Short Communication

1,4-Phenylenediamine based covalent triazine framework as an electro catalyst

Sivalingam Gopi, Murugavel Kathiresan[*]

Electro Organic Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630003, Tamil Nadu, India

A B S T R A C T

Herein, we report the synthesis of 1,4-phenylenediamine based covalent triazine framework (CTF) by reacting cyanuric chloride with 1,4-phenylenediamine under basic conditions. The as synthesized polymeric framework was characterized by solid state ^{13}C-CPMAS and ^{15}N NMR, FT-IR, Raman, SEM, TEM, UV-Vis and N_2 sorption isotherm. Commercially available glassy carbon electrode is modified with the as synthesized polymer and its electro catalytic activity towards the reduction of nitrobenzene and oxygen evolution reaction (OER) is studied. Performance of the bare CTF material resembles the performance of commercial GC (glassy carbon) electrode.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Covalent organic frameworks (COF) are covalently linked special class of micro porous organic polymers constructed from organic/organic-inorganic compounds [1]. The nature of porosity changes according to its linker functionality and core unit [2,3]. Classical synthetic chemistry allows precise control over their architecture and pore size by changing the geometry of the linking monomer units suited for different applications [4]. Nevertheless, classical synthetic chemistry lacks in accomplishing precise control over the porosity and crystallinity of these materials [5]. Because of the void and functional groups present in their structure, they act as a cage wherein the pores were used for capturing or storing the guest molecules guided through non-covalent interactions [6]. Their unusual properties such as light weight, highly ordered porous structure and conductivity makes them find applications in the fields of gas adsorption/storage [7,8], sensing [9], catalysis [10] and in energy storage devices [11]. Although wide range of COF's constructed from different functionalities were reported till date, most of the report deals with their gas storage applications with few studies focusing on other applications [12]. Because of their porous nature, they possess large surface area and were exploited as catalysts in organic synthesis [13] and in electrochemical applications [14].

Covalent Triazine Framework (CTF) constitute a family of COF possessing a central/branching triazine units in their network structure [15]. Being first reported by Thomas and co-workers via trimerization of aromatic nitriles in molten $ZnCl_2$, they exhibit high nitrogen content and their rigid aromatic network renders very high thermal and chemical stability delivering them an excellent catalytic activity [16]. Apart from conventional trimerization reaction using nitriles, CTF's can also be synthesized from melamine, cyanuric chloride and substituted triazines [15]. CTF based networks and its composites were widely exploited for multifarious applications such as gas storage [17,18], catalysis [19—21], energy storage [22—24], etc. [25—28] Guskos et al. reported an EPR (electron paramagnetic resonance) study on covalent layered network by condensing cyanuric chloride with 1,4-phenylenediamine [29]. Probably this was the only report available on phenylenediamine based covalent triazine framework system, however in their report, authors did not focus on the extensive characterization of their network [29]. Also the reaction time was too low (1 h) to form an extended network. In this communication, we report the synthesis of new **PD-CTF** (1,4-Phenylenediamine-Covalent Triazine Framework) constructed from 1,4-phenylene-diamine and cyanuric chloride under basic conditions [30]. The as prepared materials were characterized by ^{13}C-CPMAS and ^{15}N NMR, FT-IR, Raman, SEM, TEM, UV-Vis, fluorescence and N_2 sorption isotherm. Further, its electro catalytic application towards the reduction of nitrobenzene and oxygen evolution reaction has been evaluated.

* Corresponding author.
 E-mail addresses: kathiresan@cecri.res.in, kathiresan.murugavel@gmail.com (M. Kathiresan).

2. Experimental section

Cyanuric chloride,1,4-phenylenediamine and anhydrous K_2CO_3 were purchased from Sigma Aldrich and were used as such. Solvents used were of AR grade and were used as such.

2.1. Characterization techniques

^{13}C and ^{15}N CP-MAS measurements were carried out on a Bruker Avance 400 spectrometer operating at 100.6 MHz for ^{13}C and 40.53 MHz for ^{15}N using a Bruker 4 mm double resonance probehead at a spinning rate of 10 kHz. The morphological structures of the prepared fabrics were captured using Scanning Electron Microscope (SEM) of TESCAN, VEGA 3 with Bruker Detecter, Zeck Republic. FTIR analysis was carried out in BRUKER - TENSOR 27 (Optik GmbH) using RT DLaTGS (Varian) Detector. Transmission Electron Microscope Tecnai 20 G2 (FEI make), Netherlands, was used to analyze the surface morphology. Raman spectra were recorded using a high resolution Renishaw Raman microscope employing a He-Ne laser of 18 mW at 633 nm.

Cyclic voltammetry was carried on an autolab PGSTAT 302N workstation at room temperature in a standard three-electrode cell. The working electrode was a glassy carbon disk (area = 0.07 cm^2, Sinsil) and the counter electrode was a Pt wire. The reference electrode was Ag/AgCl/KCl (3 M) electrode. For the reduction of nitrobenzene, we used 0.1 M phosphate buffer (pH 7.4) as the electrolyte and the CV was recorded at a scan rate of 50 mV/s. Since nitrobenzene is insoluble in buffer solution, we added 2 mL of methanol to the buffer solution (2 mL methanol + 3 mL buffer). The solution was degassed with Nitrogen for about 15 min prior to each measurement. Oxygen evolution reaction was carried out at room temperature using 1 M KOH as the electrolyte at a scan rate of 10 mV/s.

2.2. Electrode modification

5 mg of **PD-CTF** sample was added to 600 μL methanol, 400 μL water and 5 μL nafion solution (nafion concentration 0.1%) and the suspension was sonicated for 2 h to obtain a uniform suspension. GC (0.07 cm^2) electrode was with 10 μL suspension by drop cast method and the modified electrode was dried at room temperature overnight.

2.3. Synthesis of **PD-CTF**

The synthesis follows a reported procedure as shown in Scheme 1 [30]. 1,4-phenylenediamine (2.9 g, mmol) was dissolved in 100 mL anhydrous 1,4-dioxane. To this solution, anhydrous K_2CO_3 was added and the solution was cooled down to 15 °C under nitrogen atmosphere. To this cooled solution, cyanuric chloride (5 g, 27 mmol) dissolved in 100 mL 1,4-dioxane was added drop wise over 2 h. Then the solution was warmed to room temperature over 1 h and the solution was refluxed at 90 °C for 72 h. Finally, the pale brown precipitate obtained was filtered, washed several times with water, methanol and acetone. The resulting precipitate was dried under vacuum to yield the title compound **PD-CTF** as a brown powder (Yield: 90%).

3. Results and discussion

3.1. Characterization

PD-CTF was synthesized by following a reported procedure [30]. The polymeric network yield was around 90% suggesting the successful conversion of monomer which is further confirmed by solid state ^{13}C NMR and ^{15}N NMR. ^{13}C CP-MAS solid state NMR (Fig. 1a) of the **PD-CTF** sample showed three peaks at 166.6, 136.6, and 123.1 ppm ascribed to the three sp^2 carbons of the CTF. We did not observe any residual cyanuric chloride or 1,4-phenylene diamine peaks. This confirms the complete polymerisation of cyanuric chloride and 1,4-phenylenediamine [31]. Besides ^{15}N solid state NMR (Fig. 1b) of the framework confirmed that there were two different nitrogen atoms present in the sample, peak at −120.3 ppm is ascribed to the triazine 'N' and the peak at −116.2 ppm is attributed to the 'NH' of the 1,4-phenylenediamine.

The successful formation of the CTF was further confirmed by FT-IR analysis (Fig. 2a) and Raman spectroscopy (Fig. 2b). FT-IR confirms the formation of network structure. In Fig. 2a, peaks at 1554 cm^{-1}, 1380 cm^{-1}, and 1233 cm^{-1}, indicates the presence of triazine and benzene structure. N-H stretch at 3357 cm^{-1} and 3282 cm^{-1} indicates the presence of two different 'N' atoms present in the sample. The absence of C-Cl stretching vibration at 850 cm^{-1} confirms the absence of cyanuric chloride. C-C and C-N stretching and bending vibrations are observed in the finger print region.

Ordered/disordered structures of carbon can be easily probed by Raman spectroscopy as it fingerprints a material structure based on the changes in vibrational mode [32]. Liu et al.'s study on the DCB and TCT (1,4-dicyano) and TCT (2,4,6-tricyano-1,3,5-triazine) based CTF polymers is the only available Raman report on triazine based CTF's [32]. **PD-CTF** polymer showed strong G line and D line at 1558 cm^{-1} and 1385 cm^{-1} respectively, and overtone bands were observed at 2675 cm^{-1} and 3051 cm^{-1} (Fig. 2b). Characteristic Raman bands for carbon are

i) 1580 cm^{-1} − G line assigned for E_{2g} photon of sp^2 carbon atoms
ii) 1350 cm^{-1} − D line, assigned for breathing mode of κ-point photons of A_{1g} symmetry

and overtones of D line and G lines (2D line) were observed at 2700 cm^{-1} and 3250 cm^{-1} respectively [32]. Our results matches well with Liu et al.'s report [32]. These results possibly indicate that **PD-CTF** polymer have 2D layer like structure resembling graphene nanosheets.

The porous nature of the sample was determined by measuring N_2 adsorption-desorption analysis at 77 K (Fig. S1). The isotherm resembles type III isotherm with a BET surface area of 34 m^2/g. The pore dimension indicates that the sample contains a large fraction of mesopores and a smaller fraction of macropores and the details are given in the supporting information (Fig. S1). The PXRD measurement of **PD-CTF** showed that the material is amorphous in nature with a 2θ value of 25° (Fig. S2). The broad diffraction peak at 25-27° is ascribed to the stacking of layered conjugated aromatic systems [28,33]. Further, we analyzed the morphology of **PD-CTF** via SEM and TEM analysis (Fig. 3a−d). SEM showed a filamentous network structure (Fig. 3a and b). Both the SEM and TEM images of **PD-CTF** revealed that the typical porous network is formed and clearly showed the existence of small mesopores along with macropores consistent with the BET results.

The thermal stability of the sample was analyzed by thermo gravimetric analysis under Nitrogen atmosphere. TGA profile suggests that the sample is thermally stable upto 250 °C after which there is a gradual weight loss until 450 °C (16% weight loss) which could be attributed to the loss of water or solvent molecules from the sample. (Fig. S3). Another gradual weight loss was observed until 600° C (35% weight loss) attributed to the decomposition of organic moiety. Further, photo physical properties of the polymeric sample was studied by UV-Vis and Fluorescence spectroscopy (Figs. S4 and S5). UV-Vis of the solid sample showed maximum absorption at 260−340 nm and this was assigned to π-π* transitions of the **PD-CTF** [28] after which there was a steady decline in