Indian Journal of Chemistry
Vol. 56A, August 2017, pp. 821-825

Notes

Single walled carbon nanotubes decorated vanadyl phthalocyanine composite for electrochemical oxygen reduction in fuel cells

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Received 8 May 2017; revised and accepted 20 July 2017

Vanadyl phthalocyanine (VOPc) has been immobilized on single walled carbon nanotubes by the adsorption process and characterized using UV-vis spectroscopy, infrared spectroscopy and X-ray diffraction techniques. Electrochemical characterization of VOPc immobilized SWCNTs (SWCNTs-VOPc) has been done by coating an aqueous colloid of SWCNTs-VOPc on glassy carbon electrode (represented as GC/SWCNTs-VOPc). GC/SWCNTs-VOPc exhibits a pair of peaks at –265 and –97 mV (at 20 mV s^{-1} in 0.1 M H_2SO_4) due to the characteristic redox process, $V^{IV/III}$ of VOPc. Further, electrocatalytic reduction of oxygen is analysed using GC/SWCNTs-VOPc electrode by cyclic voltammetry. GC/SWCNTs-VOPc electrode efficiently reduces oxygen in 0.1 M H_2SO_4 with a low onset potential of 0.16 V. Also, GC/SWCNTs-VOPc exhibits significant storage stability, retaining 91% of its original catalytic reduction current after 10 days storage at room temperature in air and dry conditions.

Keywords: Electrochemistry, Electrocatalysis, Oxygen reduction, Fuel cells, Cyclic voltammetry, Single walled carbon nanotubes, Vanadyl phthalocyanine

For the past few decades, metal phthalocyanines (MPcs) have attracted considerable interest of researchers, particularly in the context of the development of new functional materials for various applications.[1] MPcs can be prepared through easy synthetic routes, and they exhibit stable electrochemical characteristics.[2] MPcs also demonstrate potential applications in electrophotography, photovoltaics and in the development of microelectronic devices.[1a] Vanadyl phthalocyanine (VOPc) has been extensively investigated in recent times to formulate metallophthalocyanine based catalysts.[1a, 3] Due to its excellent thermal stability, stable electrochemical characteristics and efficient catalytic properties,[4] VOPc is selected in this work for the development of carbon nanotubes based composite for electrocatalytic reduction of oxygen.

The exceptional electrical and mechanical characteristics of single walled carbon nanotubes (SWCNTs) have received wide spread attention in recent years in several areas of research including electrocatalysis and fuel cell applications.[5] It is a unique nano-sized material, which finds various applications due to their exceptional properties.[6] Due to the subtle electronic properties of SWCNTs, it is used as electrode materials for electrochemical sensing and fuel cell applications.[5a, 5b, 7] Taking into account the extraordinary features of SWCNTs and VOPc, the combination of SWCNTs and VOPc is expected to present promising electrochemical applications.

Nanomaterials based electrocatalysts have been extensively explored for fuel cell applications over the past decades because of their high electrocatalytic activity towards the reduction of oxygen.[8] The breakdown of molecular oxygen (O_2) into water (H_2O) with electron and proton transfer reactions is generally termed as oxygen reduction reaction (ORR).[5d, 9] ORR is the most important cathodic process in fuel cells.[10] ORRs have generated interest due to their wide application in the energy converting systems like fuel cells and air batteries.[5d, 11] However, due to the high dissociation energy of oxygen, ORRs follow slow kinetics, which decreases their practical applicability.[8b, 10] Despite active research for years, the reaction mechanism of ORR is not known clearly (i.e. without any ambiguities) which is a serious drawback in the improvement of high performance energy conversion systems.[10, 12] Hence, the study of high performance ORR kinetics is important for the development of efficient and cost effective catalysts for these systems. The use of electrocatalyst can decrease the activation energy and lower the overpotential of the reduction process.[8b, 12,13] Presently, Pt-based catalysts are used as cathode materials in fuel cells, however the high cost of Pt based catalysts drives the search of alternate catalysts for ORR. In the present work, VOPc modified SWCNTs composite (SWCNTs-VOPc) coated glassy carbon (GC) electrode has been prepared, and its applicability for the ORR is explored.

Experimental

Single walled carbon nanotubes (SWCNTs) were supplied by Reinste Nano Ventures Private

Limited, India. N,N′-dimethylformamide (DMF) was purchased from SD Fine, India. Vanadyl phthalocyanine (VOPc) was procured from Sigma-Aldrich. All other chemicals were of analytical grade and used as received. Triply distilled water was used for all the experimental needs.

All the electrochemical experiments were carried out with CHI-660C electrochemical workstation (CH Instruments, USA). Glassy carbon (GC) electrode (diameter of 3 mm), Pt wire, and Ag/AgCl electrode were used as working, counter, and reference electrodes, respectively. To remove the dissolved oxygen, the electrochemical cell solution was purged with nitrogen for 20–25 min. For ultrasonication, Toshcon ultrasonic cleaner (Toshniwal process instruments Pvt. Ltd. India) was used. UV-vis spectra were recorded with 0.1% suspension of the respective material in dichloromethane on a UV-vis scanning spectrophotometer (2802 PC UNICO, USA). FT-IR spectra were recorded on a Perkin Elmer spectrophotometer using KBr pellets. Powder XRD data were collected on Advance D8 diffractometer (Bruker, Germany).

SWCNTs-VOPc composite was prepared by the following procedure. Typically, 50 mg of SWCNT was taken in 20 mL DMF and ultrasonicated for 30 min. Further, VOPc (0.05 m*M*, 0.0289 g) was added to the SWCNTs-DMF suspension. This reaction mixture was ultrasonicated for a further 30 min. Then this mixture was stirred for 24 h at room temperature. After 24 h the product, SWCNTs-VOPc composite, was filtered, washed with DMF, and kept under vacuum dry condition for 48 h.

For the preparation of the modified electrode, typically, 1.0% colloid of SWCNTs-VOPc was prepared in DMF and ultrasonicated for 30 min. GC electrodes were cleaned with micropolish alumina powder on Buhler felt-pad, washed with triply distilled water, ultrasonicated for 5 min and air dried. About 5.0 µL suspension of 1.0% SWCNTs-VOPc was applied on the GC electrode surface using drop casting method and after drying, 5.0 µL of polystyrene (0.1% in chloroform) was coated. Then this modified electrode (GC/SWCNTs-VOPc) was kept for 4 h at room temperature. A similar procedure was followed for the preparation of the GC/SWCNTs. In addition, GC/VOPc electrode was also prepared for comparison purpose by drop casting a solution of VOPc (10.0 µL, 1.0 m*M* in DMF) on GC electrode followed by another coating of polystyrene (5.0 µL, 0.1% in chloroform). The electrodes were allowed to dry in air for 4 h at room temperature condition.

Results and discussion

UV-vis spectra of MPcs generally show strong absorption band in the visible region at about 670 nm and weak band at about 340 nm representing Q band and B or Soret bands, respectively. Both bands (Q and B) occurs due to π→π* transition.[4b, 14] The complex formation of phthalocyanine with metal generates a slight blue shift in the Q band. It occurs because of the decrease in the electron density due to the presence of metal. It has been observed that the high electronegative metal ions will create more blue shift.[4b, 15] Figure 1 (curve 1) shows the UV-vis spectrum of VOPc, representing the two characteristic bands at 344 and 680 nm for B and Q bands, respectively.[14-15] Generally UV-vis spectrum of SWCNTs[7, 8a] shows no specific absorption bands (Fig. 1 (curve 2)) however, the composite SWCNTs-VOPc exhibits bands similar to VOPc (Fig. 1 (curve 3)). The existence of similar Q and B bands in the UV-vis spectrum of SWCNTs-VOPc indicates that no (or negligible) change occurs in the VOPc after its adsorption onto SWCNTs. It also indicates that the VOPc remains in the active form in the composite and viable for other studies/applications.

The molecular structure and characterization of VOPc are well documented in literature.[1a, 16] The FT-IR spectra of the VOPc, SWCNTs and SWCNTs-

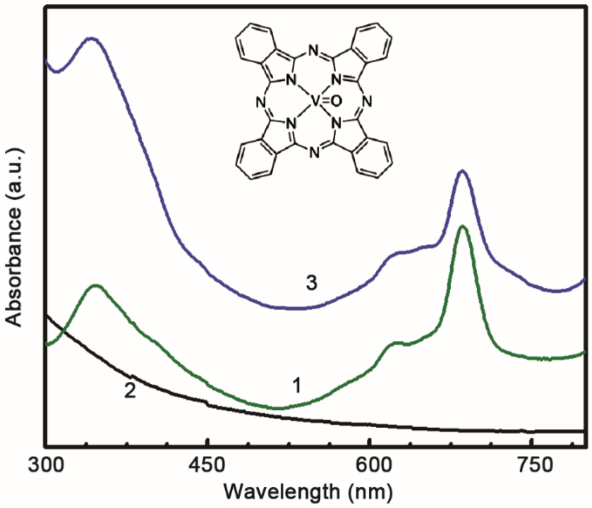

Fig. 1 — UV-vis spectra of VOPc in dichloromethane (1), SWCNTs (0.1% in dichloromethane) (2), and, SWCNTs-VOPc (0.1% in dichloromethane) composite (3). [Inset represents the molecular structure of VOPc].

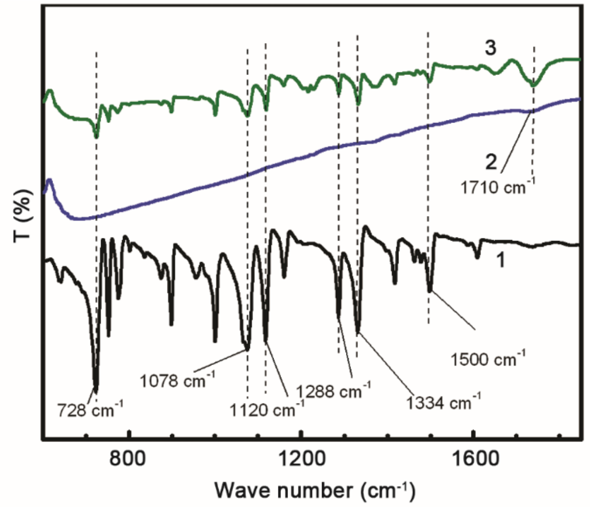

Fig. 2 — FT-IR spectra of VOPc (1), SWCNTs (2), and, SWCNTs-VOPc composite (3).

VOPc are shown in Fig. 2. The bands in the characteristic fingerprint region of VOPc can be assigned as follows: band at 728 cm^{-1} for out-of-plane deformation, 1078 cm^{-1} for $C_{aromatic}$-H vibrations (in plane deformation), 1120 cm^{-1} for C-H vibrations (in plane deformation), 1288 cm^{-1} for symmetric vibrations of isoindole fragments, 1334 cm^{-1} for –C=C–N= (nitrogen mesoatoms and pyrrole fragments) and 1500 cm^{-1} for vibrations of nitrogen (bridging) mesoatoms (Fig. 2 (curve 1)).[1a, 16] The band around 1710 cm^{-1} corresponds to carboxylic or carboxylate group of SWCNTs.[5b] The characteristics fingerprint bands of VOPc are observed at similar positions in the SWCNTs-VOPc composite also, indicating the intact integration of the VOPc onto SWCNTs (Fig. 2 (curve 3))[6, 17] which is well supported by the UV-vis study also.

Powder XRD patterns of VOPc, SWCNTs and SWCNTs-VOPc are shown in Fig. 3. The characteristic peak of VOPc observed at 7.5° (2θ) corresponds to the (010) plane. Possibly the next order of weak reflection is observed at 16° (2θ).[1a, 16a] Additional diffraction peaks are observed at 22.4°, 25.4°, 28.5° for VOPc. SWCNTs shows its characteristic diffraction signals at 26.7° and 43.0° due to (002) and (101) planes respectively, which arise due to the planes of hexagonal graphite structures.[5c, 18] The characteristic peaks of VOPc and SWCNTs are present in the powder XRD of the SWCNTs-VOPc indicating the presence of VOPc in the SWCNTs-VOPc composite. On the basis of the above studies (UV-vis spectra, FT-IR and powder XRD), it may be concluded that the VOPc is integrated intact onto the SWCNTs. The SWCNTs-VOPc composite has characteristic features of both materials, indicating that the integration process does not alter the structural and conformational behaviour of the VOPc during composite preparation.

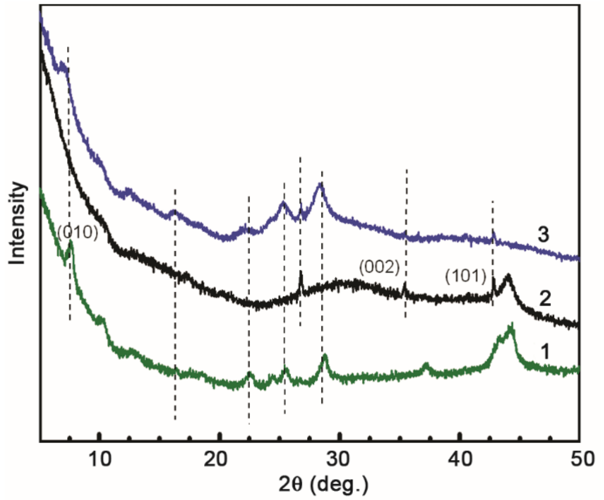

Fig. 3 — Powder XRD patterns of VOPc (1), SWCNTs (2), and, SWCNTs-VOPc composite (3).

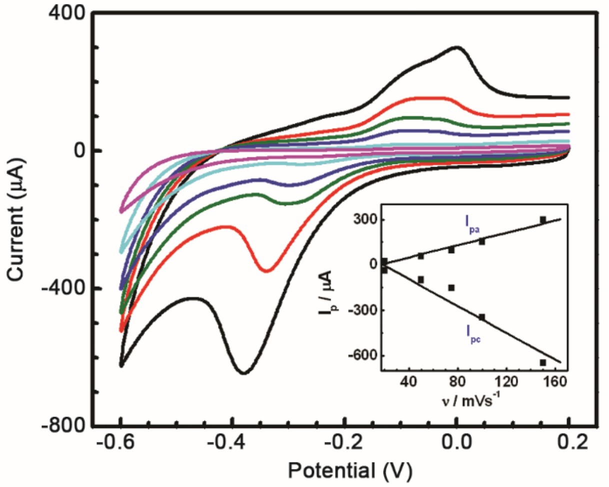

Fig. 4 — CV response at GC/SWCNTs-VOPc in 0.1 *M* H_2SO_4 with varying scan rates from 10-150 mV s^{-1}. [Inset represents the plot of anodic and cathodic peak currents with scan rates].

Cyclic voltammetry (CV) analysis of GC/SWCNTs-VOPc electrode was performed in 0.1 *M* H_2SO_4 with varying scan rates from 10–150 mV s^{-1} (Fig. 4). It is observed that the anodic and cathodic peak currents increase with increase in scan rates. This increase in peak current with scan rates represents a linear relationship (inset of Fig. 4) which corresponds to surface confined process.[19] A pair of peaks is observed in the CV response of the

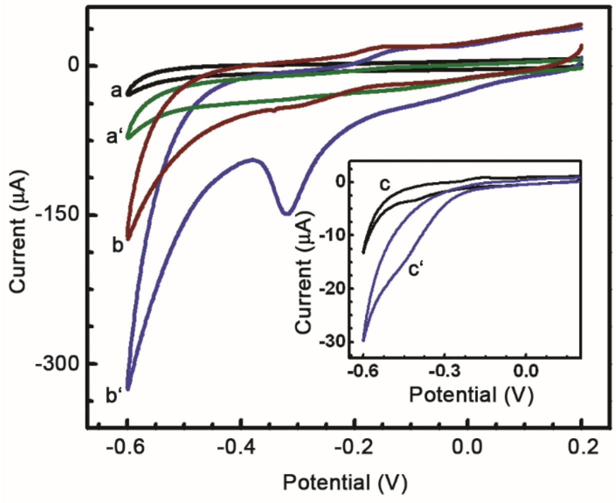

Fig. 5 — CV response of GC/SWCNTs (a, a′), GC/SWCNTs-VOPc (b, b′) in nitrogen (a, b) or oxygen (a′, b′) saturated conditions in 0.1 *M* H_2SO_4 at the scan rate of 20 mV s^{-1}. [Inset represents the CV curves of GC/VOPc under similar experimental conditions in nitrogen (c) or oxygen (c′) saturated solution].

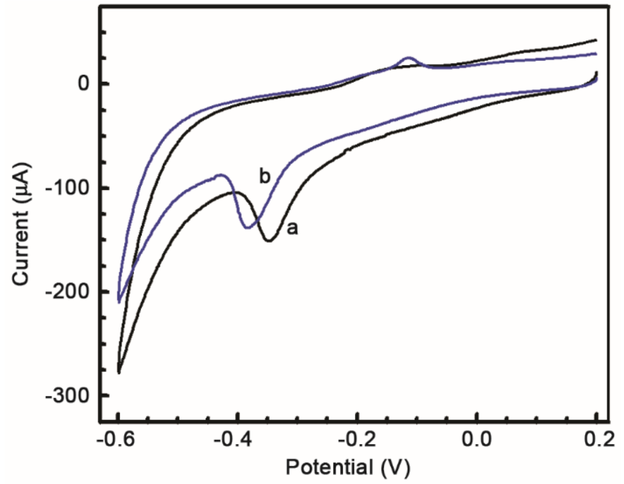

Fig. 6 — CV response of GC/SWCNTs-VOPc in oxygen saturated condition on (a) day 1, and, (b) on day 11 in 0.1 *M* H_2SO_4 under the same experimental conditions.

GC/SWCNTs-VOPc electrode at –97 and –265 mV for oxidation and reduction, respectively (at a scan rate of 20 mV s^{-1}). The reductive peak at –265 mV corresponds to $V^{IV} \rightarrow V^{III}$ and oxidation peak at –97 mV occurs due to $V^{III} \rightarrow V^{IV}$.[20] However, the I_{pa}/I_{pc} ratio was found to be 0.54, which is close to quasi reversible process.[19]

ORR at GC/SWCNTs-VOPc was performed in 0.1 *M* H_2SO_4 using CV technique with the scan rate of 20 mV s^{-1} (Fig. 5). It is observed that GC/SWCNT does not show any characteristics response in CV in N_2 saturated condition. However, GC/SWCNTs-VOPc in nitrogen saturated condition shows the redox signal as mentioned above.

In oxygen saturated condition, a small increase in reduction current at 30.2 µA is observed with GC/SWCNTs. However, GC/SWCNTs-VOPc shows high increase in reduction current (151.1 µA). The onset potential observed for ORR at GC/SWCNTs and GC/SWCNTs-VOPc are 0.11 and 0.16 V, respectively. This decrease in onset potential towards more positive potential and increase in high reduction current signifies excellent ORR at GC/SWCNTs-VOPc.[10, 13, 21] To verify the role of SWCNTs in the ORR activity, we performed the ORR at GC/VOPc under similar condition (inset of Fig. 5). GC/VOPc shows a very small increase in reduction current (14.9 µA) in oxygen saturated condition with an onset potential of –0.21 V, which is low as compared to GC/SWCNTs and GC/SWCNTs-VOPc. It signifies that the presence of SWCNTs enhances the oxygen reduction efficiency at GC/SWCNTs-VOPc electrode. It is observed that though GC/VOPc shows electrocatalytic reduction of oxygen, it is not prominent. GC/SWCNTs-VOPc shows high efficiency for ORR. On the basis of onset potential and high current, GC/SWCNTs-VOPc has high efficiency for oxygen reduction over the GC/SWCNTs and GC/VOPc electrodes.

The stability of GC/SWCNTs-VOPc has been analysed by storing the electrode in air and room temperature conditions for 10 days. Figure 6 represents CV response of GC/SWCNTs-VOPc in oxygen saturated condition for the first day and on the 11th day in 0.1 *M* H_2SO_4 at a scan rate of 20 mV s^{-1}. It is observed that the current signal for ORR at GCSWCNTs-VOPc does not alter very much even after storing the electrode for 10 days. GC/SWCNTs-VOPc retains the ORR current by 91% after storing it for 10 days with a small shift in peak potential (0.032 V) indicating the high storage stability of the modified electrode.

In the present study, a composite using SWCNTs and VOPc has been prepared by a simple equilibration/adsorption process and immobilized on the GC electrode. Spectroscopic characterizations by UV-vis, XRD and FT-IR show the nature of VOPc adsorbed on SWCNTS. The SWCNTs-VOPc coated GC electrode exhibits high efficient ORR in 0.1 *M* H_2SO_4 compared to SWCNTs coated electrode and VOPc film on GC electrode. In addition, SWCNTs-VOPc coated GC electrode shows significant stability for 10 days in room temperature under air dry condition. Due to the low onset potential (0.16 V), high sensitivity and good stability observed for the SWCNTs-VOPc, this material has the potential for high performance ORR. SWCNTs-VOPc coated GC electrode can be used as an alternative for other ORR catalysts used in fuel cells and also for trace level oxygen sensing.

Acknowledgement

Generous funding from DST (SR/NM/NS-2012/2013(G)) and UGC (UPE), New Delhi, India, is gratefully acknowledged. We are thankful to Prof. Frank Marken, University of Bath, UK for his help and support.

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