

Electrochemical synthesis of highly ordered polypyrrole on copper modified aluminium substrates

Ashoka Siddaramanna^a,

N. Saleema^b,

D.K. Sarkar^a,

^a Centre Universitaire de Recherche sur l'Aluminium, University of Quebec at Chicoutimi, Saguenay, Quebec G7H2B1, Canada

^b Aluminum Technology Centre, National Research Council of Canada, University East, Saguenay, Quebec G7H8C3, Canada

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Highlights

- Highly ordered polypyrrole has been synthesized on Cu modified Al surface.
- A model for ordered polypyrrole growth on Cu modified Al surface has been proposed.
- Polypyrrole ordering on Cu(1 0 0) plane is due to the similar inter-monomer distance of PPy with Cu–Cu inter-atomic distance.

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.

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

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], [4], [5], [6], [7] and [8]. Additionally, copper modified poly(tetrafluoroethylene) films have also been used as substrates for the deposition of PPy [9] and [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 was then performed at a potential of 1.7 V [9] and [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.

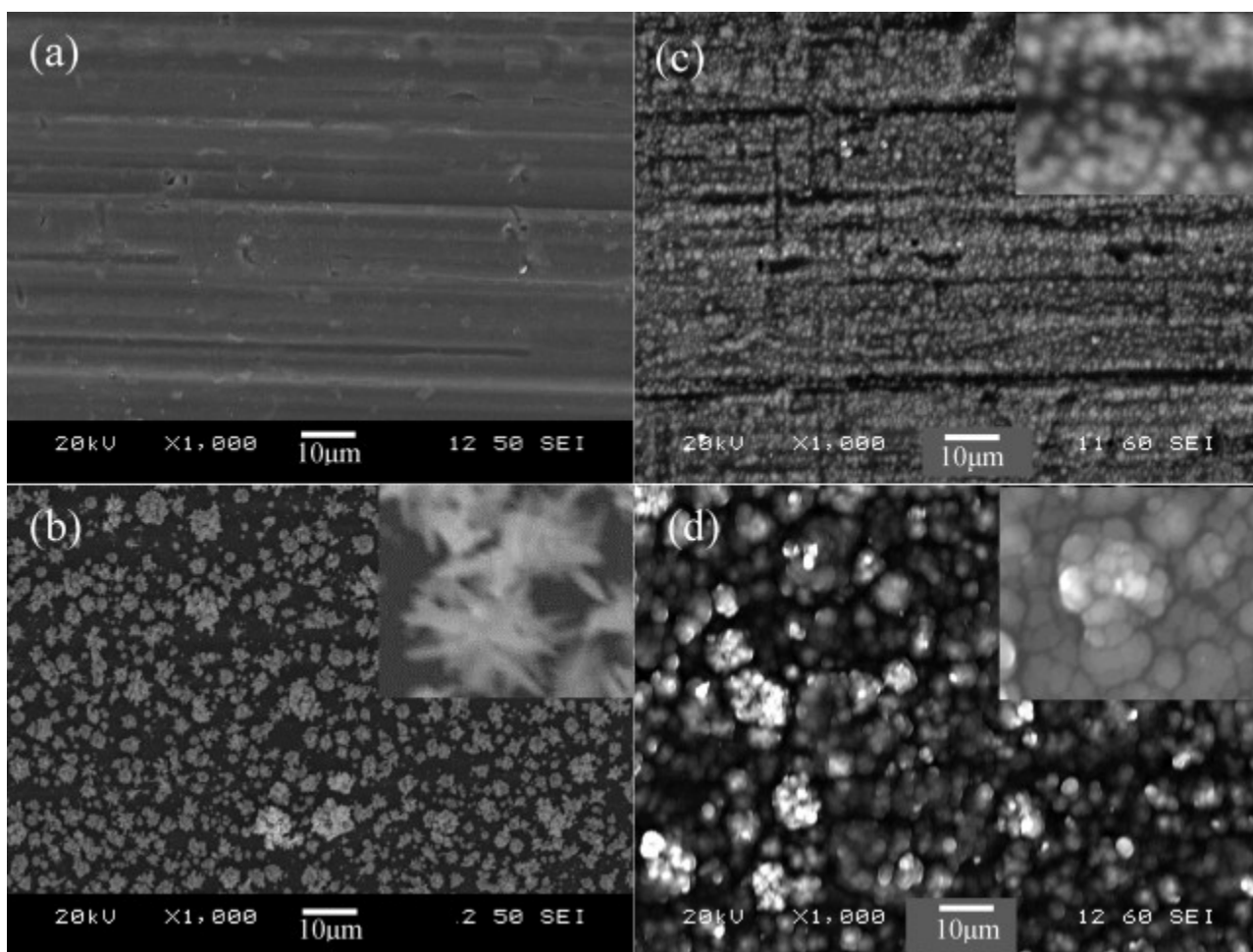


Fig. 1.

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 .

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 $\text{C}=\text{C}$ in-plane bending of pyrrole ring and $\text{C}-\text{H}$ 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 $\text{C}-\text{H}$ in-plane ring bending and the deformation of the five-membered ring which contains the $\text{C}=\text{C}-\text{N}$ deformation. The peaks appeared at 1550 and 1478 cm^{-1} arise from the pyrrole ring vibration [17] and [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 of 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].

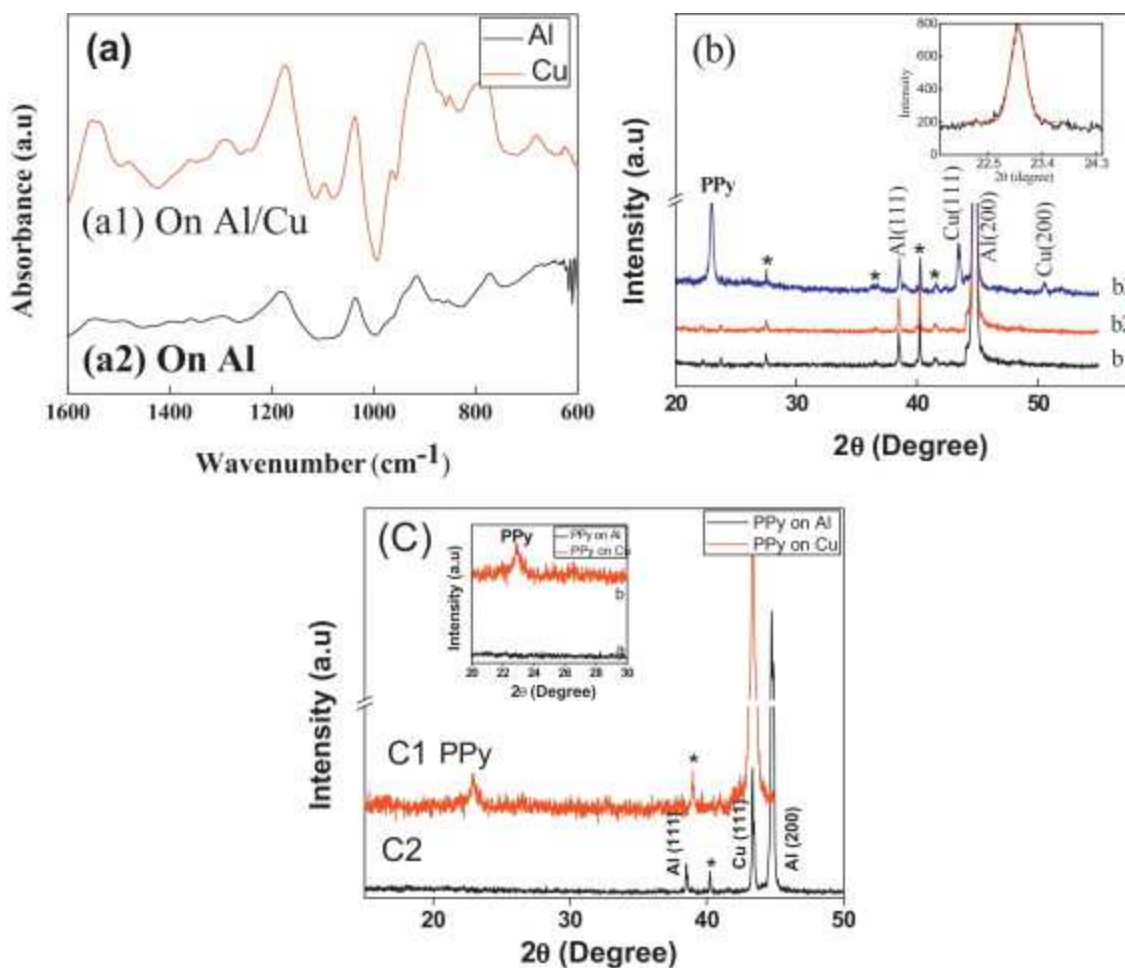


Fig. 2.

(a) FTIR spectrum of PPy deposited on aluminium (a1) and copper modified aluminium substrate (a2), (b) XRD patterns of as-received aluminium substrate (b1), PPy deposited on aluminium substrate (b2), PPy deposited on copper modified aluminium substrate (b3), (c) PPy deposited on bare copper substrate (c1) and copper modified aluminium substrate treated electrochemically under identical condition without pyrrole (c2).

*Represents inter-metallic compounds of Al substrate; the inset of Fig. 2(b and c) shows the peak at 23° fitted with Pseudo-Voigt function and XRD pattern between 20° and 30°, respectively.

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 43.32° and 50.45° , respectively, arising from copper films (JCPDS-01-085-1326) as well as the two representative peaks of aluminium (b3 of Fig. 2(b)). However, additionally, a sharp and intense peak at 2θ angle of 23° appeared only on the PPy deposited copper modified aluminium substrate which is attributable to the formation of highly ordered PPy on these surfaces. This indicates that the deposited PPy is highly ordered on copper modified aluminium substrate.

The peak profile shape could be fitted reasonably well using Pseudo-Voigt function (inset of Fig. 2(b)) and the corresponding FWHM is found to be 0.31° . This observed XRD peak is much sharper than those reported previously (FWHM 10°) for PPy [8], [17], [20] and [21]. The calculated d-spacing using Bragg's equation on our PPy films deposited on copper modified aluminium surfaces is found to be 3.8 \AA and this value is consistent with those reported previously [8] and [21].

PPy deposition on bare copper substrate has also been carried out under similar condition to compare the effect of deposited copper on PPy orientation and we have observed the presence of the same characteristic peak at 2θ angle of 23° representing PPy (c1 of Fig. 2(c)). However, the observed peak on bare copper substrate surface has a lower intensity and sharpness as compared to the PPy deposited on freshly deposited copper on aluminium surface. C2 of Fig. 2(c) shows the XRD pattern of the copper deposited aluminium substrates. In the XRD pattern, we have not observed any peaks corresponding to the contaminations of inter-metallic compounds (Cu–Al), copper oxides (CuO/Cu₂O) and copper oxalates.

The mechanism of the formation of highly ordered PPy on copper modified aluminium substrate is not fully understood. However, based on the work reported in the literature and our experimental results, we have proposed a possible model to explain the highly ordered nature of PPy on copper modified aluminium surfaces. It has been reported that PPy is linear and completely planar, and that the planes of the aromatic units are preferentially aligned [22]. The inter-monomer distance in the linear chain of PPy is equal to 3.65 \AA [23] and [24]. It can be found that the copper–copper inter-atomic distance at the (1 0 0) plane is 3.6 \AA [JCPDS-00-004-0836]. Surprisingly the inter-atomic distance of copper–copper and inter-monomer distance of PPy is nearly the same (1.3% mismatch). This matching between the inter-monomer distance in PPy and inter-atomic

distance of Cu(1 0 0) plane is believed to provide a highly oriented PPy on copper modified aluminium surfaces. This observation was indirectly evidenced in a previous work by Sarkar et al. where they observed the well faceted Cu(1 0 0) cubic morphology of copper on PPy thin films [15]. On the other hand, XRD result shows that the Cu(1 1 1) is the highly intense peak. The copper–copper inter-atomic distance at Cu(1 1 1) plane is 5.09 Å and the corresponding lattice mismatch with respect to monomer–monomer distance in PPy is found to be 28%. Based on these XRD investigations, the ordered PPy on copper modified aluminium surface has been schematically presented in Fig. 3, by taking into account of the inter-atomic distance of Cu(1 0 0) planes and inter-monomer distance of PPy. The morphological evolution of PPy deposited on copper modified aluminium surfaces as compared to surfaces without PPy and without copper modification; the presence of characteristic IRRAS peaks with increased peak intensity on the copper modified various surfaces as compared to the PPy deposited on aluminium alone; and the XRD pattern evidencing the sharp and intense peak at 2θ value of 23° leads to the conclusion that conducting PPy has been deposited on the copper modified aluminium surfaces via a simple electrochemical polymerization process.

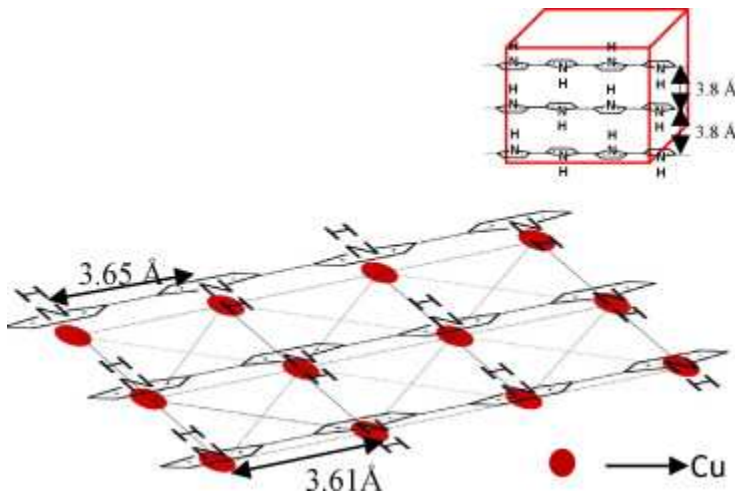


Fig. 3. Schematic representation of the orientation of PPy on Cu(1 0 0) plane. The inset shows the PPy orientation in 3D. Red Dots represent Cu on Cu(1 0 0) plane.

4. Conclusion

Conducting polypyrrole thin films have been synthesized by a simple electrochemical deposition process on as-received aluminium and copper modified aluminium

substrates. The structural, chemical and morphological characterization performed using XRD, IRRAS and SEM, revealed the presence of highly ordered conducting PPy on copper modified aluminium substrates. An in-depth XRD investigation led to the modelling of a schematic of the highly ordered PPy growth on copper modified aluminium surfaces.

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