Paper No. SS33



ELECTROCHEMICAL PERFORMANCE OF GRAPHENE OXIDE DEPOSITS ON 316L STAINLESS STEEL

J. Manovasuki

¹Department of Analytical Chemistry, University of Madras, Guindy Campus, Chennai 600 025. *manobujima@gmail.com*

Rani P George , K. Ravichandran , T.M. Sridhar and U. Kamachi Mudali

Department of Analytical Chemistry, University of Madras, Guindy Campus, Chennai 600 025. ²Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102

ABSTRACT

Graphene is a new generation materials filled with novel surface properties that enhance its application as a wonder material. It basically consists of a two dimensional carbon processing a sp² hybridised structure. The recent biocompatibility study indicates its non toxicity towards cells coupled with its superior mechanical, electronic and chemical properties. Failure of metallic implants due to corrosion and mechanical degradation is an area of concern in their use as long term load bearing devices. In the present work graphene oxide (GO) was coated on the commonly used implant alloy 316L SS by electrophoretic deposition (EPD). The deposition was carried out from a 1% suspension of GO in water. The electrochemical performance of the coatings were carried out in artificial saliva. The surface of the deposits were characterized for their crystalline properties using XRD and vibrational states using Raman and FTIR spectroscopy. The bone deposition properties were characterized by immersing in simulated body fluids. The results indicate an improved performance of the graphene oxide coatings on stainless steel.

Keywords: Graphene oxide, 316L SS, EPD, Anticorrosion

NIGIS * CORCON 2017 * 17-20 September * Mumbai, India

INTRODUCTION:

Graphene oxide (GO) is a two dimensional material derived from graphene by introducing covalent C - O bonds. The bulk from of GO, conventionally named graphite oxide [1]. Graphene oxide (GO) consists of a hexagonal carbon network with both sp² and sp³ hybridized carbons with hydroxyl and epoxide functional group on its basal plane, and carbonyl and carboxyl groups on the edges.

Graphene is thermally and chemically stable in ambient air up to 400°C and exceptionally transparent; more than 90% transmittance is observed for four-layer graphene [2]. Graphene based materials demonstrate excellent electrochemical and optical properties as well as the capability to adsorb a variety of aromatic biomolecules through a $\pi - \pi$ stacking interaction and/or electrostatic interaction, which make them ideal materials for constructing biosensors and loading drugs [3]. It is very easily functionalized thanks to abundant oxygen containing groups. It has also been used as photothermal agent for cancer treatment with encouraging therapeutic outcomes due to its high, intrinsic near-infrared (NIR) absorbance [3]. It has excellent chemical inactivity, high electrical conductivity, high optical transparency, good thermal stability and extraordinary flexibility.

Raman et. Al., showed that copper coated with graphene using chemical vapor deposition was one and a half orders of magnitude more resistance to electrochemical degradation than uncoated copper. Anticorrosion layers compared of composite films also have been introduced. Singh et al. fabricated robust graphene reinforced composite coatings that had excellent corrosion resistance using aqueous cathodic EPD and oxidation and corrosion resistant hydrophobic GO-polymer composite coatings on copper by EPD [2]. Recently, several authors reported that atomic thin layer of graphene prepared by chemical vapor deposition (CVD) was able to inhibit corrosion of the metals in electrolyte Na₂SO₄ and NaCl Although graphene has been certified as an effective protection coating, CVD method will raise the procedure intricacy and cost. To the best of our knowledge, no effort was paid on using electrophoretic deposition of GO to protect metals from corrosion. Moreover, Ruoff et al. have demonstrated that EPD method can be utilized to deposit graphene films with lower oxygen content in the GO suspension. EPD method shows a number of obvious advantages over painting and dusting especially in the preparation of thin films from charged colloidal suspensions due to its high deposition rate, good thickness controllability, good uniformity, no need of binders and simplicity of scaling up

Electrophoretic deposition (EPD) is a two-step process in which charged particles in suspension move toward an electrode of opposite charge due to the influence of an electric filed and then deposit to form a compact film. EPD is a versatile technique that can be applied to any powdered solid that forms a stable suspension, it operates successfully with a widely range of particle size, from micro- to nanometric particles (colloidal suspensions) [4].EPD has recently been attracting attention as a powerful method for the fabrication of nano-structured, thin ceramic composite films on conductive substrate, and it is simple and cost effective [2]. EPD is also applicable to polymer molecules, as well as to diverse particulate geometries, including equiaxed particles, nanotubes, nanoplatelets and nanorods. The versatility extends to almost any substrate morphology from flat or cylindrical to porous, fibrous or three dimensional (3D), and to a wide range of (conductive) materials. An aqueous medium has economical and environmental advantages over organic solvents and can be used for the deposition of materials [4].

In the present work, synthesized graphene oxide (GO) deposited on 316L stainless steel by using Electrophoretic deposition method and the electrochemical performance of the prepared GO layer was characterised.

NIGIS * CORCON 2017 * 17-20 September * Mumbai, India

EXPERIMENTAL PROCEDURE:

PREPARATION OF GO SOLUTION FOR EPD:

GO was synthesized from synthetic graphite powder (< 20 μ m, synthetic, Aldrich) by a modified hummers method. The received graphite powder (1g) was added to a solution of NaNO₃ (0.5g) in concentrated H₂SO₄ (23 mL) and after 2 h stirring KMnO₄ (3g) is gradually added to a mixture of solution in ice bath and vigorous stirring for 12 h to increase the oxidation degree of the graphite powder, and then, a mixture of solution was diluted with deionized water (500mL) and the 30% H₂O₂ (5mL) was added to the GO solution. The prepared solution was thoroughly washed using deionized water with 3 to 5 times and then solution was centrifuged and dried.

С	Mn	Si	р	S	Cr	Мо	Ni	N	Fe
<0.03	<2.0	0.75	0.045	0.03	16-18	2-3	10-14	0.10	Bal.

TABLE 1:Composition of 316L Stainless Steel

TABLE 2:Composition of 314 Stainless Steel

С	Mn	Si	р	S	Cr	Ni	Fe
0.25	2	1.5-3	0.045	0.03	23-26	19-22	Bal.

SUBSTRATE AND SUSPENSION PREPARATION:

316L SS electrodes of 10 x 10 x 3 mm size samples were mechanically polished using silicon carbide papers from 120 to 1000 grit. Polished 316L SS was used as a anode and 314 SS sheet of mm dimension were used as an cathode. The polished samples were washed completely with soap solution followed by distilled water, and dried at room temperature. 0.5% of GO in distilled water was taken in a 100mL beaker. The suspension was sonicated for 2 h to get uniform dispersion of the particles. Adjust the pH was 1.0- 2.0 with using dilute hydrochloric acid. Then, the suspension was stirred with a magnetic stirrer for 1 h.

NIGIS * CORCON 2017 * 17-20 September * Mumbai, India

ELECTROHPHORETIC DEPOSITION:

In this process, grapheme oxide was first depressed in deionized water and sonicated for 2 h at room temperature. The 316L SS was used as a working electrode and Type 314 SS was used as a counter electrode for the EPD. These electrodes were dipped in suspension and distance between the two electrodes was less than 1 cm and connected to a DC power supply (Jayam electronics). The working and counter electrodes were then used as the anode and cathode, respectively. The EPD was developed on a 1 cm² surface area of metallic substrate. The another side and edges of the substrate were masked with a Teflon tape. EPD was performed at various EPD condition with different voltages and deposition times. EPD process was carried out at 6 V using a DC voltage source at room temperature. After EPD for 1 -3 minutes the graphene oxide deposited. The coated samples were weighed before and after deposition. The changes in weight gain of substrate due to GO coatings were measured. The coating parameters were optimized by means of electrochemical studies.

CHARATERIZATION TECHNIQUES:

The as obtained coatings were characterized by XRD, RAMAN spectra, SEM and EDAX. The XRD analysis of unsintered and sintered GO coated on 316L SS was characterized by XRD (Bruker model D8) Cu k α radiation λ 1.5406 Å to determine the phase purity of the coatings. Raman spectra were analysed (double granting monochromator and photon counting system) to study the characteristics of GO coatings. The surface morphology of the coating was taken with FESEM (Model CARL ZEIS SUPRA 55) and the compositional analysis was carried out with the EDAX system attached to FESEM. The sintered and unsintered samples are characterized by ATR-IR to determine the functional groups present in the substrate.

CORROSION PERFORMANCE STUDIES:

The anti corrosion performance of GO – EPD – coated 316L SS was evaluated by the potentiodyanamic polarization method using Biologic-SP240 during immersion in 3.5% NaCl solution. A saturated calomel electrode (SCE) was used as reference electrode and graphite was used as counter electrode respectively.

The electrochemical measurements for both uncoated and GO coated 316L SS samples are Open Circuit Potential (OCP) time measurements, potentiodyanamic anodic polarization and electrochemical impendence spectroscopic studies (EIS).

RESULTS AND DISCUSSION:

FT-IR ANALYSIS OF COATED SAMPLES ON 316L SS:

Test samples were prepared by mixing approximately 0.2 g of graphene powder together with 1 g of spectroscopic grade Potassium Bromide (KBr) and then pressing them into a disk at a pressure of 8 Pa. Infrared spectra were recorded in the 650–4000 cm⁻¹ region. The recorded spectra for graphene is presented in Figure.1 FTIR foot print shows strong peak at ~1628 cm⁻¹ for aromatic C=C. This is because of back bone skeleton of graphene planes. A strong peak at ~ 2920 cm⁻¹ was obtained for C – H. Broad bands were observed in between ~3100-3500 cm⁻¹ which confirms the presence of –OH functionality. This was confirmed by strong peak at ~1107 cm⁻¹ in finger print region. Along with primary aliphatic hydroxyl functionality there is presence of aromatic phenolic – OH showing peak in between 1150-1300 cm⁻¹.





RAMAN SPECTRA FOR COATED SAMPLES ON 316L SS:

Raman spectroscopy is a non-destructive technique that is widely used to obtain structural information about carbon-based materials. Raman spectroscopy can provide a quick and effective way for structure and quality characterization of graphene. The peaks at 1358 cm⁻¹ (noted as D band), 1599 cm⁻¹ (G band), are presented in the spectrum (Figure.2) of the graphene samples. The D band of graphene associates with the existence of defects: the lower intensity of D peak, the fewer defects of the graphene layer. The graphene band is E2g mode of graphite, which is due to the sp²-bonded carbon atoms in a two-dimensional hexagonal graphite layer.



Figure.2: Raman spectra for GO and GO coated on 316L stainless steel

SEM ANALYSIS OF GO AND GO COATED ON 316L STAINLESS STEEL:

GRAPHENE OXIDE:

The morphology of the graphene oxide given in Figure.3. The nano size graphene sheets are clearly visible. The micrographs also prove the graphene oxide sheets and they are laced one over the other.



Figure.3: SEM analysis of Graphene oxide

GO COATED ON 316L STAINLESS STEEL:

The morphology of the graphene oxide coated on 316L stainless steel is given in Figure.4. The nano size particles of these particles are clearly visible. The micrographs also prove the graphene oxide sheets and they are laced one over the other.



Figure.4:SEM analysis of GO coated on 316L stainless steel OCP ANALYSIS OF GO COATED 316L SS IN ARTIFICIAL SALIVA SOLUTION:

The open circuit potential was shifted toward the positive potentials when the graphene oxide, layers covered the surface on immersion in artificial saliva solution These transients observed of these samples were relatively high in the bare sample but quite significant in the samples covered with GO. In contrast, GO the substrate was quite stable and maintain a steady state for one hour on immersion in artificial saliva solution, thus indicating the formation of a good interface. In contrast, GO coated substrate was quite stable, with hardly any transients, thus indicating a more stable passive film.



Figure.5:OCP analysis of GO coated 316L SS in Artificial saliva

NIGIS * CORCON 2017 * 17-20 September * Mumbai, India

Electrochemical Impedance Spectroscopy:

Electrochemical measurements were carried out in saline solution to evaluate the behaviour of GO coated samples and uncoated samples in equilibrium conditions. The coated samples have higher impedance values with low capacitance when compared to uncoated sample. The optimized potential 6 V and 3 minutes shows maximum impedance, resistance and very low capacitance values while compared to other coated as well as uncoated sample.(Figure.6)



Fig. 6: EIS of GO coated and uncoated samples

CONCLUSION:

- GO was successfully synthesized using the modified Hummers method, and a GO layer was
 efficiently deposited onto the 316L stainless steel using EPD. The EPD yield linearly
 increased with increases in the applied voltage and deposition time.
- Synthesized GO were characterized by FT-IR revealed the presence of oxygen functionalities..
- GO and GO/EPD coated samples were investigated the electrochemical behavior and its corrosion stability in simulated body fluids.
- The efficiency of corrosion inhibition may be greatly enhanced by improving the reduction degree of EPD-GO and depositing highly uniform.

ACKNOWLEDGEMENT:

The authors are thankful to UGC-DAE-CSR for providing financial support to carry out this work.

NIGIS * CORCON 2017 * 17-20 September * Mumbai, India

REFERENCES:

- 1. Ayrat M. Dimiev and James M. Tou, Mechanism of Graphene Oxide Formation, ACS Nano., 2014, 8, 3060–3068.
- 2. Ji Hoon Park, Jong Myung Park, Electrophoretic deposition of graphene oxide on mild carbon steel for anti-corrosion application, Surface & Coatings Technology, 254, 167–174,.
- 3. Yuqi Yang, Abdullah Mohamed Asiri, Zhiwen Tang, Dan Du, and Yuehe Lin, graphene based materials for biomedical applications, Materials Today, 2013, 16,10.
- 4. A. Chavez-Valdez, M. S. P. Shaffer and A. R. Boccaccini, Applications of Graphene Electrophoretic Deposition. A Review, J. Phys. Chem. B , 2013, 117,1502-1515.
- Sung Jin An, Yanwu Zhu, Sun Hwa Lee, Meryl D. Stoller, Tryggvi Emilsson, Sungjin Park, Aruna Velamakanni, Jinho An and Rodney S. Ruoff, Thin Film Fabrication and Simultaneous Anodic Reduction of Deposited Graphene Oxide Platelets by Electrophoretic Deposition J. Phys. Chem. Lett., 2010, 1, 1259–1263.
- 6. Swarnima Kashyap, Shashank Mishra, and Shantanu K. Behera, Aqueous Colloidal Stability of Graphene Oxide and Chemically Converted Graphene, Journal of Nano particles, 2014
- 7. Mohsen Moazzami Gudarzi, Colloidal Stability of Graphene Oxide: Aggregation in Two Dimensions, Langmuir, 2016, 32, 5058-5068.
- Wenting He, Liqun Zhu, Haining Chen, Haiyang Nan, Weiping Li, Huicong Liu, Yan Wang, Electrophoretic deposition of graphene oxide as a corrosion inhibitor for sintered NdFeB, Applied Surface Science, 2013, 279, 416–423.
- 9. Artur M. Pinto, Inês C. Gonc , alves, Fernão D. Magalhães , Graphene-based materials biocompatibility: A review, Colloids and Surfaces B: Biointerfaces, 2013, 111, 88–202.
- **10.** S.P. Vinodhini, R.Manonmani, B. Venkatachalapathy and T.M. Sridhar, Interlayer TiO₂ HAP composite layer for biomedical applications , *RSC Adv.*, 2016, 6, 62344-55.