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Thin Film Coating of Poly(acrylic acid- vinylbenzyl chloride) as a Prime Layer for the Enhancement of Conductivity and Uniformity of PEDOT Synthesized by Vapor Phase Polymerization

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Introduction

Conductive polymers have attracted significant attention due to their unique combination of electrical conductivity, optical transparency, mechanical flexibility, and tunable electronic properties, enabling a wide range of applications in energy storage, electrochemical sensors, bioelectronics, and flexible electronic devices. These materials can be synthesized through relatively simple and cost-effective methods, while their electrical properties can be adjusted via doping and structural modifications. Among various conductive polymers, PEDOT stands out as one of the most extensively studied materials due to its high electrical conductivity, environmental stability, optical transparency, low band gap, and excellent processability[1].

PEDOT thin films are required in many advanced applications, yet their fabrication via conventional solution-based methods is often limited by issues such as solvent residues, substrate incompatibility, and poor film uniformity. Vapor-based techniques provide an effective alternative to overcome these drawbacks. In particular, vapor phase polymerization (VPP) offers advantages such as low-temperature processing, reduced solvent usage, scalability, and the ability to produce uniform and highly conductive coatings on a wide range of substrates[2].

In this study, a functional interfacial primer layer of poly(AA-VBC) was deposited via initiated chemical vapor deposition (iCVD) prior to the VPP process. This primer layer acts as an interconnecting interface between the substrate and the PEDOT film, improving oxidant distribution through its hydrophilic character and enabling in-situ doping via chlorine functionalities. As a result, the combined iCVD–VPP approach enhances the uniformity, electrical conductivity, and adhesion of PEDOT thin films, while maintaining compatibility with various rigid and flexible substrates.

Experimental

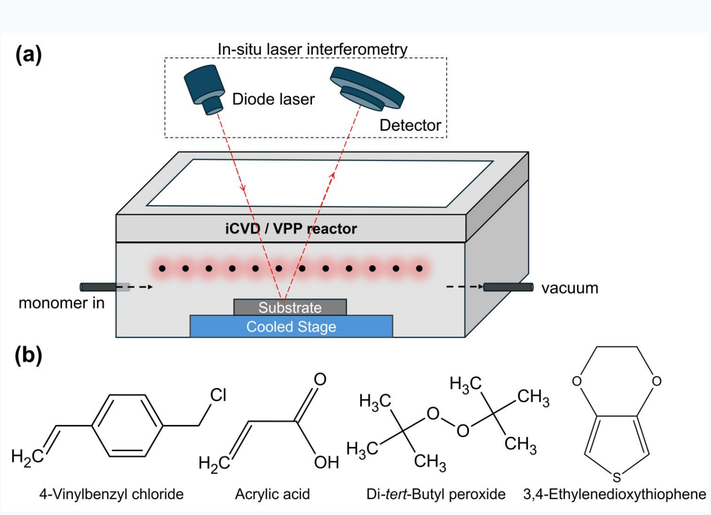

Fig. 1. (a) Schematic representation of vacuum system used for vapor deposition processes, **(b)** Chemicals Used.

P(AA-VBC) thin films were deposited on silicon and glass substrates via initiated chemical vapor deposition (iCVD) in a custom-built vacuum reactor. Acrylic acid (AA) and vinyl benzyl chloride (VBC) monomers were evaporated at controlled temperatures, while tert-butyl peroxide (TBPO) was used as the initiator. Polymerization was thermally initiated using a heated filament under low-pressure conditions. Different AA/VBC flow rate ratios were applied to adjust the copolymer composition, while substrate temperature and reactor pressure were kept constant to ensure uniform film growth.

PEDOT thin films were subsequently synthesized via vapor phase polymerization (VPP) on bare and polymer-coated glass substrates. An oxidant solution ($FeCl_3$ in 2-propanol) was first spin-coated onto the substrates, followed by exposure to EDOT vapor in a vacuum reactor. After polymerization, the films were rinsed with methanol to remove residual oxidant and unreacted species.

The chemical structure of the films was analyzed using FTIR and XPS, while surface morphology was examined by optical microscopy. Film thicknesses were monitored during deposition and measured using reflectometry. Electrical properties were determined by a two-probe method, and conductivity stability was assessed after ultrasonication.

Results and Discussion

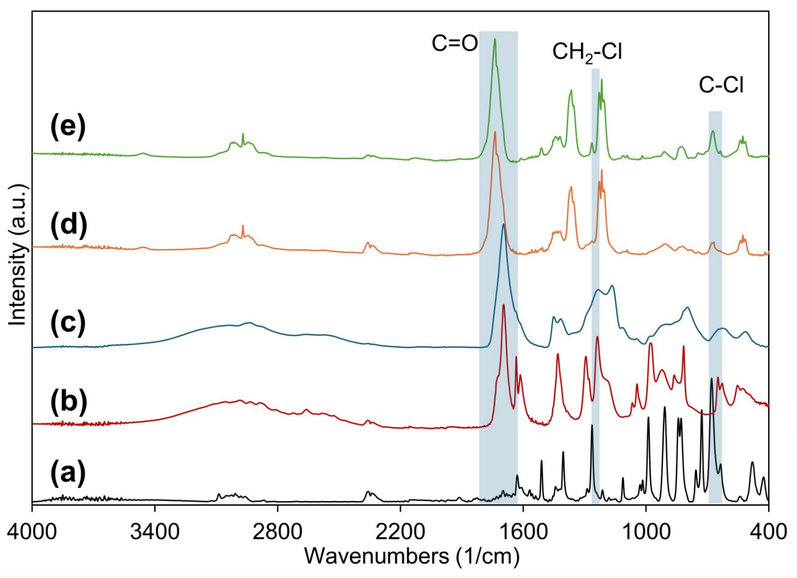

Fig. 2. FTIR spectra of the **(a)** VBC monomer, **(b)** AA monomer, **(c)** PAA homopolymer, **(d)** CP1 and, **(e)** CP2 copolymer.

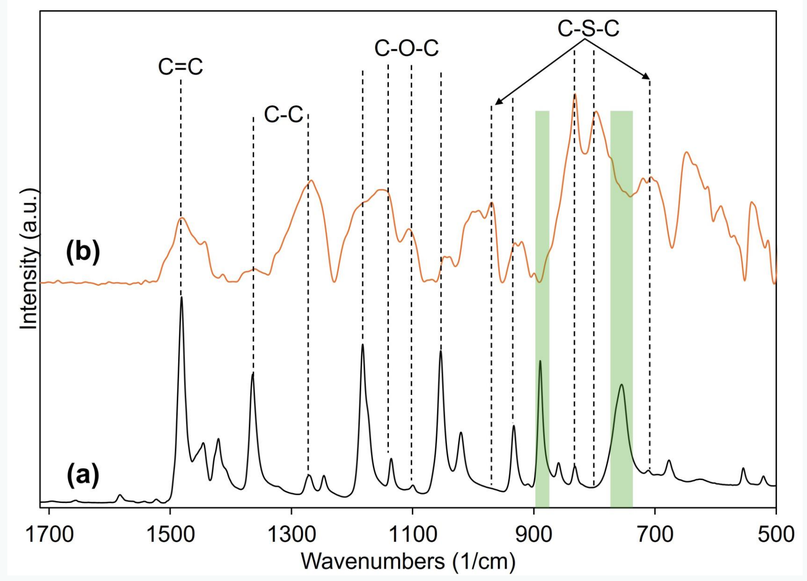

Fig. 3. FTIR spectra of the **(a)** EDOT monomer, and **(b)** PEDOT deposited by VPP.

Different AA/VBC flow rate ratios (2:1 and 1:1; denoted as CP1 and CP2) were used to adjust the composition of the P(AA-VBC) copolymer films, while the total monomer-to-initiator ratio was kept constant. The introduction of VBC significantly increased the deposition rate compared to the PAA homopolymer, indicating enhanced surface reaction kinetics, although VBC alone did not form a homopolymer. Copolymer films with a thickness of ~200 nm were successfully deposited on glass and Si substrates, serving as effective primer layers for subsequent PEDOT coatings.

FTIR spectra of the deposited films (Fig. 2) confirmed successful copolymerization, as evidenced by the disappearance of the C=C vibration peak and the presence of characteristic functional groups of both AA and VBC. Increasing VBC content resulted in higher intensity of C–Cl related peaks, verifying its incorporation into the copolymer structure[3].

For PEDOT films, FTIR analysis (Fig. 3) showed the absence of monomer-specific peaks and the presence of characteristic thiophene ring and ethylenedioxy group vibrations, confirming successful polymerization via VPP. Overall, these findings demonstrate that the combined iCVD–VPP approach enables controlled copolymer formation and the fabrication of uniform, conductive PEDOT thin films with improved structural integrity and performance[4].

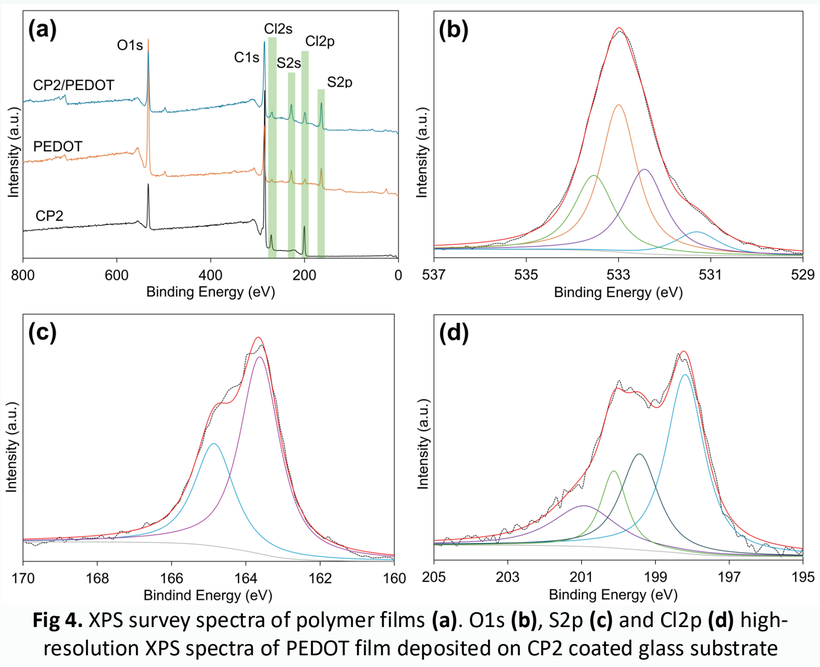

Fig 4. XPS survey spectra of polymer films **(a)**. O1s **(b)**, S2p **(c)** and Cl2p **(d)** high-resolution XPS spectra of PEDOT film deposited on CP2 coated glass substrate

The chemical structure of the films deposited via iCVD and VPP was further analyzed by XPS (Fig. 4). The survey spectra (Fig. 4a) revealed the presence of C, O, and Cl elements in the CP2 copolymer film, while PEDOT-based films additionally exhibited S signals, confirming successful polymer formation. Notably, the Cl (2p) peak intensity was higher for PEDOT deposited on CP2-coated substrates compared to pristine PEDOT, indicating enhanced incorporation of chloride species.

Moreover, the presence of the CP2 interlayer increased the intensity of the S (2p) peak, suggesting improved conjugation length and enhanced doping during oxidative polymerization. High-resolution spectra (Fig. 4b–d) further confirmed the chemical structure: O (1s) peaks were attributed to O–H, C–O–C, C=O, and Fe_2O_3 species, while S (2p) peaks corresponded to the characteristic C–S–C bonds of PEDOT. The Cl (2p) spectra showed contributions from both Cl^- ions in PEDOT and C–Cl bonds originating from the VBC units in the copolymer[5].

Table 1. Atomic percentage values calculated from the XPS survey spectra

Atomic %	CP2	VPP-PEDOT	CP2/PEDOT
S2p	-	7.50	10.95
Cl2p	7.07	1.98	4.51
Fe2p	-	0.59	0.91
C1s	80.57	49.72	64.28
O1s	12.37	40.21	19.34

Quantitative analysis (Table 1) demonstrated that PEDOT films deposited on CP2-coated substrates exhibited higher S and Cl atomic percentages compared to pristine PEDOT, indicating increased doping level and longer conjugation chains. These findings are consistent with FTIR results and confirm that the P(AA-VBC) interlayer enhances the structural and electrical properties of PEDOT films.

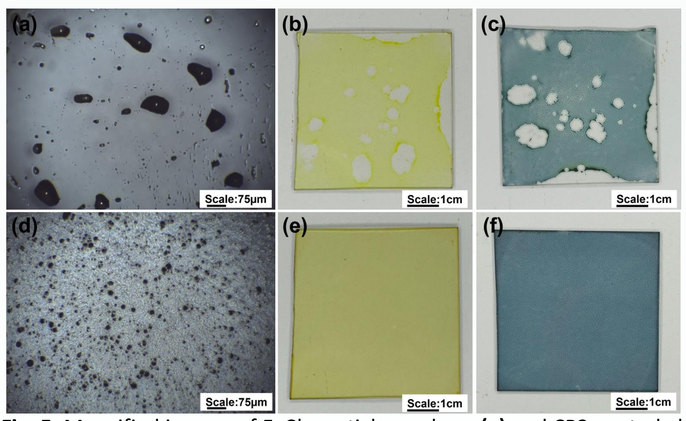

Fig. 5. Magnified images of $FeCl_3$ particles on bare **(a)** and CP2-coated glass **(d)**, together with the photographs of the corresponding $FeCl_3$ and PEDOT films deposited on bare **(b, c)** and CP2-coated **(e, f)** glass.

Optical microscopy images (Fig. 5a–d) show that oxidant coating is more uniform on CP2-coated surfaces, whereas bare glass exhibits large agglomerates (Fig. 5a). This improvement in oxidant distribution led to the formation of more uniform PEDOT films, a finding confirmed by both microscopic images and visual observation (Figure 5e–f). In contrast, PEDOT films deposited on bare glass showed significant non-uniformities and surface defects (Fig. 5b–c).

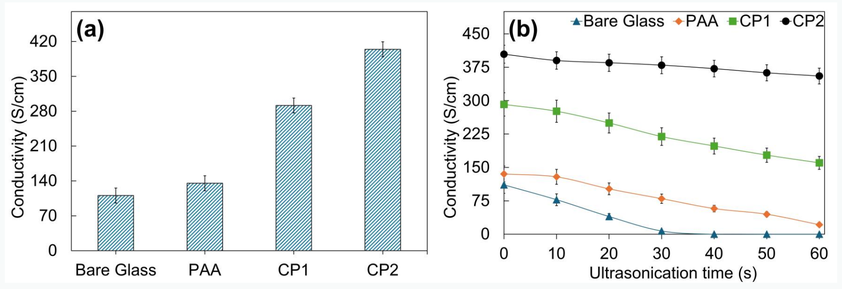

Fig. 6. The electrical conductivity of VPP-PEDOT on bare and polymer-coated glass **(a)**, and the effect of ultrasonication time on conductivity values **(b)**.

PEDOT conductivity increased from 110 S/cm (bare) to 135 (PAA), 292 (CP1), and 404 S/cm (CP2) (Fig. 6a), mainly due to improved film uniformity and Cl^--induced doping from the P(AA-VBC) layer.

Under ultrasonication, conductivity loss was 100% (bare), 84% (PAA), 45% (CP1), and only 12% (CP2) after 60 s (Fig. 6b), showing significantly enhanced stability and adhesion. This improvement is attributed to strong interfacial interactions, likely covalent bonding between PEDOT and the VBC-containing copolymer.

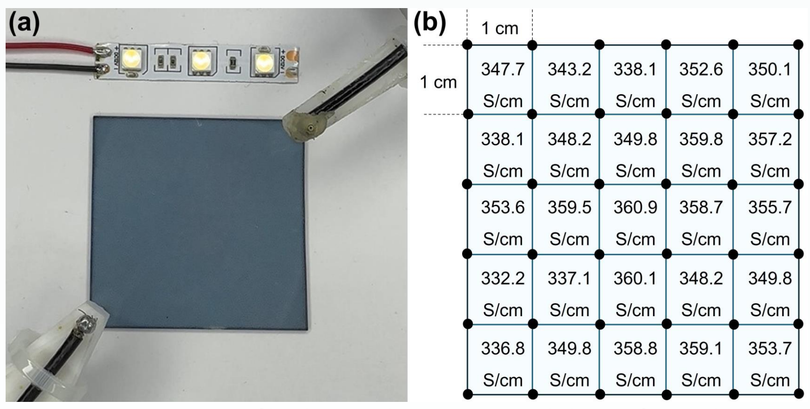

Fig. 7. Large-area PEDOT film deposited on a CP2-coated glass surface with powered LED lights **(a)**, and conductivity values measured at 25 different measurement areas **(b).**

A large-area (5 × 5 cm^2) PEDOT film on CP2-coated glass showed sufficient conductivity to power an LED (Fig. 7a). Conductivity mapping across 25 regions (Fig. 7b) revealed uniformity values of 45.63% (bare), 97.75% (PAA), 96.22% (CP1), and 95.86% (CP2). The high uniformity (>90%) is attributed to the primer layer enabling a more homogeneous oxidant coating.

Conclusion

P(AA-VBC) copolymer layers deposited via iCVD prior to PEDOT coating significantly improved the conductivity, uniformity, and durability of VPP-PEDOT films. AA units enabled uniform oxidant coverage, while VBC-derived Cl^- ions provided in-situ doping, leading to enhanced electrical performance. As a result, PEDOT films exhibited up to ~4× higher conductivity and ~96% uniformity over large areas (5 × 5 cm^2).

These findings demonstrate that the P(AA-VBC) primer layer is an effective strategy to improve the performance of PEDOT coatings and can be extended to various substrates for practical applications.

Acknowledgement

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