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# Graphene quantum dot functionalized by chitosan and beta-cyclodextrin as a new support nanocomposite material for efficient methanol electrooxidation

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ABSTRACT

Current needs for sustainable energy have popularized the development and use of fuel cell technology. Catalysts are vital fuel cell components, and in recent years research efforts have focused on the development new types of catalysts. This work describes application of a novel nanocatalyst based on graphene quantum dot functionalized by chitosan (GQD-CS) and β-cyclodextrin (GQD-$\beta$-CD) towards electrooxidation of methanol in alkaline solution. The catalysts were prepared by cycling the glassy carbon electrode in solutions containing graphene quantum dot and chitosan. The synergistic effects and catalytic activity of the modified electrodes were investigated by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). It was found that, in the presence of methanol, the modified electrodes [(GQD-CS-GCE) and (GQD-$\beta$-CD-GCE)] exhibited a significantly higher catalytical response for methanol oxidation compared to the other samples. The anodic peak currents showed a linear dependency on the square root of the scan rate, which is a characteristic of a diffusion controlled process. The graphene quantum dots functionalized with chitosan and β-CD electrodes is further extended to the demonstration of novel electrocatalyst through the transfer of the electrode fabricated by bare GQDs. For comparison of the recognition efficiency, other electrodes including bare GCE, and GQDs-GCE were used for the control experiments. Comparison of recorded CVs and CHs in the presence of methanol using GQD-CS-GCE, β-CD-GQDs-GCE shows $\Delta E_p$ was decreased as GQD-CS-GCE > GQDs-β-CD-GCE > GQDs-GCE. The higher peak current observed in the presence of GQD-CS-GCE, GQDs-β-CD-GCE clearly indicates β-CD and CS essential roles in the observed electrocatalytical behavior. In general, the attachment of chitosan and β-cyclodextrin to structure of GQDs provides new opportunities towards the direct methanol fuel cell application.



## 1. Introduction

At present, the ever-increasing use of energy, and especially of fossil fuels, is a major source of air pollution. As a result, there is a search for alternatives to fossil fuels, and fuel cells have attracted much attention due to their minimal pollutant emissions. Fuel cells are currently used in a wide range of portable, stationary and transport applications, and direct methanol fuel cells (DMFCs) are a particularly promising clean, portable power source. As such, DMFCs have received considerable interest with regard to applications in automobiles and portable consumer electronics [1] as well as other mobile and stationary devices [2,3]. This is because of their high efficiency, very low emissions and potential to act as renewable fuel sources with fast and convenient refueling, simple operation and ease of fuel storage and distribution. In addition, the low operating temperature of a DMFC (typically < 95 °C) allows for easy start-up and rapid responses to changes in the load or operating conditions [4]. A considerable number of studies have been devoted to the electrocatalytic oxidation of methanol, which is of paramount importance in the development of DMFCs [5]. One

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approach to the design of DMFCs is to use alkaline solutions [6], since there are many associated advantages, such as increased efficiency [6,7], a wider selection of possible electrode materials, almost no sensitivity to surface structures and negligible poisoning effects [8,9]. However, because the kinetics of methanol oxidation are generally unfavorable, a catalyst is required to improve the oxidation efficiency. Electrocatalysts based on Pt [10–12]. and Pt alloys [13–18] have been developed and used as anode catalysts for methanol oxidation in DMFCs [19], and have been shown to exhibit good activity for methanol oxidation. Unfortunately, these materials are too expensive for practical applications. Therefore, many attempts have been made to examine the catalytic activity of less expensive materials.

With the development of nanotechnology, nanomaterials have attracted substantial interest because of their unique optical, electrical, thermal and catalytic properties. These properties originating from quantum-size dimensions could change with their sizes and shapes. Since graphene was isolated from highly oriented pyrolytic graphite using the mechanical exfoliation method known as the "Scotch-tape method", which was reported by Geim and Novoselov in 2004 [20], research into graphene's characteristic and potential application has grown exponentially due to its excellent mechanical, thermal, optical and electrical properties [21]. Recently, graphene-based nanomaterials such as graphene oxide (GO) [22], graphene nanoribbons (GNRs) [23] and graphene quantum dots (GQDs) [24] have gained interest in various fields of research. GQD with tunable sizes, *ie.,* 2.2 ± 0.3, 2.6 ± 0.2, and 3 ± 0.3 nm especially displays unique optical and electrical properties due to the quantum confinement effect [25]. GQD is a chemically inert, low toxicity and low cost nanomaterial compared to other nanomaterials. Moreover, it is a water-soluble nanocarbon [26]. Therefore, GQDs are attractive for use in analytical chemistry applications, particularly in spectroscopy [27–30] and electrochemistry [31].

Owing to the exciting properties such as high electrical conductivity, high surface area, tunable photoluminescence and excellent dispersion in various solvent, graphene quantum dots (GQDs) have emerged as promising material for energy storage devices and fuel cells [32]. On the other hand, GQDs can be functionalized especially with oxygen containing groups such as hydroxyl, carboxyl and epoxy groups which can greatly enhance their hydrophilia and biocompatibility. One of important cases for this purpose is chitosan (CS). Chitosan is a linear polysaccharide composed of randomly distributed β-(1–4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating shrimp and other crustacean shells with the alkali sodium hydroxide. CS has been gradually used for constructing catalysts due to its attractive properties that include excellent film-forming ability, high permeability, good adhesion, nontoxicity, cheapness and a susceptibility to chemical modification. It also facilitates the electron transfer after its swelling in the reaction mixture due to its hydrophilic nature [33,34]. Besides, chitosan can be used as a dispersant to form stable GQDs -chitosan composite which can form a stable film on the electrode surface. CS as a polysaccharide biopolymer, which displays excellent film-forming ability, high water permeability, good adhesion, and susceptibility to chemical modifications due to the presence of reactive amino and hydroxyl functional groups.

Other cases for functionalization of GQDs is cyclodextrin (CD.(CDs with their largely hydrophobic cavities of variable size and numerous ways of chemical modification are the subject of intensive electrochemical research including both their behavior in homogeneous solutions and in thin films attached to the electrode surfaces [35–37]. Therefore, CDs are employed in electrochemical devices and electrocatalysts for the direct electrooxidation. On the other hand, literature review show that, integration of CDs to the structure of electroactive materials such as graphene based materials can be enhancing their electrical conductivity [38]. These improved performances encouraged us to explore the possible leading role played by the presence of ß-CD/graphene or its conductive derivatives such as graphene quantum dots (GQDs) and functionalized GQDs. GQDs increase the contact area with the analyte, so they could increase the electrochemical active surface to interact with some electroactive analytes [39]. Since the increase in geometric surface area is very important parameter in electrocatalysis, therefore modification of different substrates (such as glass, carbon, graphite *etc.*) by GQDs can increase the rate of electrochemical reaction. Therefore, integration of ß-CD into GQDs can be provide by the zero-dimensional structure of the deposited films and greatly increases Faradic currents. Thus, in this paper, a nanocomposite of graphene quantum dot-β-cyclodextrin was fabricated on the surface of glassy carbon electrode by using one step electrodeposition method.

Excellent properties of GQDs and the advantages of CS and ß-CD have received more attention for preparation of high performance electrode materials [40]. It was for these reasons that we decided to explore the possibility of using the GQDs-CS system as a platform for the direct methanol fuel cell application. In this paper, GQDs-CS and GQDs- ß-CD were fabricated on the surface of glassy carbon electrode by using one step electrodeposition method. The redox behavior of prepared electrode was then characterized by cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. The kinetics of charge transfer and mass transport processes across the interface were studied. In general, CS-GQDs show excellent electrocatalytic activities toward electrooxidation of methanol and great application potential in direct methanol fuel cell application.

## 2. Experimental details

### 2.1. Chemicals and reagents

All chemicals were purchased from Merck (Darmstadt, Germany) and used without further purification. Alumina slurry was purchased from Beuhler (Illinois, USA) and raw material of Methanol was purchased from Merck (Germany).

### 2.2. Apparatuses and methods

Electrochemical measurements were carried out in a three-electrode cell setup. The system was run on a Personal Computer using NOVA1.7 software. Saturated Ag/AgCl as a reference electrode and the counter electrode (also known as auxiliary electrode), which usually made of an inert material was platinum. All potentials were measured with respect to the Ag/AgCl which was positioned as close to the working electrode as possible by means of a luggin capillary. Glassy carbon electrode (GCE) (from Azar electrode Co., Urmia, Iran) was used as the working electrode. The transmission electron microscope (TEM) images were obtained on Leo 906, Zeiss, (Germany). Atomic force microscopy (AFM) experiments were performed at contact mode by Nanowizard AFM (JPK Instruments AG, Berlin, Germany) mounted on Olympus Invert Microscope IX81 (Olympus Co., Tokyo, Japan). UV–Vis spectroscopy was performed by Cecil, Cambridge, (UK). X-ray powder diffraction (XRD) measurements were performed using Siemens, D500, (Germany). Dynamic light scattering (DLS) were obtained using Malvern 3500 ZS. Spectrofluorimetery test was performed using Jasco, FP-750, (Tokyo, Japan).