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Self-assembly Structure of Poly(o-methoxyaniline) on Ball Milling Graphite Surface

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ABSTRACT

Poly(o-methoxyaniline) is an important polymer due to highly water dispersible and easily processible compare to other poly-aniline group polymers. But it properties is not so superior to apply in numerous energy related application and it has some difficulty due to degrade during the device application. Graphene is the good material due to possess good environmental stability, large surface area and highly conducting property. So, to enhance the properties and application, I combine both materials in very facile way. In this manuscript ball-milling graphite is used due to it has more rough surface that help to easily combine with P. Here only highlighted about the synthesis of a self-assembly structure of polymer in ball-milling graphite surface.

Keywords: Poly(o-methoxyaniline), Graphite, Ball-milling, Self-assembly structure.

INTRODUCTION

The numerous units of monomer are joined together to form polymer and it has no restriction for chain length such a way that it can prolong to indefinitely. At initial stage, polymers are familiar as none conducting, high resistivity and low manufacturing cost materials. After few years later, new category polymers have been synthesized and it has excellent conductivity. These polymers are recognized as ‘conducting polymers’ and its properties is almost similar to the metal hence it’s familiar as ‘synthetic metal’. Conducting polymers (CPs) has huge applications in industry and it can apply in academic purpose due to find new properties. CPs has different form such as different bases and various salts are prepared via chemical reaction or by cyclic voltammetry at particular potential. Among the various form only emeraldine salts are conducting and its conductivity depend upon the doping level. We have different types of conducting polymer and can be categorized as linear (polyethylene, polyacetylene, polythiophene, polypyrrole, polyindole and polyaniline) and non-linear ((Poly(p-phenylene vinylene) (PPV)). In general the CPs is amorphous and stable that is not soluble in maximum polar, non polar solvent. The above properties have delayed the utilized of CPs and hence research are continuing to find more easily processible CPs. Up to now various methods have been established to improve processibility such as side chain functionalization and emulsion polymerization. To increase the solubility in both polar and non polar solvent, the monomers should be design by alkyl, alkoxy, carboxylate, sulfonate, boronate groups such as ortho-methoy aniline, suphonated aniline etc. The substitution of polymer chain as a result decreases the strictness of the polymer backbone and increasing the polarity but substitution effect creates negative impact on conductivity due to lost its planarity. Generally we used two types of polymerization technique one electrochemical polymerization and other is chemical polymerization. Chemical synthesis polymer has great advantage over electrochemical polymerization due to it is facile and excellent production yield.[1-4]

Pure Graphene is the carbon and hydrogen containing material and honeycomb structure. Every single carbon atom are four bonding environment among them three are σ bond and rest is Π and ~1.42 A° is distance separation of carbon atoms. Graphene has several structures, therefore opto-electronic properties variation is clearly observed. Graphene is a stacking structure of single layer and many single layers are stacking to form multilayer graphene and it is familiar as graphite. Layers structure of graphene is highly conducting and no band gap observed. Graphene can be exhibited in 1D, 2D, 3D, 0D structure such as nanoribbon, graphene, graphene gel, quantum dots respectively. The structure variation of graphene can be utilized in various applications purpose such as different pollutions control treatment, bio-medical, opto-electronic and energy devices etc. Actually graphene can be used in all ground due to it has various structural forms.[5-7]

Conducting polymers and graphene both have immense advantages on the subject of properties and applications. Pure graphene belongs to 2D structure with huge surface area and generally p type with high conductivity and on the other hand CPs has well conductivity with n type, good solubility depending upon functional groups and polymer backbone, active redox property. Polymer in emeraldine base (EB) form is non-conducting and it is difficult to measure in instrument but emeraldine salt (ES) form is conducting and it depend upon the doping level as for e.g. the conductivity of poly (o-methoxyaniline) (EB) varies from 10^{-2} to 10^{-1} S cm^{-1} when it is doped with HCl or CF_3COOH.[4,8-11] It is reported that poly(o-methoxyaniline) has average molecular weight (M_v) of 20900 and it is highly soluble in polar solvent and also can tune the doping level by changing the experimental conditions.[4,8-11] But recently researchers have found enchantment or sometimes generate new properties and applications when both are formed composite materials in different experimental conditions. These results have found due to synergistic effect of graphene and CPs. Here in this article I have discussed about the self-assembly structure of poly(o-methoxyaniline) (P) on ball-milling graphite (BG) surface.

Preparation of BG

The ball-milling (B) experiment has been carried out by Pulverisette 6, Fritsch in ammonia gas under speed 500 rpm. First 5 g graphite was placed into a container and added small size balls and saturates it with ammonia. After that container is perfectly closed and placed in the ball-mill machine, and rotate at high speed for 2 days. After finishing ball milling, the high pressure generated inside the ball milling jar and it was slowly released via a gas outlet. The ball milling materials was then clean-up constantly with aqueous HCl to washout the metallic impurities and then neutralized by NH_4OH and dried in a vacuum oven.

Synthesis of POMA–graphite composite

In this synthesis first we made two solutions that we may define as portion 1 and portion 2. Portion 1 contain 0.152 g $(NH_4)_2S_2O_8$ and 3 g LiCl in 18.3 mL H_2O and then added 1.675 mL 12(N) HCl solution. Portion 2 made by 500 mg BG with 1.35 mL OMA and 7.0 g LiCl in 2.5 mL 12 (N) HCl and 26.0 mL H_2O. The addition of portion 1 (dropwise) in the portion 2 was performed at -30°C and then whole container was placed at -18°C for 48 hours. After reaction completion, washed constantly with double distilled water and dried at 30°C.

Instruments

Morphologies experiment was performed by field emission scanning electron microscopy (JSM6700-FESEM, JEOL). X-ray photoelectron spectra were recorded with ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4 × 10-10 mbar using a monochromatic Al Kα X-ray beam (1486.60 eV). Fourier transform infrared spectroscopy (FTIR) was carried out with PerkinElmer Spectrum GX FTIR system. The UV-Vis absorption study was characterized in UV-2450 spectrophotometer (Shimadzu).

Cyclic voltammetry (CV) was performed by using a VersaSTAT3 AMETEK model (Princeton Applied Research TN) potentiostat/galvanostat employing a standard three-electrode electrochemical cell that consisted of a sample loaded glassy carbon as the working electrode, Ag/AgCl as the reference electrode and platinum gauze as the counter electrode. Glassy carbon electrodes (GCE) of 3.0 mm in diameter were polished with finer emery paper and 0.1, 0.3 µm Al_2O_3 powder. This working electrode was cleaned in an ultrasonic bath for 1 min and dried in air for use. In a typical process for sample loading, 1 mg sample solution was separately made in 0.5 mL H_2O by sonicated in an ultrasonic bath for 10 min to get a homogeneous solution. Then 10 µL of sample was separately coated on GCE and dried in vacuum at 30°C for 30 minute. After that 3 µL Nafion solution was added on the sample coated GCE electrode and then vacuum dried at 30°C for 30 minute. Electrochemical experiments were carried out at room temperature in 1 M aqueous H_2SO_4 solution as the electrolyte.

RESULT AND DISCUSSION

The SEM micrographs (Fig. 1(a)) of graphite (G) shows sheet like structure. BG exhibits sheet like bulk morphology with cracking surface (Fig. 1(b)). During B of graphite in ammonia gas generate ammonia functionalized G with more cracking surface. PG shows that self-assembly structure of P in BG surface (Fig. 1(c, d)). So, BG is the good platform to grow polymer self-assembly structure at low temperature.

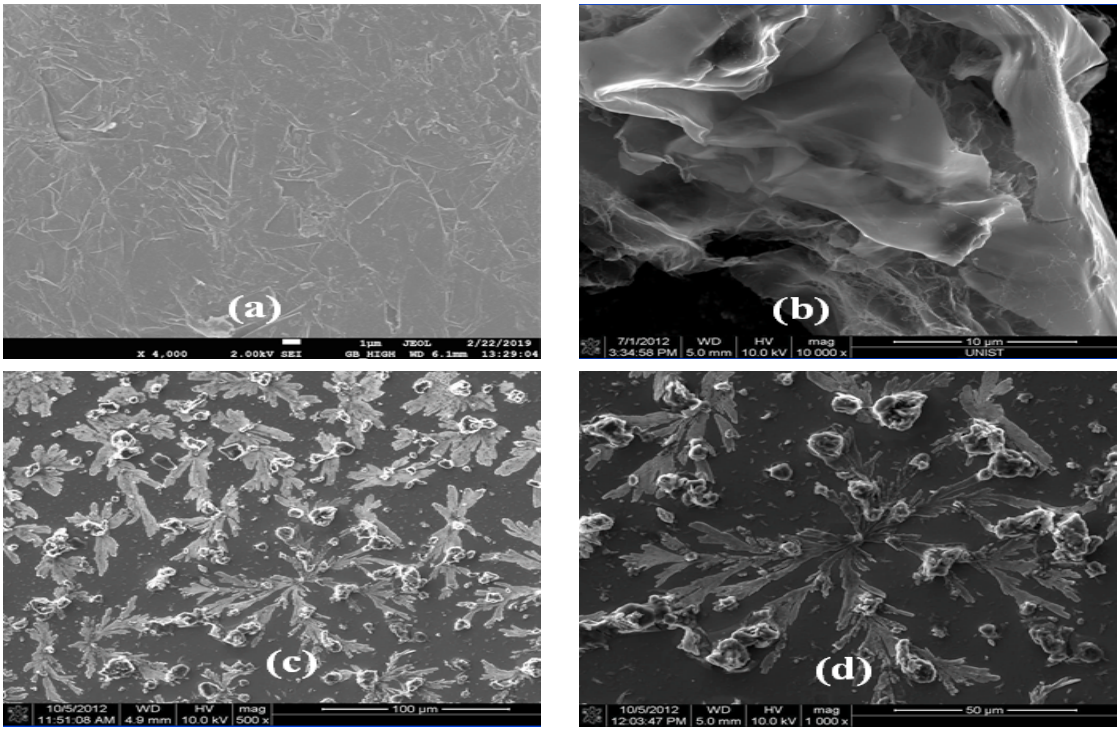

Fig. 1. SEM morphologies (a) G, (b) BG, and (c, d) different magnification images of PG

It is already reported that the P (emeraldine salt, ES) shows peak at 340 nm due to π–π^* transition of benzonoid ring, 440 nm peak for polaron to π^* band and ~ 650 nm peak arise due to benzonoid to quinonoid ring.[4,8] PG show at same position peaks like P (ES), So I can concluded that P (ES) structure remain intact in PG. BG has no characteristic UV-vis peak.

FTIR spectra (Fig. 3) of the P observed at 1590 and 1493 cm^{-1} peaks due to the carbon carbon double bond stretching of quinoid and benzenoid rings. The 1260 cm^{-1} peak is recognized to the C -N$^+$ stretching vibration of polaron structure and it justify with UV-Visible spectra (Fig. 2). The peak at 1019 cm^{-1} arises for C-O-C linkage. G shows a prominent peak at 1632 cm^{-1} for C=C skeleton of graphite. BG shows peak at 1583 cm^{-1} and 1206 cm^{-1} attributed to vibration of N-H and C-N bond. In PG the peak at 1578 and 1190 cm^{-1} observed for N-H and C-N bond and these bands position are little be shifted compare to BG due to self-assemble structure of P in BG surface.[9,12]

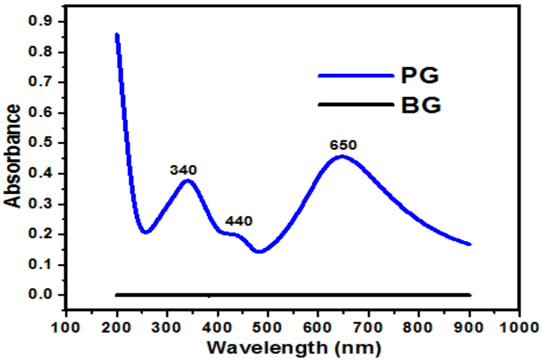

Fig. 2. UV-Vis spectra of PG and BG

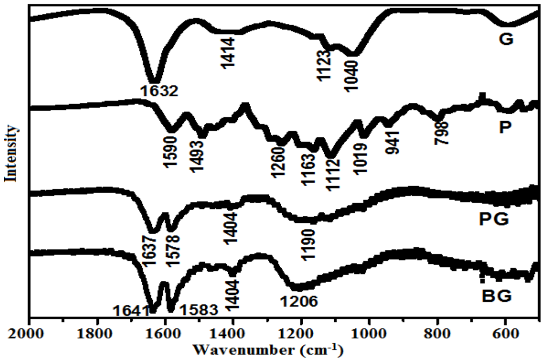

Fig. 3. FTIR spectra of G, P, PG and BG samples

Not only FTIR spectra but also X-ray photoelectron spectroscopy (XPS) can be utilized for functional groups and doping environment prediction. The XPS spectra (Fig. 4) observed that carbon (C), nitrogen (N) and oxygen (O) and consequent peaks of C 1s, N 1s and O1s at 285.0, 401.0 and 533.0 eV, respectively. In pure G only C1s peak observed but in case of PG the peak at 401.0 eV is little bit shifted to 399 eV due to formation of self-assembly structure of P on BG surface.[13]

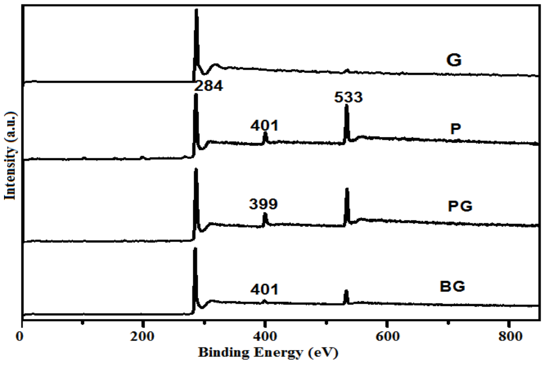

Fig. 4. XPS survey spectra of G, P, PG and BG samples

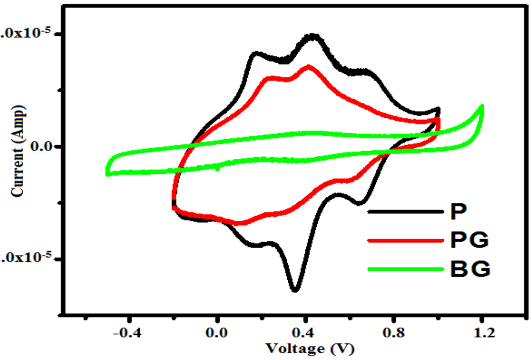

Fig. 5. CV plots of the P, PG and BG in 1 (M) H_2SO_4 electrode solution at 5mV s^{-1}

Charge storage behavior has observed from CV curves. Fig. 5 shows that charge storage capacity of PG is higher than BG due to polymer help to introduce its pseudo capacitance property to the BG.

CONCLUSION

This manuscript are completely described about the formation of self-assemble structure of polymer on BG surface. This synthesis method can create a common platform for helping us to attach of conducting polymer in graphite surface under low temperature. It is very important to link between two conducting wire due to enhancement of various properties and can apply in some energy related field.

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Declaration of competing interest

The authors declare that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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