

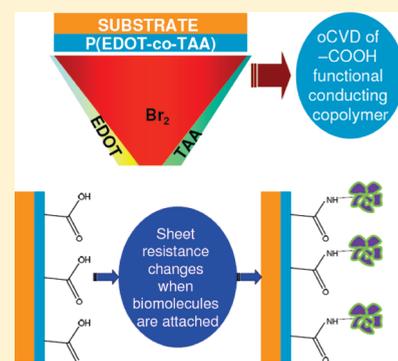
# Single-Step Oxidative Chemical Vapor Deposition of –COOH Functional Conducting Copolymer and Immobilization of Biomolecule for Sensor Application

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**ABSTRACT:** A platform for fabrication of conductive copolymer based resistive biosensor on nonconductive substrate is demonstrated. The –COOH functional groups in the copolymer of thiophene-3-acetic acid (TAA) and 3,4-ethylenedioxythiophene (EDOT) was employed for immobilization of a biomolecule. The sheet resistance of the conductive copolymer thin films significantly increased upon immobilization of the biomolecule. In terms of the fabrication method, application of bromine as an oxidant in this oxidative chemical vapor deposition (oCVD) technique considerably improved the conductivity of the copolymer and also notably reduced the polymer synthesis steps. This low temperature oCVD process shows promises for coating any substrate, for example, paper, plastics, silicon and glass with highly conducting, conformal polymeric films for the future applications in fabricating flexible biosensor devices.

**KEYWORDS:** oxidative chemical vapor deposition, conducting copolymer, EDOT, thiophene-3-acetic acid, resistive biosensor



## INTRODUCTION

In recent years, conducting, semiconducting, light-emitting or -absorbing conjugated polymers have become major areas of research interests because of increasing demand for flexible electronic devices. Various attempts to synthesize and fabricate polymeric conducting materials are being reported. Conjugated polymers have many applications including organic photovoltaic devices,<sup>1,2</sup> light-emitting diodes (LED),<sup>3,4</sup> chemical sensors,<sup>5–7</sup> biosensors,<sup>8,9</sup> biomedical devices,<sup>10</sup> optoelectronic devices,<sup>11</sup> EMI shielding,<sup>12</sup> and in many others, including future devices that have not been dreamt of yet.

The development of conducting polymers, particularly for sensors; both chemical and biosensors, involve immobilization of analyte detecting molecules to the polymer backbone. Achieving this requires a highly conductive polymer with at least one derivatizable functional group. Preparation of conducting polymers or copolymers with different types of functional groups, for example, amine (–NH<sub>2</sub>), carboxylic acid (–COOH), hydroxyl (–OH), azide (–N<sub>3</sub>) groups have been reported.<sup>6,13–16</sup> Among them, thiophene-3-acetic acid (TAA) monomer with –COOH group has gained interest to prepare functionalized conducting polymer or copolymers. The free –COOH groups of TAA have been used to immobilize different small molecules and inorganic nanoparticles as well for bio and chemical sensor applications respectively.<sup>6,14,15,17</sup> The reported conductivities of the pure TAA polymers or copolymers are low, in the range of  $1 \times 10^{-6}$  S/cm. It is well understood that the specificity and concentration of the analyte binding molecules govern the sensitivity of a sensor. However, higher conductivity in the polymer backbone allows the excitons hop around a higher conjugation length and scan more analyte molecules, and thus it results in a higher signal-to-noise

ratio.<sup>18</sup> Therefore, highly conductive functional polymers are necessary to significantly enhance the sensitivity of a sensor.

Fabrication of most of the devices consisting of conducting polymers requires conformal thin film preparation for reproducible and consistent properties. The traditional methods to synthesize and form thin films on a solid support are limited by the insoluble nature of the polymers.<sup>19</sup> Electrochemical synthesis of conductive polymers is well-studied and it has proven its capability to deposit thin polymeric functionalized conductive films of poly-TAA and other polymers and copolymers.<sup>14,15,20</sup> The major constraint of electrochemical technique is that it requires starting with a conductive substrate. However, resistivity-based sensors typically require the conductivity of the conducting polymer to be measured independent of the substrate. Thus, nonconducting substrates, such as plastics or glass are favored for sensor applications, substrates that cannot be coated by the electrochemical method.

Oxidative chemical vapor deposition (oCVD) has been shown to grow uniform and conformal conducting polymers and copolymers on different substrates.<sup>6,17,21–23</sup> The stability and modulation of conducting properties of the polymeric films deposited by oCVD have been reported.<sup>23,24</sup> The previous work to form –COOH functionalized conducting copolymer by oCVD involved copolymerization of TAA with pyrrole<sup>17</sup> and EDOT.<sup>6</sup> In both the cases, iron chloride was employed as the oxidant. The conductivities of the iron chloride deposited copolymers were very low, of the order of  $\sim 0.1$  S/cm. In addition, use of iron chloride as oxidant involved an extra postpolymerization treatment of the

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polymer to remove unreacted iron chloride and other byproducts from the deposited thin films by rinsing it with a polar solvent, usually methanol. The removal of excess iron chloride as contaminant in the polymeric film is an important step because it may interfere with the device fabrication and performance. To avoid these postpolymerization treatments and contamination from residual iron chloride, researchers have employed a more volatile oxidant, bromine, to polymerize EDOT by oCVD.<sup>21</sup> Gaseous bromine acts both as an oxidant and as well as dopant in the polymerization steps.

The previous attempt to make a resistance-based sensor device, as reported by Vaddiraju et al., involved synthesis of –COOH functional conductive copolymer using iron chloride as an oxidant and attachment of metal nanoparticles. Covalently linked metal nanoparticles in the metal–polymer hybrid system improved the conductivity of the system and also provided the platform for sensing volatile organic compounds.<sup>6,17</sup> Once the –COOH groups are used for attaching the nanoparticles, they no more contribute to the sensing property of the system.

In the current work, we report fabrication of a pure polymeric platform for resistive biosensor on nonconducting substrate. For the proof of concept, here we show that the sheet resistance of the conductive polymer film significantly changes when a biomolecule is attached to the system. For this, we describe the synthesis and characterization of conducting copolymeric thin films of EDOT and TAA by oxidative chemical vapor deposition (oCVD) method. In order to make this synthesis single-step and

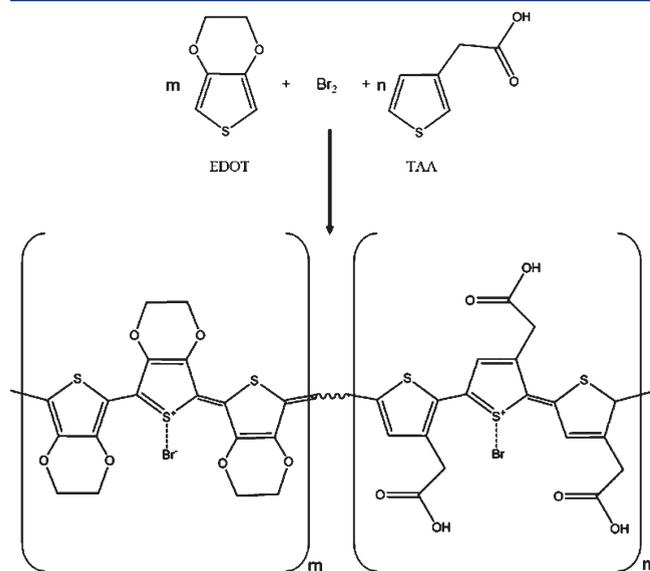
completely dry, bromine vapor was used during the polymerization process as an oxidant in lieu of using iron chloride. Bromine vapor employed during the polymerization also doped the copolymer. Therefore, no further steps were required to achieve the conductivity in the conjugated copolymers. Structures of the monomers and the copolymer are shown in the Figure 1. The copolymer thus deposited using bromine showed conductivity values 2 orders of magnitude higher than the previously reported oCVD grown copolymer of EDOT and TAA using iron chloride. The copolymerization of TAA with EDOT provided a stable and a highly conductive film with a functional group, here –COOH group and finally the free –COOH groups were employed for covalent immobilization of protein for resistance-based sensor applications. Thus, we report the application of oCVD to synthesize –COOH functional highly conducting copolymer thin films in one step with no postdeposition treatments. Moreover, we show that oCVD deposited conductive film can act as a resistance-based biosensor platform by immobilizing a biomolecule on a nonconducting substrate for the first time to our best knowledge. A comparison of the metal–polymer hybrid system by Vaddiraju et al. and the current work is shown in Table 1.

Additionally, deposition of this functional copolymer in a completely dry process makes it advantageous in many applications, for example, in coating solvent-sensitive substrates, preventing damage to underlying layer in multilayered structures. Moreover, use of bromine as an oxidant makes it possible to deposit –COOH functional conducting copolymer in a continuous roll-to-roll process.

## EXPERIMENTAL SECTION

**Materials.** 3,4-Ethylenedioxythiophene (97%), thiophene-3-acetic acid (98%) and bromine (reagent grade) were purchased from Sigma-Aldrich, St. Louis, MO. The monomers and bromine were used as received. Bovine serum albumin (BSA) was obtained from Sigma-Aldrich, St. Louis, MO as well. MES buffer, pH 4.5 (2-(N-morpholino) ethanesulfonic acid) and EDC, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide were purchased from Pierce Biotechnology.

**Oxidative Chemical Vapor Deposition Using Bromine.** EDOT monomer vapor was delivered into the reactor from a side-port. Both the monomer jar and the feed lines were heated to 150 °C to avoid condensation and pressure drop in the reaction chamber. Similarly, TAA monomer vapor was delivered through a separate side-port next to the EDOT line. TAA monomer jar and the feed lines were heated to a higher temperature, ~180 °C, because the volatility of TAA monomer is very low. Pure bromine was delivered in gas phase from another feed through in the same chamber. Bromine jar and the feed lines were not required to heat because of the high volatility of bromine. The substrate temperature was maintained at 80 °C by a temperature controlled stage. The vapor pressure of the feed monomers was 150 mTorr and was controlled by a



**Figure 1.** Steps of the copolymerization of EDOT and TAA by using bromine in oCVD process.

**Table 1.** Comparison of the Current Work with Previously Reported oCVD-Deposited Conducting Copolymer in Lights of Synthesis, Properties, and Applications

	current work	previous work by Vaddiraju et al.
oxidant	Br <sub>2</sub>	FeCl <sub>3</sub>
dopant	Br <sup>−</sup>	Cl <sup>−</sup>
conductivity	~10 S/cm	0.1 S/cm
attachment chemistry	protein molecules are attached	metal nanoparticles were attached
sensing layer	pure polymeric system	metal–polymer hybrid
species detected	biomolecule	volatile organic compounds

butterfly valve. Pure PEDOT and PTAA were also deposited using bromine to compare and correlate the spectroscopic and conductive properties of the copolymer. A schematic diagram of the oCVD process using bromine is shown in Figure 2.

#### Covalent Immobilization of Bovine Serum Albumin (BSA).

A 10 mg/mL solution of BSA was prepared in MES buffer (pH 4.5). Copolymer coated silicon wafer was washed in MES buffer twice and submerged in 3 mL of the same buffer solution in a petridish. One ml of a 30 mg/mL solution of EDC in MES buffer was added to the sample followed by addition of 1 mL of BSA solution and allowed to react for 2 h at room temperature. BSA bound polymeric films on silicon wafers were washed twice with MES buffer, twice with d.i. water and finally with 1% SDS solution to remove any absorbed BSA from the film surface.

**Characterization.** The initially produced oCVD films were analyzed by FTIR spectroscopy using a Nexus 870, Thermo electron Corp.

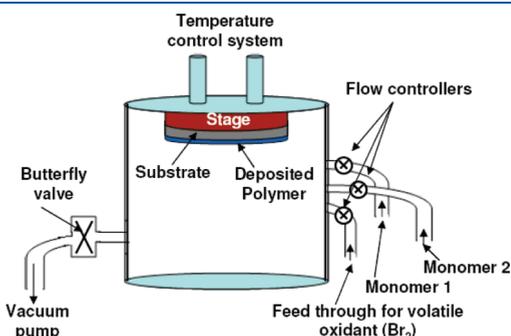


Figure 2. Schematic representation of the oCVD reactor for deposition of conducting polymer and copolymers using bromine as an oxidant.

X-ray Photoelectron Spectroscopy (XPS) data for the polymeric films were done in a Surface Science instrument (SSI, Model: SSX-100) equipped with a monochromator. The minimization of the chi-square (and the root-mean-square parameters) was the criterion for the best fit performance in CasaXPS software. The thickness and conductivity of the films deposited on glass were measured by a KLA Tenchor P-16 surface profilometer and a four-point probe (Model: Keithley SCS-4200), respectively. Scanning electron micrographs were obtained by a JEOL JSM-6060 instrument with acceleration voltage of 5 kV and a spot size of 50. Atomic force microscopy (AFM) was performed in a Veeco Nanoscope V with Dimension 3100 in tapping mode.

## RESULTS AND DISCUSSION

**FTIR Spectroscopy.** Figure 3 shows the FT-IR spectra of oCVD grown PEDOT film (A), PTAA film (B), P(EDOT-co-TAA) film (C) using bromine as oxidant and BSA attached copolymer film (D). Presence of  $1520\text{ cm}^{-1}$  peak in PEDOT in Figure 3A confirms the conjugation in the polymeric system and the peak intensity shows the degree of conjugation.<sup>23</sup> It has been found that the degree of conjugation of bromine deposited PEDOT film is much higher as compared to iron chloride deposited PEDOT film.<sup>21</sup> The peaks at  $1085$  and  $1050\text{ cm}^{-1}$  correspond to the stretching vibrations of bridged C–O in the ethylenedioxy group of EDOT and the band at  $920\text{ cm}^{-1}$  is the ethylenedioxy ring deformation mode.<sup>24,25</sup>

The IR peaks at  $1716\text{ cm}^{-1}$  (C=O),  $\sim 2900\text{ cm}^{-1}$  (CH) and a broad peak  $\sim 3300\text{--}3400\text{ cm}^{-1}$  (–OH) in Figure 3(B) are characteristic peaks for poly-TAA. The intensity of  $\sim 1520\text{ cm}^{-1}$  peak is relatively much lower as compared to PEDOT, which

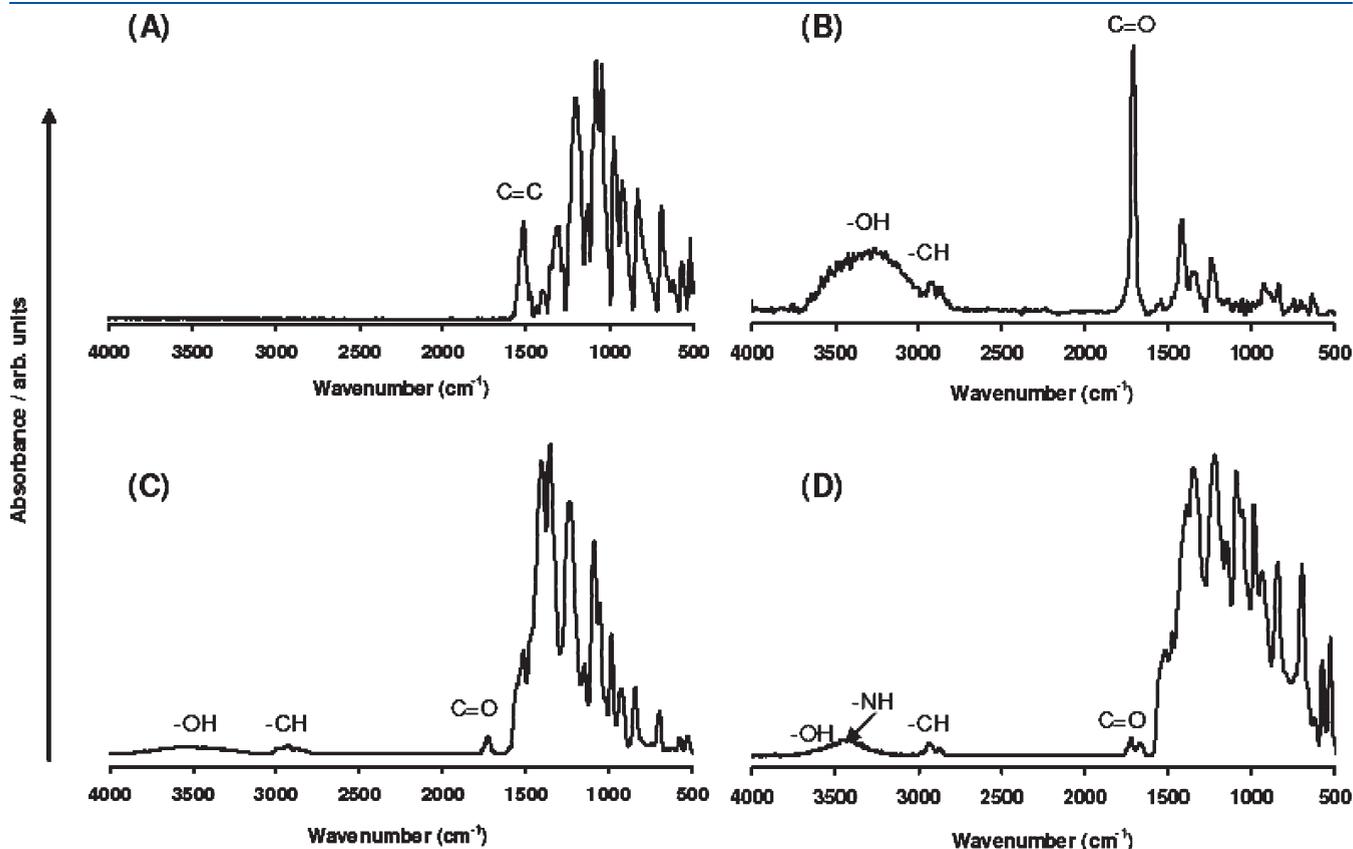


Figure 3. FT-IR spectra of oCVD-grown (A) PEDOT, (B) PTAA, P(EDOT-co-TAA) using (C) bromine as oxidant and (D) BSA-attached copolymer.

indicates less conjugation in the poly-TAA system. Figure 3C shows the FT-IR spectra of oCVD grown P(EDOT-co-TAA) film. The presence of C=O ( $1720\text{ cm}^{-1}$ ) from -COOH group and C-H ( $\sim 2900\text{ cm}^{-1}$ ) from the aliphatic -CH<sub>2</sub> group of TAA along with all the peaks of EDOT, as mentioned above, proved the presence of TAA in the copolymer. Retention of the characteristic peaks of TAA even after rinsing the polymeric films with solvents for TAA and EDOT monomers, such as methanol and THF proved that the monomers reacted with each other and the film was not a simple mixture of the either monomers.

The availability of the -COOH groups in the copolymer for biofunctionalization was verified by covalent attachment of BSA molecules by carbodiimide chemistry. Figure 3D is the FT-IR spectrum of the BSA attached P(EDOT-co-TAA) film. The immobilization of BSA to the -COOH groups were confirmed

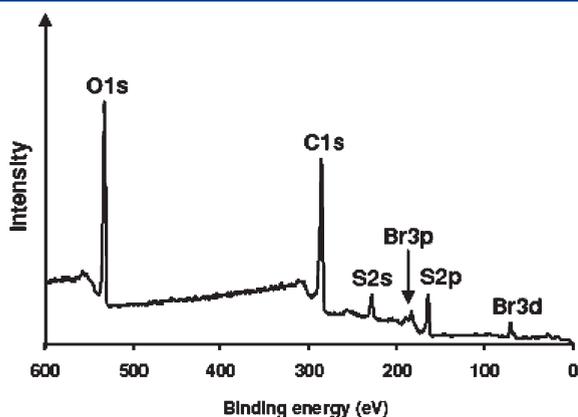


Figure 4. XPS survey scan of P(EDOT-co-TAA) showing the presence of O1s, C1s, S2s, S2p, Br 3p, and Br 3d peaks.

by the appearance of characteristic peaks of the amide bond (CO-NH) at  $1650\text{ cm}^{-1}$  and N-H stretching vibration at  $\sim 3300\text{ cm}^{-1}$ .<sup>26</sup> Almost no change in the C=O peak intensity for -COOH group was observed, because the BSA immobilization consumed only the surface -COOH groups, whereas the FT-IR spectrum is a bulk property and it reflected the free -COOH groups inside the film. It was possible to control this covalent immobilization at the surface because the oCVD grown random copolymer film did not swell, and thus no BSA molecules could enter into the bulk of the film.

**X-ray Photoelectron Spectroscopy.** XPS survey scans (Figure 4) of the copolymer showed the presence of C, O, S as the characteristic elements of the comonomers. Bromine is present as the dopant in the polymeric film. Figure 5 represents the core-electron C1s spectra of bromine deposited PEDOT, PTAA, P(EDOT-co-TAA), and BSA-attached copolymer. The C-C and C-H functional groups, i.e., carbons not bonded to any heteroatoms such as oxygen and sulfur, are centered at 284.6 eV in all of the high resolution C1s spectra in Figure 5. The other peaks in PEDOT (Figure 5A) were C-S (285.2 eV), C-O (286.3 eV), and an asymmetrical peak ( $\sim 290\text{ eV}$ ) due to the contribution from the  $\pi\rightarrow\pi^*$  shakeup transition and positively polarized or charged carbon.<sup>27,28</sup> In addition to all the peaks similar to PEDOT, PTAA has a characteristic peak at 288.6 eV that corresponds to the -COOH group in the polymer as shown in Figure 5B. The C1s spectrum of the copolymer P(EDOT-co-TAA) (Figure 5C) is deconvoluted into the similar number of peaks as in PTAA. The peak at 288.8 eV in the copolymer is due to the presence of -COOH groups from TAA comonomer.<sup>14</sup> The ratio of C-O/COOH peak areas in the PTAA is 1:1 due to the presence of two different oxygen atoms in the TAA monomer. This ratio is found to increase to 1.5 in the copolymer which might be because of the contributions of two C-O groups of

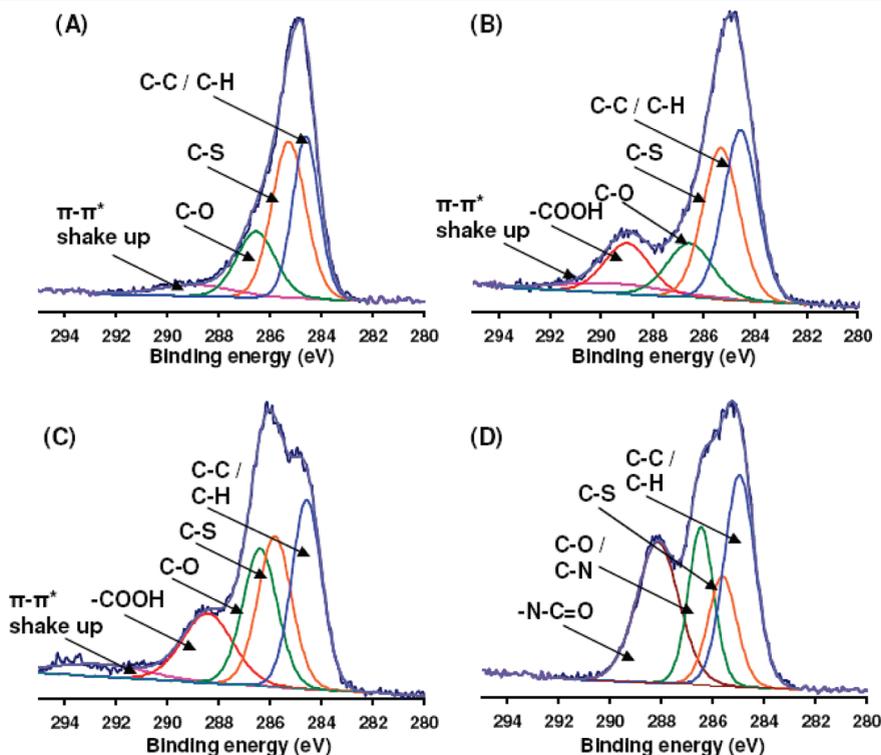


Figure 5. XPS C1s high-resolution spectra of (A) PEDOT, (B) PTAA, (C) P(EDOT-co-TAA), and (D) BSA-attached P(EDOT-co-TAA).

EDOT, one C–O group of TAA monomers and one –C=O group from TAA.

Covalent immobilization of BSA to the –COOH functional groups was also confirmed by the high resolution C1s spectrum as shown in Figure 5D. An  $\sim 1$  eV shift and an increase in the intensity of the highest energy peak are observed in the copolymer after BSA attachment. This is because of conversion of the surface –COOH groups to CONH groups and presence of the abundant amide functional groups (N–C=O) in the protein molecule.<sup>28</sup> The neighboring peak at 286 eV is due to the combination of C–O and C–N bonds present in the copolymer

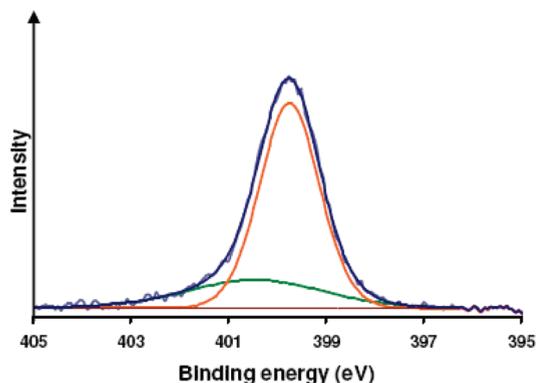


Figure 6. XPS N1s high-resolution spectra of BSA-attached P(EDOT-co-TAA).

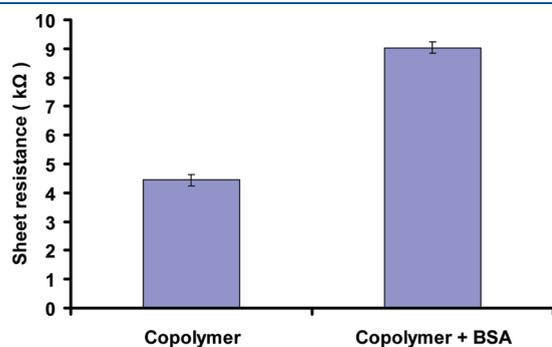


Figure 7. Change in the sheet resistance of the P(EDOT-co-TAA) after BSA immobilization.

and the BSA molecules. A characteristic N1s high resolution spectrum of the copolymer surface after BSA attachment is shown in Figure 6. Presence of characteristic peak at 399.7 eV (–NH) and 400.4 eV (N–C=O) further proved the surface immobilization of BSA to the conducting copolymer.<sup>29</sup> Here to note that no resolvable peaks were detected in the N1s region of the oCVD grown films prior to BSA immobilization (not shown).

**Conductivity Measurements.** Conductivity of oCVD deposited polymers were calculated from the sheet resistance values obtained by 4-point probe measurements and the thicknesses of the polymeric films deposited on glass. Bromine doped PEDOT deposited at 80 °C has a conductivity of 380 S/cm as previously reported.<sup>21</sup> Conductivity of bromine doped PTAA was  $1 \times 10^{-4}$  S/cm, and that of the copolymer, P(EDOT-co-TAA) was 10 S/cm. It is important to note here that only one attempt to copolymerize EDOT and TAA by methods other than oCVD has been reported. Unfortunately, the conductivity of the electrochemically synthesized copolymer was not described.<sup>31</sup> oCVD was previously successfully employed to synthesize P(EDOT-co-TAA) using iron chloride as oxidant.<sup>6</sup> However, the conductivity of the bromine deposited copolymer, as shown in this work, is much higher than iron chloride deposited polymers. Since PTAA itself is very low conducting, copolymerization of TAA with highly conducting EDOT significantly increased the conductivity of the copolymer. The conductivity of this copolymer is found to be almost 2 orders of magnitude higher than that reported for the best composition of the copolymers of pyrrole and TAA grown by oCVD process.<sup>17</sup>

It is important to note here that particularly for resistivity-based biosensor applications of conducting polymers, the sheet resistance of the polymer changes upon immobilizing a biomolecule to the polymer surface. A significant increase in the sheet resistance of the oCVD grown P(EDOT-co-TAA) using bromine was observed when BSA was attached to the copolymer, from  $4.44 \pm 0.2$  kΩ to  $9.03 \pm 0.2$  kΩ as shown in Figure 7. This >200% increase in the sheet resistance arises from the interactions of the electronic environment in the BSA molecules with the excitons in the conjugated polymer backbone. It shows the potential uses of this –COOH functionalized copolymer for fabrication of future resistive biosensor devices.

**Scanning Electron and Atomic Force Microscopies.** Morphological properties of the conducting polymer films are important for their applications, particularly for sensor applications. Since, the

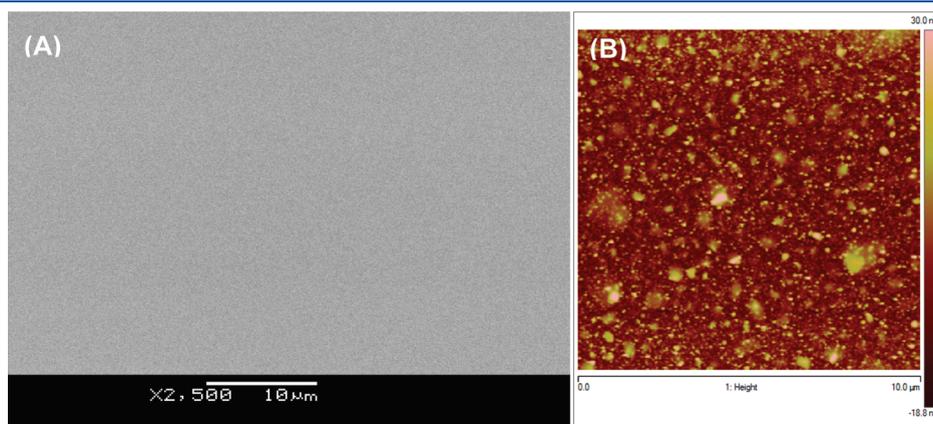


Figure 8. (A) SEM and (B) AFM images of oCVD-deposited poly(EDOT-co-TAA) on silicon wafer.

interaction of the analytes with the immobilized biomolecules is detected by the sensor, a uniform and consistent morphology is sought for the reproducibility of the sensor devices. Previously reported conducting polymers deposited by oCVD process have shown that the morphology depends on the strength of the oxidant.<sup>30</sup> For example, oCVD grown PEDOT deposited by using bromine was more uniform than iron chloride deposited PEDOT.<sup>20</sup> Figure 8 shows the surface morphology of the oCVD deposited film of P(EDOT-co-TAA) by using bromine as oxidant. SEM and AFM images at two different magnifications are shown to verify the uniformity of the copolymeric film surface deposited by oCVD method. The average root-mean-square roughness calculated from the AFM measurements is found to be  $6.6 \pm 0.2$  nm at different spots of the polymer surface.

## CONCLUSION

Attachment of a biomolecule to a conducting copolymer on a nonconducting substrate was successfully demonstrated for the first time to the best knowledge of the authors. In terms of fabrication of resistance-based biosensor, >200% increase in the sheet resistance after BSA immobilization to the copolymer is highly significant and it has a potential future applications in making flexible biosensor. Moreover, as demonstrated in this paper, use of bromine in oCVD provides an exceptionally simple route to deposit conducting PTAA and P(EDOT-co-TAA). Application of bromine as an oxidant in gas phase thus removes the solvent treatment step in oCVD deposition of conducting films using iron chloride. Using bromine as an oxidant improved the conductivity of the copolymer to  $\sim 10$  S/cm and made the deposition process completely dry. Furthermore, it is applicable to any solid substrate, not just electrically conductive ones. Successful synthesis of P(EDOT-co-TAA) by this technique provided free -COOH groups on the conducting polymer backbone and thus a convenient route to covalent attachment of target molecules via simple one-step carbodiimide reaction.

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