



# 3D-polythiophene foam on a TiO<sub>2</sub> nanotube array as a substrate for photogenerated Pt nanoparticles as an advanced catalyst for the oxygen reduction reaction

Rajashekar Badam<sup>1,2</sup> · Raman Vedarajan<sup>1</sup> · Noriyoshi Matsumi<sup>1</sup>

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## Abstract

The development of novel substrates that possess high durability, strong anchoring to catalytic metal nanoparticles and low charge transfer resistance as well as that can replace conventional carbon is of great importance. To improve the durability and reduce the cost of various energy devices, new methodologies are necessary. Therefore, we report the preparation of a macroporous hybrid material containing polythiophene electropolymerized onto TiO<sub>2</sub> nanotubes (TNT). The prepared foam-like hybrid material exhibited a very low charge transfer resistance and was further modified with novel and green photogenerated Pt nanoparticles. The material exhibited very strong metal substrate interactions, resulting in high durability during the oxygen reduction reaction (ORR). This study proposes a novel macroporous organic/inorganic hybrid material for use as an alternative material to replace conventional carbon substrates in ORR catalysts.

## Introduction

The development of very active, stable, and economically viable electrocatalysts is the main bottleneck in realizing efficient alternate energy technologies, such as fuel cells and Li-air batteries. Although Pt nanoparticles (nps) are extremely active, the high cost involved in their preparation as well as the instability of the catalysts are two principle reasons for the continued interest in this area of research. Various factors, such as electrooxidation of carbon substrate, dissolution, Ostwald ripening and aggregation [1] of nps, can inhibit their commercialization. Therefore, an electrochemically stable catalyst support with tailorable morphology is needed. The multifaceted functionalities of

conducting polymers endow this material with the potential for becoming a substrate for electrocatalysts [2].

Conducting polymers have gained much attention and been extensively investigated since their discovery in 1970s. The ease of their synthetic procedures allowed for tailoring of their electrical conductivity as well as the chemical and mechanical stabilities. Owing to improvement in these intrinsic properties of the conducting polymers, they have been employed in a broad range of applications, including charge storage devices, electrochromic devices, modified electrodes, anticorrosion coating, and molecular transistors [3–6]. Among the many conducting polymers that have been studied, polythiophene (PTh) and its derivatives are of great interest. Their high electrochemical stability in stringent oxidizing or reducing electrolytes makes PTh a good choice for various electrochemical applications. PTh has evolved as a promising catalyst support material for various electrochemical applications. Schrebler et al. [7] modified PTh by decorating Pt and Pt/Pb metal nanoparticles for the electrooxidation of formic acid. In this study, the PTh support offered high electrochemical stability, and the composite containing PTh was an effective alternate supporting material compared to conventional carbon supports. Yassar et al. [8] electrodeposited Pd onto PTh and studied the oxygen reduction reaction (ORR) characteristics by varying the particle size of the Pd nps. Several other researchers have also reported that PTh is a

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✉ Noriyoshi Matsumi  
matsumi@jaist.ac.jp

<sup>1</sup> School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

<sup>2</sup> Surface Science Laboratory, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya, Aichi 458-8511, Japan

very stable host polymer matrix [9, 10]. PTh, which possesses attractive features, such as good mechanical, chemical, and electrochemical stability especially in the presence of strong acids or bases, can be recommended for application as a catalyst support material in the ORR.

From a synthetic point of view, electropolymerization of thiophene is one of the most frequently used methods for the preparation of porous conducting polymers [11]. Rationally, electrochemical polymerization of thiophene delivers several advantages compared to conventional chemical polymerization techniques. Electrochemical polymerization allows for facile tailoring of the thickness of the polymer by controlling the number of deposited layers and provides a degree of control over the pore wall dimensions and morphology [12–14]. Second, the polymerization rate can be precisely controlled to achieve highly compact polymers [12], and very good contact with the conducting substrates can be achieved, which is essential for the fabrication of electrical devices [15]. In addition, electropolymerization provides selectivity in choosing the site of polymerization. Kowalski et al. [16] reported the site-specific deposition of polypyrrole into the gaps in the tube walls rather than inside the tubes of a TiO<sub>2</sub> nanotube array.

In general, the conducting polymers can be fabricated into shape-specific macroporous structures by employing templates with specific chosen dimensions. Ordered macroporous or tubular polymeric nanostructures can be fabricated by employing colloidal crystals [12, 17, 18], anodic aluminum oxide [19–22], and TiO<sub>2</sub> nanotube (TNT) [23] arrays. In recent years, TNT has attracted much interest in the research community due to the ability to control geometric and functional properties with simple anodization preparation methods. Recent studies have reported the preparation and investigation of polymer/TNT nanoarchitectures with unique geometries [16, 24, 25].

Many studies on the electropolymerization of conducting polymers have reported the use of a surfactant to enhance the wettability of the electrode, control the diffusion of the monomer, and vary the geometrical arrangements by serving as soft template [26–29]. In a recent study, the mechanism and role of the surfactant structure on the morphology of electropolymerized PTh were elucidated. The long dodecyl aliphatic chain in the surfactant electrostatically interacts with the monomer, leading to controlled diffusion of the monomer to the electrode and alignment of the polymer chains [30]. Ionic liquids have attracted much interest in the past decade, especially their use in synthesis. The physical and chemical properties of ionic liquids depend on their tunable structure. Therefore, these properties can be tailored. Moreover, their negligible volatility, good electrochemical stability, and flame resistance make them suitable for use in electropolymerization methods [31, 32]. Therefore, we propose that the dodecyl aliphatic chain-

linked imidazolium-based ionic liquid is a suitable surfactant and vector agent for electropolymerization.

In our recent study [33], TiO<sub>2</sub> exhibited promising photoreduction of a metal salt to form metal nps on a conducting substrate, and the resulting catalyst exhibited high ORR catalytic efficiency with a very low Pt content. In view of these results, a three-dimensionally ordered PTh foam was electropolymerized using a TNT array as the template and an imidazolium-based ionic liquid as the vector to enable directional diffusion of the monomer to the electrode. Pt nps were decorated onto this conducting polymer/TNT array hybrid material using a novel photoreduction method [33]. This report highlights the preparation of novel three-dimensional (3D) PTh foam electropolymerized using an ionic liquid as a vector onto a TNT template and Pt decoration using a novel green photoreduction method.

## Experimental procedures

### Materials

The Ti and Pt metal electrodes were purchased from The Nilaco Corporation, Japan. Ammonium fluoride, dodecyl bromide and 1-methyl imidazole were obtained from Wako Chemicals, Japan. Ethylene glycol and perchloric acid were purchased from Kanto Chemicals, Japan, and thiophene was obtained from TCI, Japan. All the chemicals were used as obtained without any purification.

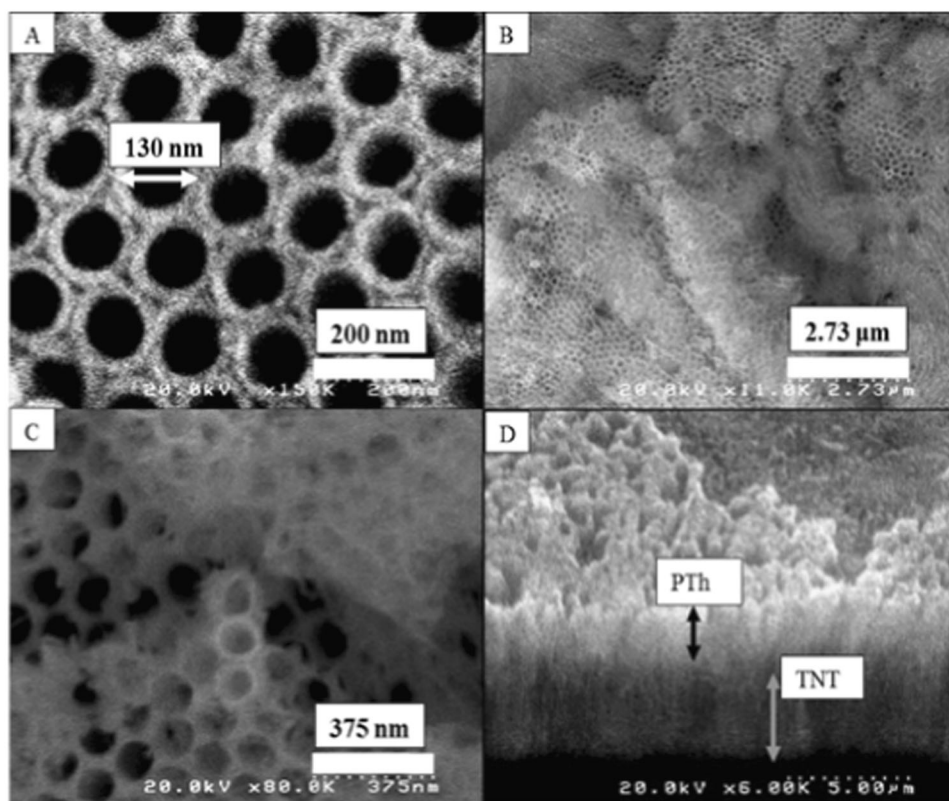
### Preparation of TNT array

The TiO<sub>2</sub> nanotube array was prepared using a standard anodization method. The Ti chip that was used for the anodization process was hand polished with 600 grit sand paper, and the oxide layer was removed by washing the chip in a hydrofluoric acid: nitric acid: water (1:3:16 volume ratio) mixture. This chip was degreased by washing the Ti chip in methanol. The cleaned titanium metal strip was anodized at a DC voltage of 50 V with constant ultrasonication for 2.5 h in an aqueous ethylene glycol solution containing 0.5 wt.% NH<sub>4</sub>F using a platinum strip as the cathode. After the TNT was grown on the Ti strip, it was washed with methanol and sintered at 300 °C to prepare the TiO<sub>2</sub> as a single anatase phase and eliminate all the organic contaminants.

### Preparation of 1-methyl- 3-dodecyl imidazolium bromide (DMImBr)

DMImBr was prepared according to a previously reported procedure [34, 35]. Briefly, methylimidazole was treated

**Fig. 1** SEM micrographs of TNT showing the tube dimensions, a polythiophene foam grown on TNT b and c and cross-sectional view of PTh-TNT hybrid d



with dodecylbromide (1:1.2 molar equivalents, respectively) in acetonitrile at 80 °C. The solution was refluxed under a nitrogen atmosphere for 48 h. The volatile material was removed, and the resulting material was recrystallized using an ethyl acetate and n-hexane mixture to yield a soft crystalline material. DMImBr was successfully prepared with a yield of 85%. The structural determination of DMImBr was performed using <sup>1</sup>H-NMR spectroscopy on a Bruker BioSpin Avance III 400 MHz instrument.

### Electropolymerization of thiophene using TNT as a template

The electropolymerization was conducted using a conventional three-electrode system. TNT was used as the working electrode, Ag/Ag<sup>+</sup> electrode was employed as a reference, and a platinum chip was used as the counter electrode. DMImBr was used as a vector rather than the typical surfactant. Thiophene (0.1 M) was electropolymerized from a solution consisting of 0.1 M 1-methyl-3-dodecylimidazolium bromide in acetonitrile with 0.1 M aq HClO<sub>4</sub>. The potential was cycled between -2 V and 0 V vs. Ag/Ag<sup>+</sup> at a scan rate of 50 mV/s. This cycling was carried out 50 times. After the polymerization, the TNT chip was washed with acetonitrile to remove any contamination from the reaction mixture and vacuum dried at room temperature to afford PTh/TNT. To understand the morphological

dependence of the polymer on the use of DMImBr and TNT, control experiments were carried out using a similar electropolymerization technique, either 1) in the absence of DMImBr or 2) Ti instead of TNT (see ESI for details).

### Photoreduction of Pt onto PTh-TNT hybrid

The Pt nanoparticles were generated using a metal salt reduction procedure similar to that used in our recent study [33]. Here, the PTh-TNT hybrid on the Ti chip was immersed in 100 mL of deionized water containing 800 μL of a 0.045 M aq. chloroplatinic acid solution and irradiated by a simulated solar light with an intensity of ~1 sun (100 mW cm<sup>-2</sup>) for 5 h under constant stirring of the metal salt solution at room temperature. After the photoreduction process, the chip with PTh-TNT was cleaned with water and dried under vacuum at room temperature for overnight. The resulting Pt-PTh-TNT was further characterized to study its physical and electrochemical characteristics.

Elemental characterization of TNT and Pt-PTh-TNT was performed using an X-ray photoelectron spectroscopy (XPS) technique using an S-probe 2803 instrument. The morphology of the as-prepared TNT and PTh-TNT was studied using scanning electron microscope (SEM) (Hitachi S-4500). The transmission electron microscopy (TEM) measurements were performed to gain insight into the growth of PTh on TNT as well as the particle size and

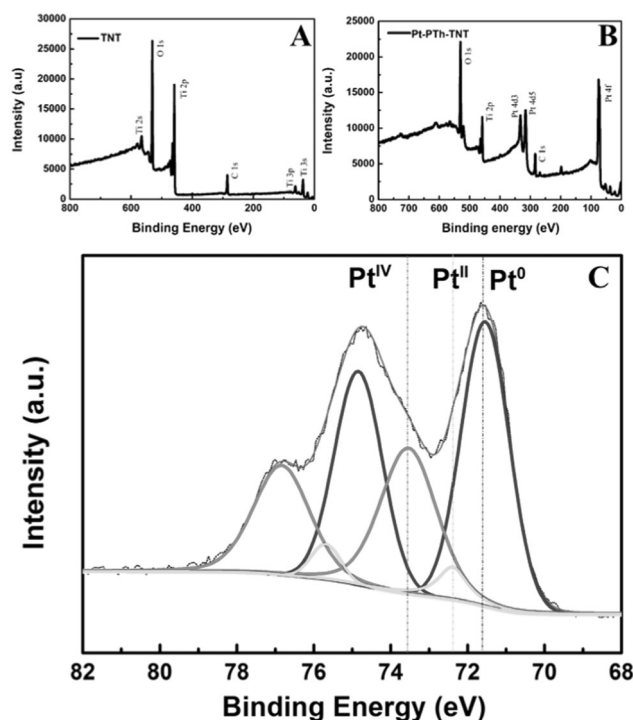
distribution of the Pt nps. The change in the charge transfer resistance before and after polymerization was studied using electrochemical impedance spectroscopy (Biologic VSP).

In addition, the electrocatalytic activity of Pt-PTh-TNT was studied based on its ORR behavior using cyclic voltammetry (CV). The ORR studies were performed using a conventional three-electrode system, where the electrocatalyst on the TNT chip was used as the working electrode (area of 2.3 cm<sup>2</sup>), a platinum chip was used as the counter electrode, and 3 M Ag/AgCl was used as reference electrode (the potentials were later normalized to a normalized hydrogen electrode) at 25 °C in 0.1 M aq. HClO<sub>4</sub>. CV was performed by sweeping the voltage between 0.02 and 1.67 V vs. normal hydrogen electrode (NHE) at a sweep rate of 20 mV s<sup>-1</sup> in an oxygen-saturated 0.1 M HClO<sub>4</sub> solution at 25 °C.

## Results and discussion

The SEM micrographs of TNT and PTh-TNT are shown in Fig. 1. Figure 1a shows the tubular morphology of TNT with a 130 nm diameter. Individual tubular demarcation was observed. Figure 1b–d show the micrographs of the PTh-TNT composite. The difference in the contrast between Fig. 1a, b confirmed the growth of the polymer. The individual tubular nature was not observed in Fig. 1b, c but a foam-like morphology was observed. For TNT and PTh foam, the tube diameter was in the same range (i.e., 130 nm), which indicates that TNT acted as a template. The tube diameter of TNT determines the pore size of the PTh foam. The cross-section shown in Fig. 1d illustrates the demarcation of PTh and the TNT substrate. The thickness of the PTh foam was approximately 2.01 μm, and the length of TNT was determined to be 3.23 μm in Fig. 1d.

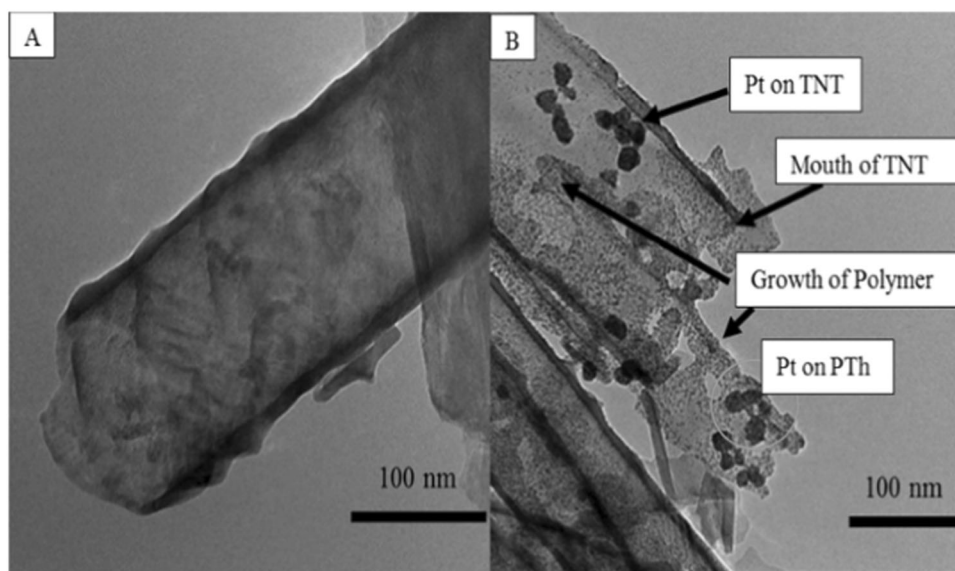
The micrographs were also studied to determine the morphological changes in the absence of DMImBr from the reaction mixture and TNT as the template (Fig. ESI1; for micrographs) in two separate experiments. Based on the SEM micrographs, the foam-like morphology was not observed in either case (Fig. ESI2; Ti instead of TNT). Therefore, the TNT template and the presence of the ionic liquid as a vector were essential for the formation of the PTh foam. A surfactant with a similar aliphatic chain exhibited electrostatic interactions with the monomer. The surfactant with a long chain length tends to move slower than the monomer towards the working electrode. These types of interactions can result in alignment of the polymer chain on an electrode [30]. Therefore, the change in the morphology was due to controlled directional diffusion of the monomer. It is important to note that the ionic liquid acted as a conventional surfactant. Next, Pt nps were photogenerated using a green synthetic method as previously mentioned.



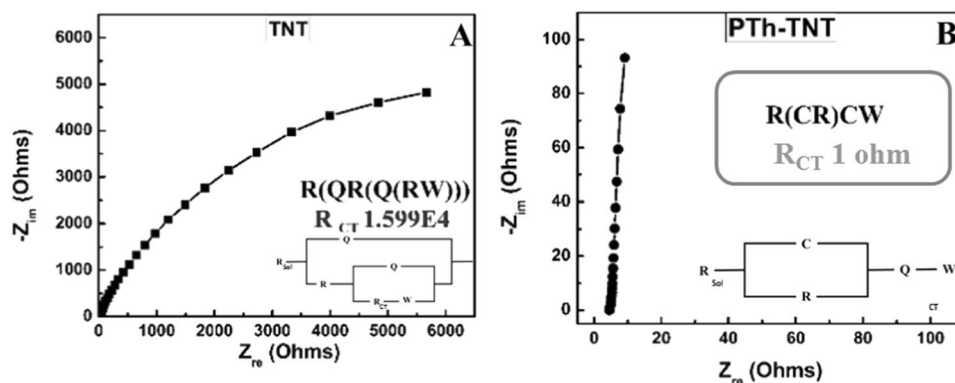
**Fig. 2** XPS survey spectra of TNT **a** and Pt-PTh-TNT **b**. Deconvolution of high-resolution Pt 4f peak of Pt-PTh-TNT showing the Pt<sup>0</sup> and Pt<sup>IV</sup> valence states **c** (Color figure online)

The elemental composition of TNT and Pt-PTh-TNT was studied using XPS. Figure 2 shows the survey spectra of TNT and Pt-PTh-TNT. The survey spectrum of TNT (Fig. 2a) contained typical peaks for Ti 3s, Ti 2p, C 1s, O 1s, and Ti 2s at their respective binding energies. The survey spectrum of Pt-PTh-TNT contained peaks corresponding to Pt 4f, 4d<sup>5/2</sup>, and 4d<sup>3/2</sup> and an increased C 1s peak intensity along with the typical TNT peaks. Based on the XPS data, the calculated amount of photodeposited Pt (Fig. 2b) was determined to be ~10 wt%. Further XPS analysis was employed to determine the various valence states of Pt in the prepared hybrid material. The high-resolution core level spectra of the Pt 4f peak provided valuable information on the various oxidation states of Pt. In addition, these spectra provided insight into the strong metal–substrate interaction (SMSI) based on analysis of the binding energies of Pt<sup>0</sup>. Figure 2c shows the high-resolution Pt 4f peak of Pt-PTh-TNT, consisting of 3 peaks at 71.6, 72.3, and 73.5 eV that correspond to Pt<sup>0</sup>, Pt<sup>II</sup>, and Pt<sup>IV</sup>, with Pt<sup>0</sup> being the predominant state. The positive shift in the binding energy of Pt<sup>0</sup> compared to that in a similar ORR catalyst with conventional carbon was determined to be approximately 0.4 and 0.2 eV higher than Pt–graphite–TiO<sub>2</sub> and Pt–CNT–TiO<sub>2</sub>, respectively [33]. In both Pt–graphite–TiO<sub>2</sub> and Pt–CNT–TiO<sub>2</sub>, Pt was decorated using the same photoreduction method, and the only difference was that graphite and CNT were replaced with PTh. In comparison to

**Fig. 3** TEM micrographs of TNT **a** and Pt-PTh-TNT **b** (Color figure online)



**Fig. 4** Nyquist plots of TNT **a**, PTh-TNT **b** and their RCT values given in the inset along with the equivalent circuit (Color figure online)

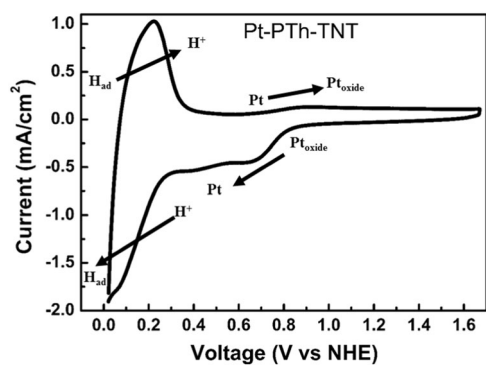


the recently reported Pt/BC (Pt decorated on graphite-rich boron carbide) [36] that exhibits very high activity and cyclability, Pt-PTh-TNT exhibited a similar binding energy of 71.6 eV. In these two reports, the high ORR activity and durability of Pt were due to its SMSI. Similarly, the current XPS results indicate successful photodecoration of Pt on PTh and provided insight into the strong adherence and electronic interaction between Pt and PTh, leading to high ORR activity and durability.

In addition, the TEM analysis provided insight into the detailed morphological aspects of TNT as well as the growth pattern of PTh on TNT and Pt np size and distribution on PTh-TNT. Figure 3a shows the TEM micrograph of bare TNT (prior to electropolymerization), in which the tube diameter was determined to be  $\sim 130$  nm. TNT had smooth edges without any particle-like material in the as-prepared TNT. However, the Pt-PTh-TNT (Fig. 3b) exhibited growth of a thin polymer along the length of TNT and higher than the TNT with an open pore mouth. These results are consistent with the results obtained from the

SEM micrographs. Pt nps of the same size ( $\sim 10$  nm) were observed on TNT as well as PTh, indicating that the novel green photogeneration of metal nps is possible for any conducting substrate coated onto TNT. Therefore, interfacial photoinduced charge transfer to the preadsorbed conducting polymer can efficiently control the rapid recombination of the photogenerated charges of TNT. This spill-over of electrons from the TNT onto the highly conducting polymer matrix tends to travel over the conducting matrix until it finds a suitable reducing species (in this case, chloroplatinic acid) to form Pt nanoparticles.

The interaction with the electrolyte helps to reduce the interface boundaries, which affects the overall catalytic performance of the electrode [37, 38]. Therefore, interfacial studies are important for validating the catalytic performance of the electrode using electrochemical impedance studies. In addition, our previous study on Pt-FAB [37] provided insight into the correlation between the ORR catalytic activity and the absorptive properties of catalysts. Therefore, to evaluate the charge transfer resistance of



**Fig. 5** : Cyclic voltammogram of Pt-PTh-TNT in a  $N_2$ -saturated 0.1 M  $HClO_4$  solution at a scan rate of  $20\text{ mV s}^{-1}$

PTh-TNT, electrochemical impedance spectroscopy (EIS) studies were carried out.

The EIS studies for the PTh-TNT catalyst substrate were performed using a conventional three-electrode system using Pt wire as the counter electrode and a Ag/AgCl reference electrode in a nitrogen-saturated 0.1 M  $HClO_4$  solution at the open-circuit potential. These results were compared to that for the bare TNT chip prior to electropolymerization. The EIS results are shown in Fig. 4 as Nyquist plots for TNT and PTh-TNT. These results were fit to an equivalent circuit (inset in Fig. 4a, b), which revealed a substantial change in the  $R_{CT}$  value of TNT ( $1.599E4$  ohms) and PTh-TNT (1 ohms). According to one of our recent studies, Pt-FAB (Pt/C) exhibited very high ORR activity compared to that of commercial Pt/C (20% Pt-Vulcan XC-72) due to its low  $R_{CT}$  of 22.8 ohms, which is nearly 20 times less than that of commercial Pt/C (i.e., 378.8 ohms) [37]. Therefore, with a  $1\ \Omega$   $R_{CT}$  value, a catalyst made using this conducting substrate would be extremely active.

The SEM and TEM results indicate that during the electropolymerization of thiophene, the ionic liquid (DMImBr) in the reaction mixture modulates the morphology. The presence of the ionic liquid was necessary for enabling electropolymerization over the TNT template. For a substrate to act as a template, suitable wetting agents, such as surfactants, must be used. In the current strategy, the environmentally benign ionic liquid acted as the wetting agent as well as a vector to afford PTh foam. In addition, this substrate was successfully decorated using a novel green reduction process that leads to the formation of Pt nanoparticles with very good adherence to the substrate. The obtained Pt nanoparticles exhibited enhanced SMSI. SMSI can drastically alter the electronic states or the Fermi level of the Pt nanoparticles, which influences the ORR activity as well as the durability of the materials. Finally, the impedance studies revealed extremely low charge transfer resistance values, which make PTh-TNT an ideal substrate for replacing carbon substrates in ORR catalysis.

The CV studies were carried out to evaluate the ORR behavior of the prepared sample. The cyclic voltammogram shown in Fig. 5 exhibit a typical Pt-carbon-type profile with Pt fingerprint peaks for hydrogen adsorption ( $H_{ad}$ ) and desorption peaks as well as oxygen evolution and reduction peaks. The hydrogen desorption peak was used to study the electrochemical active surface area (ECSA) of the studied materials (details are given in ESI). The ECSA of the materials was determined to be approximately  $60.6\text{ m}^2/\text{g}$ . The ECSA of the material was determined to be nearly twice that of Pt-Vulcan XC-72 (commercial sample from Sigma Aldrich,  $30.6\text{ m}^2/\text{g}$ ). The oxidation of carbon, which typically occurs at approximately 1.2–1.6 V, was negligible, indicating that the polymer is stable in the electrooxidation region of carbon. Electrooxidation of carbon in the stringent ORR conditions is the main reason for the instability of the catalyst. The current catalyst, which exhibits much less electrooxidation of the substrate, will enable results in a highly stable catalyst. The important characteristics of the catalyst include (a) SMSI, which enables strong anchoring of the nps to the substrate that inhibits dissolution, Ostwald ripening, and aggregation of nps; (b) a high ECSA, which activates the catalyst particles; (c) much smaller charge transfer resistance, which enables a high catalytic activity; and (d) negligible electrooxidation of the substrate until 1.6 V vs. NHE, leading to a highly durable catalyst system. The material was very active in the ORR due to its very low charge transfer resistance and macroporous structure.

## Conclusion

A novel 3D PTh foam was prepared by electropolymerization using DMIMBr (ionic liquid) as the wetting agent and vector as well as TNT as the tubular template. Photoactive TNT in the presence of an electronically conductive polymer hybrid allowed for a green photoreduction process that was similar to that of our previous study. XPS analysis of the photogenerated Pt nps indicated very high SMSI characteristics, resulting in high durability during the ORR. Finally, EIS studies revealed that this hybrid exhibited much less charge transfer resistance and a high ORR activity was also observed (with an ECSA twice that of its commercial counterpart).

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no competing interests.

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