CHAPTER II

Synthesis Techniques

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SYNTHESIS TECHNIQUES

This chapter includes:

- Introduction
- Hummer's method for the preparation of graphene oxide
- Chemical functionalization method for the synthesis of rGONS/β-CD nanocomposite
- Wet chemical method for the synthesis of metal (Ag, Au)/metal oxide (ZnO, CuO) nanoparticles decorated rGONS/β-CD nanocomposite
- Methodology of electrochemical sensing studies for nitrophenol isomers
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2.1. INTRODUCTION

In recent years carbon nanomaterials functionalized with polymer and metal/metal oxide nanoparticles plays a predominent role for the development of nanotechnology sensor applications. Several approaches have been employed for the synthesis and surface functionalization of graphene oxide nanomaterials to govern their superior electrochemical properties [1-2]. The modified Hummer's method provides the high surface area graphene oxide nanosheets with good electrical conductivity property compared to other chemical synthesis methods [1] [3]. The approach for the surface functionalization of graphene oxide is highly important to ensure the stability and surface interaction of polymer and metal/metal/oxide nanoparticles with graphene oxide nanosheets for appropriate electrochemical functions. Several physical and chemical methods are available for the synthesis of uniformly dispersed shape, size and stable metal/metal oxide nanoparticles and polymer functionalized reduced graphene oxide nanosheets. Among them, chemical synthesis of metal/metal oxide nanoparticles embellished polymer functionalized reduced graphene oxide nanosheets is found to be a facile method.

This chapter comprehensively describes the modified Hummer's method for the synthesis of graphene oxide nanosheets, chemical reduction method for the chemical functionalization of β-cyclodextrin polymer with reduced graphene oxide nanosheets and wet chemical method for the decoration of metal/metal oxide nanoparticles with β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets. It also describes the preparation methodology of phosphate buffer solution and glassy carbon electrode surface that have been employed as an electron transfer medium in the electrochemical reaction mechanism.

2.2. SYNTHESIS OF GRAPHENE OXIDE

Graphite powder (<20 μm, synthetic), sodium nitrate ($NaNO_3$), concentrated sulphuric acid (H_2SO_4, 95-97%), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) are purchased from Himedia, India. All the chemicals are used as received and all the reaction solutions are prepared using double distilled water.

2.2.1. Synthesis procedure

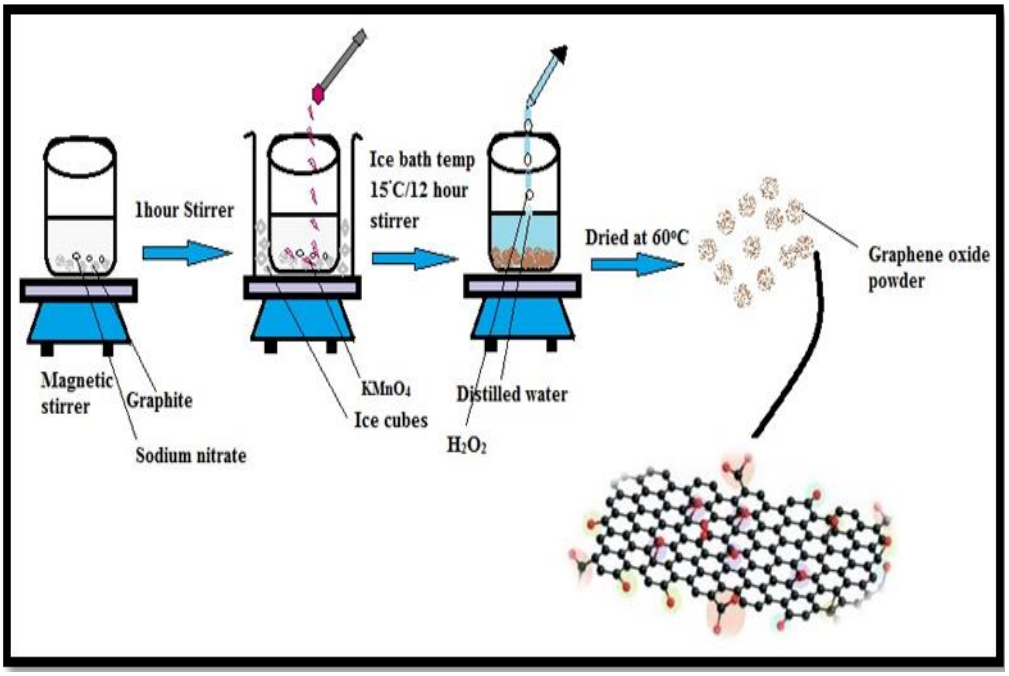

Figure.2.1. Schematic diagram of synthesis of graphene oxide using modified Hummer's method

Graphene oxide nanosheets (GONs) are synthesized using modified Hummer's method through the oxidation of graphite powder and the Figure.2.1 shows the

schematic representation of the synthesis of graphene oxide. The stepwise synthesis is given as follows:

About 2 g of synthetic graphite powder (GO) and 1 g of sodium nitrate ($NaNO_3$) are taken and mixed in a 50 mL of concentrated sulphuric acid solution (H_2SO_4) (95-97%). The reaction mixture is stirred for 1 hour at room temperature and potassium permanganate ($KMnO_4$) of about 6 g is slowly added to the reaction suspension. The rate of addition of potassium permanganate is carefully governed to keep the reaction temperature below 15˚C using ice bath condition. The mixture is stirred at 35˚C keeping in ice bath for 12 hours. The colour of the reaction suspension has become pasty brownish. The suspension is then diluted with very slow addition of 500 ml of double distilled water and the colour of the reaction suspension changed into brown colour. The suspension is finally treated with 10 ml of hydrogen peroxide to finish the oxidation reaction by resulting in yellow colour. Then the reaction mixture is undisturbed for two days to get a fine precipitate of graphene oxide suspension. The reaction mixture is further purified by washing it thoroughly by centrifugation with double distilled water followed by diluted (10 %) hydrochloric acid (HCl) and then with deionized water several times until the pH of the reaction suspension becomes neutral and dried at 60˚C for 12 hours. The graphene oxide (GONs) nanosheets are finally obtained as a powder [1] [4].

2.3. SYNTHESIS OF β-CYCLODEXTRIN FUNCTIONALIZED REDUCED GRAPHENE OXIDE NANOSHEETS

The synthesized graphene oxide nanosheet powders (GONs) are taken. The chemical reagents such as β-cyclodextrin (β-CD), hydrazine hydrate (N_2H_4), ammonia solution (NH_4OH) and hydrochloric acid (HCl) are purchased from Himedia, India and all the chemical reagents used are of analytical grade and used without further purification.

2.3.1. Synthesis procedure

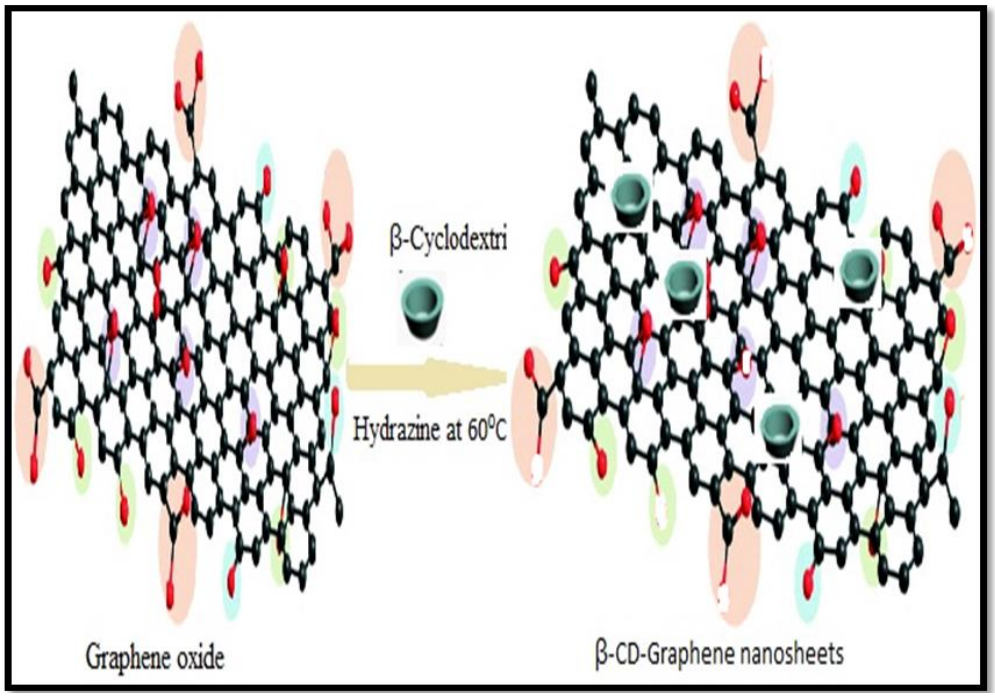

Figure.2.2.Schematic illustration of chemical functionalization of β-CD onto the rGONS

The β-cyclodextrin functionalized reduced graphene oxide nanosheets (rGONS/β-CD) are prepared by the following procedure and the schematic representation of the synthesis of rGONS/β-CD is shown in the Figure.2.2. About 0.1 g of synthesized graphene oxide powder is taken and thoroughly ultra-dispersed in a 50 ml of double distilled water using ultrasonicator for 1 hour. Simultaneously, 0.6 g of β-cyclodextrin powder is dissolved in 50 ml of deionized water and stirred for 1 hour at room temperature. Then the dispersed β-cyclodextrin solution is added into the graphene oxide suspension dropwise. In order to obtain a homogenous reaction suspension, 50 μL of hydrazine hydrate is added in the GO/β-CD suspension, followed by the addition of 300 μL of ammonia solution. The reaction mixture is then stirred vigorously at 60˚C for 4 hours. The pH of the reaction suspension is maintained at 10 using HCl/NaOH. The stable black dispersion solution is obtained and kept undisturbed over a night. Finally, the reaction suspension is washed thoroughly with doubly distilled water till all un-reacted chemical compounds are removed from the synthesized rGONS/β-CD suspension and then dried at 60˚C for 4 hours to get a fine powder form of rGONS/β-CD nanocomposites [5-6].

2.4. SYNTHESIS OF METAL (Ag / Au) / METAL OXIDE (ZnO / CuO) NANOPARTICLES DECORATED β-CYCLODEXTRIN FUNCTIONALIZED REDUCED GRAPHENE OXIDE NANOSHEETS

Silver nitrate ($AgNO_3$), Gold III chloride trihydrate ($HAuCl_3.3H_2O$), Zinc acetate dihydrate ($C_4H_6O_4Zn.2H_2O$), Copper II acetate monohydrate ($CH_3COO_2C_4.H_2O$) and sodium borohydrate ($NaBH_4$) are purchased from Himedia, India. All the chemicals used are of analytical grade reagents and are used without further purification. Double distilled water is used throughout the experiments for solution preparation.

2.4.1. Synthesis procedure

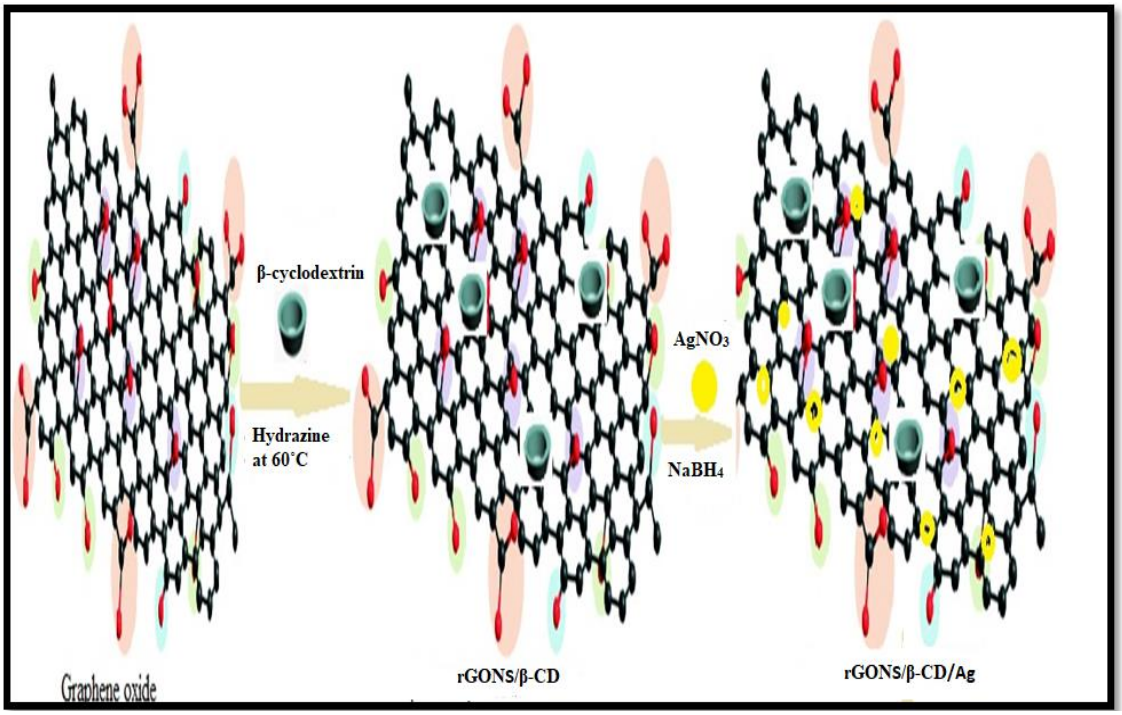

Figure.2.3.Schematic illustration of decoration of silver nanoparticles on the β-CD functionalized rGONS

Figure.2.3. shows the Schematic illustration of decoration of silver nanoparticles on the β-CD functionalized rGONS. The β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets (rGONS/β-CD) are synthesized by taking 50 mg of synthesized graphene oxide in a beaker containing 50 ml of water, then dispersed using ultrasonicator for 1 hour to obtain a homogeneous brown suspension. The β-

cyclodextrin of about 0.6 g is taken in a 50 ml of water and stirred for 2 hours. The dispersed β-cyclodextrin solution is then added into graphene oxide suspension followed by the addition of hydrazine hydrate and ammonia solution and the pH of the reaction suspension is maintained at 10 by using HCl. Then, the reaction mixture is stirred for 4 hours at 60˚C and washed thoroughly using deionised water and dispersed in a 50 ml of water.

The metal (Au/Ag) / metal oxide (ZnO/CuO) nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets are synthesized by taking, 0.002 M of metal/metal oxide precursor ($AgNO_3$ or $HAuCl_3.3H_2O$ or $C_4H_6O_4Zn.2H_2O$ or $CH_3COO_2C_4.H_2O$) in a 50 ml of water and stirred for 2 hours. The dispersed metal/metal oxide precursor solution is then added dropwise into the dispersed rGONS/β-CD suspension. About 0.005 M of sodium borohydrate ($NaBH_4$) is taken in a 30 ml of water and stirred for 2 hours. The dispersed $NaBH_4$ solution is then added into the above reaction mixture to reduce metal/metal oxide precursor into metal/metal oxide nanoparticles. The reaction suspension is then allowed to stirrer for 4 hours at 80˚C. Finally, the reaction mixture is centrifuged using distilled water. The centrifuged reaction suspension is then dried under vacuum to produce a fine powder of metal/metal oxide nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanocomposites. The similar procedure is carried out to produce different concentrations such as 0.004 M, 0.006 M, 0.008 and 0.01 M of metal/metal oxide nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets [7-8].

2.5. PREPARATION OF PHOSPHATE BUFFER SOLUTION

Potassium dihydrogen phosphate (KH_2PO_4) and dipotassium hydrogen phosphate (K_2HPO_4) are purchased from Hi media, India. All the chemical reagents used are of analytical grade and used without purification.

2.5.1. Synthesis procedure

The electrochemical investigations on the detection of ortho-, para- and meta-nitrophenol isomers are performed using phosphate buffer solution as an electrolyte medium, which acts as an electron transfer medium. The preparation of phosphate buffer solution with the pH range from 4.5 to 8.5 is described as follows:

The buffer solution with the pH of 4.5 is prepared by taking 0.1 M of potassium dihydrogen phosphate (KH_2PO_4) dissolved in 200 ml of double distilled water and dispersed using magnetic stirrer. The pH of dispersed solution is measured using pH meter and it is found to be 4.5. The preparation of buffer solution with the pH of 8.5 is as similar as the preparation of buffer solution with the pH of 4.5. In contrast, dipotassium hydrogen phosphate (K_2HPO_4) is employed instead of potassium dihydrogen phosphate (KH_2PO_4). The buffer solution with the pH values ranged between 4.5 and 8.5 is obtained by the mixture of almost equal amount of K_2HPO_4 and KH_2PO_4 solution. To get the buffer solution with high accuracy, the pH value of the electrolyte medium is measured using pH meter for the addition of each drop of K_2HPO_4 and KH_2PO_4 solution [9].

2.6. PREPARATION OF MODIFIED ELECTRODES

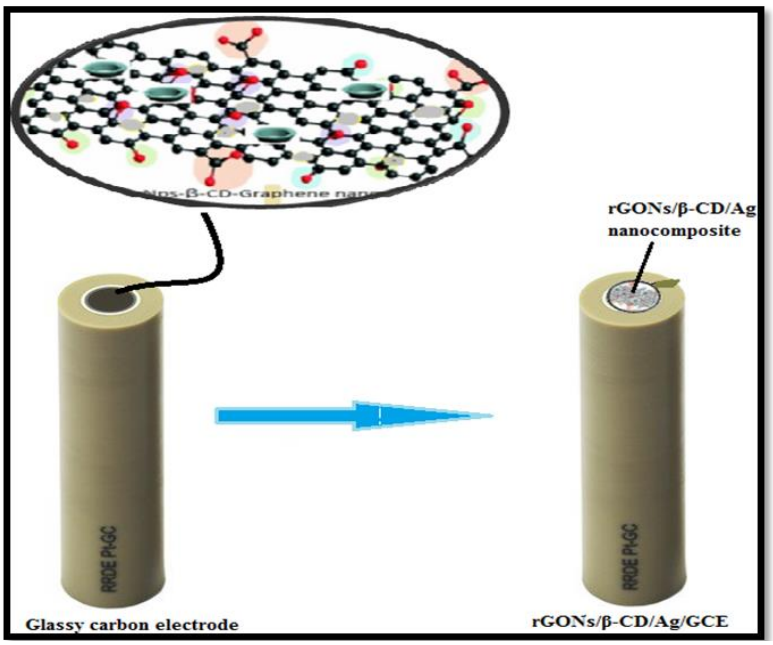

Figure.2.4.Schematic illustration of surface modification of GCE using synthesized nanocomposites

Glassy carbon electrode (GCE) with a geometrical area of 0.07 cm^2 is employed as a working electrode for the detection of nitrophenol isomers in all the electrochemical investigations. The investigation made on bare or unmodified glassy carbon electrode does not show any electrochemical redox behaviour with the nitrophenol isomers under optimized electrochemical conditions. Hence, it is necessary

to modify the surface of glassy carbon electrode using any other nanomaterials. Therefore, the synthesized nanocomposites such as graphene oxide nanosheets, β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets and metal (Au, Ag) / metal oxide (ZnO, CuO) nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets are used for the surface modification of glassy carbon electrode. The schematic representation of the preparation of surface modified glassy carbon electrode is shown in the Figure.2.4. The step wise surface modification of glassy carbon electrode is described as follows:

Before the surface modification, the working area of glassy carbon electrode is attentively polished with alumina slurry. After polishing, the surface of glassy carbon electrode is rinsed and ultrasonicated using double distilled water and ethanol for 3 minutes each, to eliminate the alumina residues employed for polishing and then dried under vacuum. Then the working area of the electrode surface is modified by drop casting the synthesized nanocomposites [10]. About 2 mg of synthesized nanocomposite is taken in sample holder and dispersed using 2 ml of double distilled water. In order to produce a uniformly modified electrode surface, the nanocomposites need to be dispersed completely in an aqueous medium. From the highly dispersed solution, about 10 μL of nanocomposite is taken using micro pipette and drop casted onto the surface of glassy carbon electrode, and then allowed to dry at room temperature [11].

2.7. CONCLUSION

This chapter describes the methodology used for the synthesis of graphene oxide nanosheets, β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets and different concentrations of metal (Au, Ag) / metal oxide (ZnO, CuO) nanoparticles decorated β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets. It also explains the methodology for the preparation of buffer solution and modified glassy carbon electrode employed for the electrochemical detection performance.

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