at 1040 cm^{-1} has been assigned to a combination of C—H in-plane ring bending and the deformation of the five-membered ring which contains the C=C—N deformation. The peaks appeared at 1550 and 1478 cm^{-1} arise from the pyrrole ring vibration [17,18]. The PPy deposited on as-received aluminium substrate also reveals similar IRRAS peaks as shown in Fig. 2(a2). From Fig. 2, it is clear that the intensity of the PPy peaks on copper modified aluminium surface is higher than that of the PPy deposited on aluminium surface alone. This difference in the intensity if the IR peaks indicates that the thickness of the PPy deposited on copper modified alumina surface is higher than that of PPy deposited on aluminium surface alone. The increase in thickness of the PPy films on the copper modified aluminium surfaces is attributed to the increase in the nucleation centres for the polymerization on these surfaces as compared to the as-received aluminium [19].

Fig. 2(b) shows the XRD patterns of as-received aluminium substrate, PPy deposited on aluminium surface and PPy deposited on copper modified aluminium surface. The XRD pattern of as-received aluminium surface show two characteristic peaks at 38.47° and 44.72° of Al(1 1 1) and Al(2 0 0) planes (JCPDS-01-085-1327), respectively arising from the aluminium substrate (b1 of Fig. 2(b)). Similarly, the XRD pattern of PPy deposited on as-received aluminium also show only two characteristic peaks of aluminium as observed on aluminium surface alone with no characteristic peaks of PPy evidenced (b2 of Fig. 2(b)). The XRD pattern of PPy deposited on copper modified aluminium substrate shows two characteristic peaks of the planes of Cu(1 1 1) and Cu(2 0 0) at