Applied Innovative Research
Vol. 1, March 2019, pp. 62-65

Investigations of Gold-Graphene Nanocomposite for ORR in Aqueous Electrolytes

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Received 19 September 2018; accepted 22 January 2019

Oxygen reduction reaction (ORR) is an essential reaction step in fuel cell and metal-air batteries. The kinetics of ORR is very sluggish; it requires very high potential to occur. Many interesting articles have been published to enhance the kinetics. In this direction, we are working on metal nanoparticles modified graphene sheet. Gold nanoparticles are attached on two dimensional graphene sheets by in-situ reduction of metal ion in an aqueous reaction mixture. The synthesized nanocomposite is characterized by powder XRD, XPS and Raman spectroscopy. Microscopy image shows gold nanoparticles are attached to graphene sheets. ORR is studied in 0.1 M KOH and 0.1 M K_2SO_4 electrolytes. O_2 reduction in aqueous electrolytes produces water molecules on gold-graphene nanocomposite.

Keywords: Graphene, Gold nanoparticles, Nanocomposite, ORR, Aqueous electrolyte

Introduction

Oxygen reduction reaction is backbone of rechargeable metal-air battery and fuel cell devices[1]. ORR occurs during discharging step in metal-air batteries[2]. ORR is widely investigated in aqueous and non-aqueous electrolytes. The main issues with ORR are sluggish kinetics and multi-steps mechanism on cathode surface. The efficiency of energy storage devices mainly depends on oxygen electrode (or cathode) where ORR takes place[3].

Two dimensional graphene sheets is wonder carbon material for researchers due to its surface area, electrical conductivity, interesting mechanical properties[4,5]. Pure graphene sheets have their own limitations for catalyst applications. Current research trend is diverted towards graphene composites with metal particles[6-8], metal-free materials[9,10] and transition metal oxides[11-13]. Many articles are published on using graphene composite to enhance the kinetics of ORR. Some of interesting findings are discussed here. Badam *et al.*[14] reported Pt particles decorated defective acetylene black as an ORR catalyst. The catalytic activity Pt-acetylene back composite was more because of electrochemical surface area, low charge transfer resistance and defects on the graphitic structure[14]. Kumar *et al.*[15] published silver nanoparticles modified graphene composite as a catalyst for ORR/OER towards rechargeable Li-O_2 battery.

In this report, composite of gold particles and graphene sheets prepared in aqueous electrolyte by simple reduction process. Nanocomposite is being explored for ORR in alkaline and neutral medium keeping me mind aqueous energy storage devices. Already, gold nanoparticles are explored for ORR in aqueous as well as in non-aqueous electrolytes[16]. First time, we are reporting gold-graphene nanocomposite for ORR in aqueous electrolytes. As per our knowledge, there are no articles on gold-graphene composite for O_2 reduction in alkaline and neutral medium.

Results and Discussions

Characterizations

Formation of gold graphene nanocomposite catalyst was studied by powder XRD studies. XRD pattern of nanocomposite is presented in Fig. 1. Graphite powder was oxidized to graphite oxide using Hummer's method, where harsh acidic meduim is used to put oxygen functional groups in order to weaken non-covalent interactions between graphitic planes[17]. Then expanded graphite oxide was further converted to graphene oxide using ultrasonic waves. Finally, metal ions and graphene oxide was reduced in

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aqueous reaction mixture using $NaBH_4$ strong reducing agent. The XRD pattern of nanocomposite has reflections at two theta (2Θ); 35, 40, 62 and 76°, respectively, belongs to (111), (200), (220) and (311) planes of gold nanoparticles on graphene sheets (Fig. 1 (a)). Synthesis and characterization of gold-graphene composite is already reported in our previous article[18]. The presence of gold metal nanoparticles in nanocomposite was confirmed by XPS spectrum (Fig. 1 (b)). In full spectrum; peaks corresponding to gold 4p, 4d and 4f orbital binding energies as well as C 1s orbital regions are observed. Gold 4f region is further split into $4f_{7/2}$ and $4f_{5/2}$ peaks at 83.90 and 87.50 eV. The peak separation of 3.60 eV for gold 4f doublet confirms metallic nature of gold on graphene sheet.

TEM micrographs, particle size distribution and EDAX pattern of gold-graphene sample are presented in Fig. 1. The TEM micrographs (Fig. 1 (c)) reveals the layer of 2D graphene and nanoparticles of gold distributed uniformly. An investigation of particle size distribution suggests the presence of gold nanoparticles in 20-50 nm range. EDAX pattern indicates the presence of gold, oxygen and carbon elements in the nanocomposite (Fig.1 (d)).

Electrochemistry of nanocomposite

Electrochemistry of synthesized nanocomposite was studied in 0.10 M KOH (pH = 13) and 0.10 M K_2SO_4 (pH = 7) aqueous electrolyte with oxygen gas pursing and nitrogen gas pursing. Cyclic Voltammetry (CV) of nanocomposite coated glassy carbon electrode in 0.10 M KOH at 0.010 V s^{-1} scan rate is presented in Fig. 2a. As expected, there is no redox peak after pursing N_2 gas (Fig. 2 (a)). The oxygen reduction peak appears at -0.347 V versus mercury mercuric oxide (MMO) electrode with -0.093 mA reduction current. ORR on pure graphene sheets appears at -0.510 V with -0.0450 oxygen reduction current in 0.1 M KOH electrolyte. Linear sweep voltammetry (LSV) was also carried in 0.10 M KOH electrolyte to extract more information about the oxygen reduction reaction mechanism (Fig. 2 (b)). Mixed controlled region -0.280 to -0.400 V, where Koutecky-Levich equation is valid and diffusion controlled region -0.400 to -1.00 V, where Levich equation is used simulate for mechanistic interest.

Limiting currents due to diffusion process are -0.055, -0.072, -0.080, -0.087 and -0.097 mA, respectively, at 100, 300, 500, 800 and 2000 rotations per minute (rpm) of rotating disc electrode (RDE).

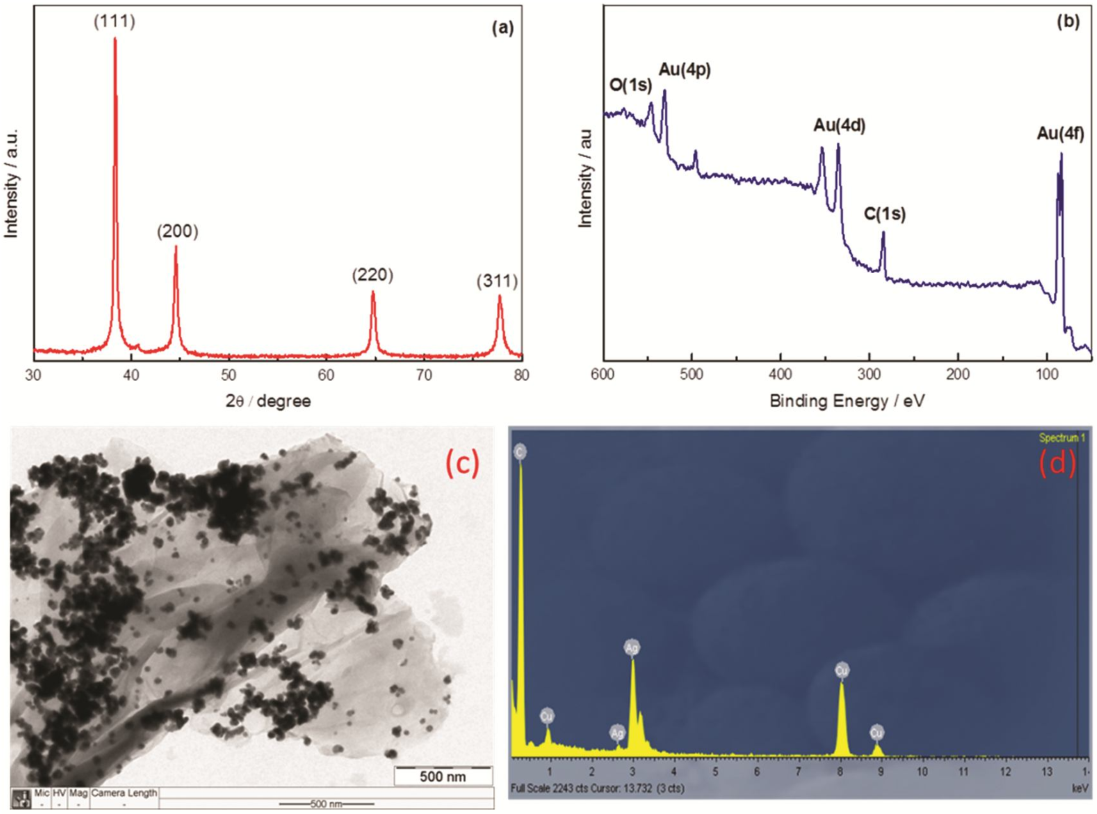

Fig. 1 – XRD pattern (a) XPS spectra, (b) TEM image, (c) EDAX pattern and (d) of composite.

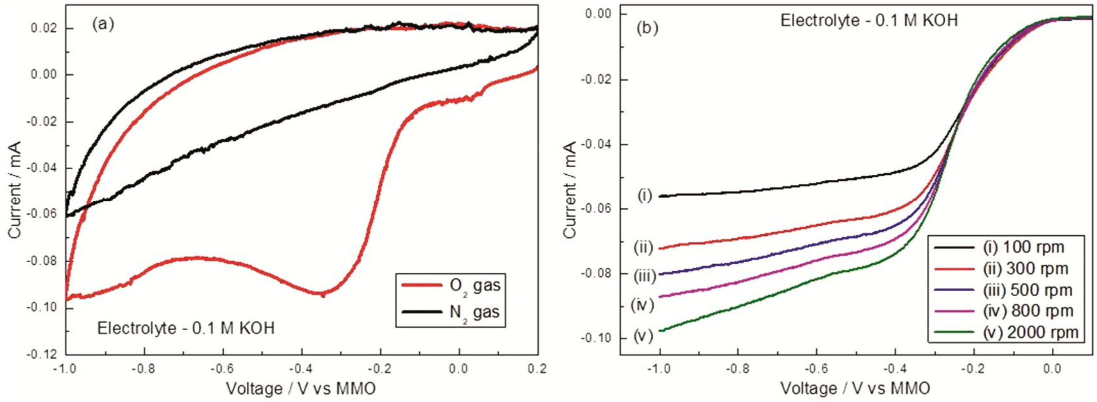

Fig. 2 – (a) CV and (b) LSV of composite sample in 0.1 M KOH.

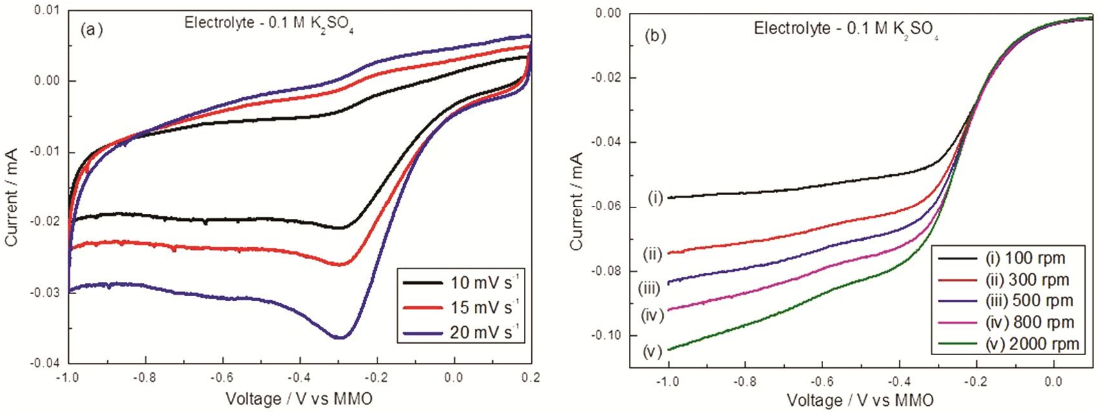

Fig. 3 – (a) CV and (b) LSV of composite sample in 0.1 M K_2SO_4.

CV of nanocomposite coated RDE electrode in neutral medium (0.10 M K_2SO_4) at 10 mV s^{-1} sweep rate in potential range from 0.20 to -1.0 V versus MMO reference (Fig. 3a). Oxygen reduction redox peak appears at -0.296 V. Redox peak current is increasing linearly with scan rate at static condition of solution according to Randles-Sevcik equation[19]. Values of O_2 reduction are -0.020, -0.025 and -0.036 mA at 10, 15 and 20 mV s^{-1} scan rate. LSV of nanocomposite in 0.10 M K_2SO_4 electrolyte at several rpm is shown in Fig. 3b. Limiting currents due to oxygen diffusion process at -1.0 V are -0.057, -0.074, -0.083, -0.092 and -0.104 mA, respectively, at 100, 300, 500, 800 and 2000 rpm of RDE.

Conclusions

Nanocomposite of gold and graphene was synthesized and characterized by many ex-situ techniques. Nanocomposite explored for O_2 reduction reaction in 0.10 M KOH and 0.10 M K_2SO_4. Generally, ORR follows two reduction pathways; two electrons step produce H_2O_2 and four electrons produce H_2O. The final product of oxygen reduction reaction was water; which was predicted by RDE studies.

Acknowledgement

The authors gratefully acknowledged to Director, CSIR-AMPRI, Bhopal, for giving permission to carry out the work. Author (Dr Surender Kumar) extends his acknowledgement to SERB, DST, GoI, New Delhi for financial support.

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