Graphene quantum dot functionalized by beta-cyclodextrin: a novel nanocomposite toward amplification of L-cysteine electro-oxidation signals

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Abstract A novel nano-composite of graphene quantum dot-β-cyclodextrin was fabricated on the surface of glassy carbon electrode (GCE) using one step and green electrodeposition method. The redox of L-Cys behavior prepared nano-composite-modified of GCE was then characterized by cyclic voltammetry, chronoamperometry, and differential pulse voltammetry. Voltammograms of the modified electrode are recorded in physiological pH (phosphate buffer solution, pH 7.4), the kinetics of charge transfer and mass transport processes across the nano-composite/solution interface were studied. The modified electrode showed an efficient electrocatalytic activity toward the oxidation of L-Cysteine (L-Cys) through a surface-mediated electron transfer. The catalytic rate constant and the L-Cys diffusion coefficient were reported. A sensitive and time-saving method (differential pulse voltammetry) was developed for the analysis of L-Cys. The proposed voltammetric method was also applied to the determination of L-Cys using graphene quantum dot-β-cyclodextrin-GCE.

Keywords Graphene quantum dot, Nano-composite, β-cyclodextrin, L-cysteine, Fabrication, Electrochemical sensor

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Introduction L-Cysteine (L-Cys) belongs to sulfur-containing amino acid molecules playing a crucial role in biological systems and food industries.1–3 L-Cys can be used for the clinical diagnosis of the disease states. For example, hair depigmentation, lethargy, edema, slowed growth, muscle and fat loss, skin lesions and weakness, and liver damage are associated with the deficiency of L-Cys.4 Therefore, it is critically important to develop novel electrode materials for sensitive determination of the trace amounts of different biomolecules, such as L-Cys in biological samples for clinical and pharmaceutical industrial applications.5–7

Various methods have been used for the determination of L-Cys, such as high performance liquid chromatography,8 capillary electrophoresis,9 chemiluminescence10,11 spectrofluorimetry12,13, and fluorimetry.14,15 However, some of these methods take the disadvantages of expensive apparatus, time-consuming, and complicated pre-concentration process, multi-solvent extraction and trained technicians. By the comparison with other methods, electrochemical method takes inherent advantages of simple operation, high sensitivity, low cost, good selectivity, easy miniaturization and in vivo real time
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Bare carbon electrode showed poor electrocatalytic activity, even no responses for the determination of l-Cys.25,26 Bulk Au and Pt electrodes usually showed high overpotential owing to the formation of surface oxide resulting in narrow linear range and low selectivity.21 Various modified electrodes with electrocatalytic properties have been prepared for the determination of l-Cys, such as graphene oxide-Au nanoclusters composites,22 metal-organic framework,23 ordered mesoporous carbon-modified glassy carbon electrode (GCE),24 boron-doped carbon nanotubes (CNTs),25 copper-based nanoscale materials,26,27 and vanadate nanoscale materials.28 Furthermore, the detection limit, linear range, and sensibility are expected to be improved. Therefore, it is necessary to explore novel electrode materials to improve the electrochemical performance for the determination of l-Cys.

On the other hand, the couple l-cysteine/l-cystine is generally used as a model for the role of the disulfide bond and thiol group in proteins in a variety of biological media.29 Therefore, it is very important to investigate the electrochemical behavior and sensitive detection of CySH.30,31 Unfortunately, at ordinary electrodes (Pt, Au, graphite), the electrochemical behaviors of CySH are poor; no electrochemical responses could be observed.32,33 It has been realized that the method to solve this problem may be to utilize new materials as electrodes; at such an electrode surface, the electrochemical responses could be simply obtained directly.34–36 Over the past decades, several carbon-based materials, including fullerene and boron-doped diamond, have been explored for the electrochemical oxidation and detection of CySH. Recently, due to their unique electronic, chemical, and mechanical properties, CNTs as a new class of carbon nanomaterials have been exploited for the electrochemical oxidation of CySH. The high electrocatalytic activity observed at CNTs is attributed to the presence of the oxygen-containing functional groups on the surface of CNTs and a large number of edge plane graphite sites within the walls and at the ends of CNTs.49,50 Besides the materials mentioned above, there has been significant interest in the development of one such novel carbon material, i.e. graphene quantum dots (GQDs).

In the recent years, GQDs has become an emerging class of the nano-carbon family, thanks to its low toxicity, it’s easy preparation, its high chemical stability, its environmental friendliness, its luminescence or its ability to transfer photo-induced electron.51,52 It has shown great promise applications in the fields of bioimaging,53–55 photo-luminescence,56 catalysis,57 and fluorescent sensor.58 In addition, GQDs have been recognized as both excellent electron donors and acceptor, making them interesting candidates for producing electrode materials.59–61 GQDs can be functionalized62 especially with oxygen-containing groups such as hydroxyl, carboxyl, and epoxy groups which can greatly enhance their hydrophilicity and biocompatibility. Therefore, GQD-based materials have significant potential for biosensor applications. Additionally, various metallic nano-composite materials have been investigated for enzymatic and non-enzymatic amino acid biosensors.63–65 Traditionally, noble metals are the favored candidates for electrochemical biosensors due to their inherent electrocatalytic activities. For example, previously we used metal nanoparticles and GO as enhanced materials to build amino acid biosensor.66 However, due to the high price and scarcity of noble metals, nano-composite materials with great performances and low costs have been intensively explored to develop new functional nanomaterials.

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.70,71 Therefore, CDs are employed in electrochemical sensing devices for the determination of selected analytes. 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.72 These improved performances encouraged us to explore the possible leading role played by the presence of β-CD/graphene or its conductive derivatives such as 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.73 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 β-CD into GQDs can be provided by the zero-dimensional structure of the deposited films and greatly increases Faradic currents. Thus, in this paper, a nano-composite of GQDs-β-cyclodextrin was fabricated on the surface of GCE using one step electrodeposition method. The redox behavior of prepared nano-composite modified of GCE was then characterized by cyclic voltammetry (CV), chronoamperometry, and differential pulse voltammetry. In the voltammograms of the modified electrode recorded in physiological pH (phosphate buffer solution (PBS), pH 7.4). The kinetics of charge transfer and mass transport processes across the nano-composite/solution interface were studied. The modified electrode showed an efficient electrocatalytic activity toward the oxidation of l-Cysteine (l-Cys) through a surface-mediated electron transfer. The catalytic rate constant and the l-Cys diffusion coefficient were reported. A sensitive and time-saving method (differential pulse voltammetry) was developed for the analysis of l-Cys. The influence factors including scan rate, l-Cys concentration in the electrochemical behaviors have been systematically analyzed. β-CD-GQDs show excellent electrocatalytic activities toward l-Cys and great application potential in electrochemical sensors.

**Experimental details**

**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 l-Cys was purchased from Merck (Germany). All solutions were prepared with deionized water. The stock solution of l-Cys (0.001 g per mL) was prepared by dissolving an accurate amount of l-Cys in an appropriate volume of 0.1 M PBS, pH 7.4 (which was also used as supporting electrolyte), and then stored in the dark place at 4 °C. Additional dilute solutions were prepared daily by accurate dilution just before use. Also the other stock solutions were
prepared by dissolving an accurate amount equal to molecular weight of each one in an appropriate volume of 1000 mL deionized water and then all stored in the dark place at 4 °C.

**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. 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).

**Synthesis of GQDs**

An easy bottom-up method was used for the preparation of GQDs. At first, GQDs were synthesized by pyrolyzing citric acid and dispersing the carbonized products into alkaline solutions. Briefly, 2 g of citric acid was put into a beaker and heated to 200 °C by a heating mantle until the citric acid changed to an orange liquid. Then, for preparing GQDs, 100 mL of 10 mg/mL NaOH solution was added into the orange homogenous liquid dropwise with continuous stirring. The obtained GQD solution was stable for at least one month at 4 °C.

**Characterization of GQDs**

Figure 1(A) and (B) presents the AFM and TEM images of synthesized GQDs. The corresponding AFM image shows a single GQD monolayer thin film. Ninety percent of the particles represent dark brown color which assigned to a size range below 10 nm. Furthermore, the DLS study represented hydrodynamic sizes of GQDs with size distribution of 5 ± 4 nm (Figure 1(C)) which findings of DLS analysis confirmed the AFM results. Figure 1(D) shows fluorescence spectra of the GQD dispersed in water at room temperature. The GQDs have a broad absorption, from 400 to 600 nm. The maximum excitation of 210 nm was obtained with an emission wavelength of ~470 nm. The maximum emission of ~480 nm was obtained with an
excitation wavelength of 400 nm. Also when the excitation wavelength changed from 340 to 420 nm, the maximum peaks were constant. This could be explained by the uniformity both in the size and the surface state of those sp\(^2\) clusters contained in GQD which was responsible for the fluorescence of GQD.

**Preparation of GQDs and β-CD-GQDs modified GCE**

GCE (2 mm in diameter) was polished to a mirror-like finish with 0.3 and 0.05 μm alumina slurry and then thoroughly rinsed with double distilled water. Then it was successively sonicated in acetone and double distilled water and was allowed to dry at room temperature. Finally, 5 mL of homogeneous GQD and β-CD-GQDs films were electrodeposited onto GCE by CV in the potential range from -1.0 to 1.0 V at a scan rate of 200 mV s\(^{-1}\) for 50 cycles (Scheme 1). After 50 repeating cycles, the three-electrode system was transferred into 0.1 M PBS (pH 7.4) containing l-Cys and cyclic voltammograms were recorded at a sweep rate of 100 mV s\(^{-1}\).

**Results and discussion**

The electrochemical behaviors of l-Cys have been analyzed by measuring the CVs at bare GCE and different modified GCEs. Figure 2 shows the CVs at bare GCE with the mixed solution of 2 mM l-Cys and 0.1 M PBS (pH 7.4), GQD and β-CD-GQD modified GCE in PBS (pH 7.4) solution with and without l-Cys. In 0.1 M PBS (pH 7.4) solution, bare GCE exhibits no electrocatalytic activities toward l-Cys. The GQD and β-CD-GQD modified GCE has also no electrochemical response only in the presence of PBS (pH 7.4) solution. Generally, an irreversible CV peaks can only be observed in PBS (pH 7.4) solution with 0.1M PBS (pH 7.4) solution were located at +0.24, +0.07 V, and +0.05, −0.47 V, respectively using polyaniline/CuGeO\(_n\) nanowires-modified GCE for the electrochemical determination of l-Cys. Different from the electrochemical responses of l-Cys at the GCEs modified using different nanoscale materials, GQD-GCE and β-CD-GQD-GCE exhibits irreversible oxidation peaks located at 0.75 and 0.62 V, respectively, in the mixed solution of 2 mM l-Cys and 0.1 M PBS (pH 7.4). Therefore, it is reasonably concluded that these CV peaks result from l-Cys because the CV peaks can only be observed in PBS (pH 7.4) solution with l-Cys. The results suggest that the β-CD-GQD-modified GCE exhibits superior performance for l-Cys oxidation.

For comparison of the recognition efficiency, other electrodes including bare GCE, and GQDs-GCE were used for the control experiments. Although the peak currents are remarkably increased at the GQDs-GCE due to the excellent electrical conductivity of GQDs, the I\(_p\) is 2 mA which is still too small to distinguish the lower concentrations of l-Cys (see Figure 2). From the above figure, it can be concluded that without active substance, bare GCE or GQDs-GCE cannot result in the successful electrooxidation of l-Cys. When β-CD containing catalyst agent is used to modify GQD-GCE, the differences in both peak currents and potential are obviously enlarged, suggesting that β-CD-GQDs can provide an acceleration center to electron shuttling. These results indicated that β-CD-GQDs film could accelerate the rate of electron transfer of l-Cys and have good electrocatalytical activity for redox l-Cys reaction of l-Cys. Therefore, β-CD-GQDs are a suitable mediator to shuttle electron between l-Cys and working electrode, and facilitate electrochemical regeneration following electron exchange with l-Cys. This observation is also linked to the high conductivity and inherent ability of β-CD-GQDs. That might be related to the excellent properties of β-CD-GQDs such as high-specific surface area and electrical conductivity. Also, the recognition efficiency is further improved at the β-CD-GQDs-GCE with a peak current ratio of 4.1 and ΔE\(_p\) of 0.8 V, it is no doubt that β-CD-GQDs play important roles in the improvement of catalytically activity of GQDs toward electrooxidation of l-Cys. As a decisive catalytic component in the composite film, β-CD-MMNPs provides a catalytic platform for selective detection.
Figure 3  (A) CVs of β-CD/GQDs/GCE in the presence of 2 mM Cys + 0.1 M PBS (pH 7.4) in different scan rates (from inner to outer): 20, 40, 60, 80, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 900, and 1000 mV s⁻¹, respectively. (B) Variation of the scan rate-normalized current (Ip/v½) with scan rate. (C) Variation of Ep vs. the logarithm of the scan rate. (D) Tafel plot derived from the current-potential curve

Figure 4  DPV of 2 mM l-Cys at β-CD/GQDs/GCE. Supporting electrolyte: 0.1 M; PBS (pH 7.4); scan rate: 50 mV s⁻¹
of l-Cys meanwhile, GQDs can amplify the electrochemical signals produced during the electrochemical sensing process. In one word, the synergetic effect of GQDs and β-CD leads to a successful and effective detection of l-Cys.

Scan rate is one of parameters significantly affecting electrooxidation of various compounds. Also, useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. Therefore, the electrochemical behaviors of l-Cys at different scan rates were investigated on the surface of β-CD-GQDs-GCE by CV. Thus, the effect of the scan rate on l-Cys electrooxidation was investigated in the range from 20 to 1000 mVs⁻¹ using CV method (Figure 3(A)). A linear relationship was obtained between the peak current and the scan rate in the range of 2–300 mVs⁻¹, which revealed that the oxidation of l-Cys was an adsorption-controlled step. Two approaches widely used to study the reversibility of reactions and to determine whether a reaction is adsorption or diffusion controlled consist of the analyses of dependences: \( I_p \) vs. \( v^{1/2} \) and \( \ln I_p \) vs. \( \ln v \). Figure 3(B) shows these plots for the oxidation peak of l-Cys in 0.1 M PBS. For reversible or irreversible systems without kinetic complications, \( I_p \) varies linearly with \( v^{1/2} \), intercepting the origin. Although, the plot of \( I_p \) on \( v^{1/2} \) presented in Figure 3(B) is linear \( (R^2 = 0.9996) \), it does not cross the origin of the axes. This is characteristic for the electroodic process preceded by electrochemical reaction and followed by a homogenous chemical reaction. In the scan rate range from 20 to 300 mVs⁻¹, peak current \( I_p \) of l-Cys electrooxidation depends linearly on square root of the scan rate \( v \) and is described by the following equation:

\[
I_p = 0.0308 v^{1/2} + 0.3377 \quad (R = 0.9911)
\]

This dependence does not cross the origin (Figure 3(B)). This fact can suggest that the electrode process of l-Cys electrooxidation isn’t controlled by diffusion and can be preceded by chemical reaction. On the other hand, a dependence of \( \ln I_p \) on \( \ln v \) is linear and described by the following equation:

\[
\ln I_p = 0.7540 \ln v - 2.500 \quad (R^2 = 0.9954)
\]

Its slope is 0.7540 and indicates adsorption control of the electrode process. A slope close to 0.5 is expected for diffusion-controlled electrode processes and close to 1.0 for adsorption-controlled processes.\(^{79-81}\)
where $I_p$ – peak current (A), $f = F/RT$, $A$ – electrode area (cm$^2$), and $C$ – bulk concentration of L-CYS (mol cm$^{-3}$). This equation allowed obtaining dependence: $\ln(I_p)$ vs. ($E_p$) is linear (Figure 3(D)) and described by the following equation: and its slope is 2.30 anodic transfer coefficient ($\beta_n$) of L-Cys electrooxidation, calculated from the Eq. (3) totals 94.2 mV. This result is close to obtained from previous method ($E_p$ vs. $\ln v$). This slope indicates also the three electron transfer to be rate-limiting, assuming a charge transfer coefficient of $\beta = 0.30$.

We also investigate the electrochemical behavior of L-Cys at GC, GQD/GC, and β-CD-GQDs-GCE electrodes at using DPV technique. Figure 4 shows the electrochemical oxidation of Cys at β-CD-GQDs-GCE electrodes at pH 7.4. As can be seen, there are two anodic peaks at $+0.02$ (peak I) and $+0.38$ V (peak II), respectively. This means the oxidation of L-Cys at pH 7.4 undergoes two processes, and the β-CD-GQDs film clearly plays an important role in the observed electrocatalytic behavior. Mao et al. reported the oxidation of L-Cys at CNT-modified electrode at pH 7.0 undergoes two processes: at 0.0 V attributed to the oxygen-containing functional groups of CNTs, and at $+0.35$ V.

**Figure 6** DPVs of β-CD/GQDs/GCE in different concentrations of L-Cys solutions (0.1 (a), 0.2 (b), 0.25 (c), 0.3 (d), 0.33 (e), 0.5 (f), 0.66 (g), 1 (h), 1.33 (i), 2 (j), and 4 (k) mM) Supporting electrolyte: 0.1 M; PBS (pH 7.4); scan rate: 20 mV s$^{-1}$
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existing on the surface of β-CD-GQD,86 which means peak II at the β-CD-GQD-GCE electrode at pH 7.4 could be logically attributed to the edge-plane-like defective sites of β-CD-GQD.

In order to evaluate the reaction kinetics, the electrocatalytic oxidation of l-Cys on β-CD/GQDs/GCE was investigated by chronoamperometry. Chronoamperometry, as well as CV has been employed for the investigation of the processes occurring via an ErCi mechanism.81 Single steps chronoamperograms were recorded by setting the working electrode potentials to desired values and were used to measure the catalytic rate constant on the modified surface. Figure 5(A) shows double steps chronoamperograms for the modified electrode in the

ascribed to the edge plane-like defective sites of CNTs,85 which are almost at the same potentials as those at the β-CD-GQD-GCE electrode of this work. This suggests the electrooxidation of Cys at β-CD-GQD-GCE and CNTs modified electrodes at pH 7.4 may have the same processes and similar mechanisms. The redox l-Cys peak pairs observed at β-CD-GQD-GCE electrode in Figure 4 can be also observed for β-CD-GQD and CNT-based materials,86 which indicates the pairs may originate from protonation/deprotonation of the oxygen-containing functional groups of β-CD-GQD.86 So the oxygen-containing functional groups of β-CD-GQDs are thus mainly responsible for peak I. There are also significant edge-plane-like defective sites

Scheme 1 Synthesis procedure of β-CD/GQDs
absence (a) and presence (b) 0.46, (c) 0.15, (d) 0.11, (e) 0.09, (f) 0.076, (g) 0.065, (h) 0.057, and (i) 0.05 M of l-Cys over a concentration range of 0.05–0.46 M. The applied potential steps were 0.55 vs. (Ag/AgCl)/V, respectively. The plot of net current vs. $t^{-1/2}$ which has been obtained by removing the background current by the point-by-point subtraction method gives a straight line, Figure 5(B). This indicates that the transient current must be controlled by a diffusion process. The transient current is due to catalytic oxidation of l-Cys which increases as the l-Cys concentration is raised. Using the slopes of these lines, we can obtain the diffusion coefficients of the drugs according to the Cottrell equation $^{21}$, p. 163

$$I = nFAD^{1/2}C^{1/2}D^{-1/2}$$

(2)

where $D$ is the diffusion coefficient, and $C$ is the bulk concentration. The mean value of the diffusion coefficients of l-Cys was found to be $2.1 \times 10^{-5}$ cm$^2$ s$^{-1}$.

The rate constants of the reactions of l-Cys and the ensuing intermediates with the redox sites of the β-CD/GQDs/GCE electrode can be derived from the chronoaerogamograms according to Eq. (6): $^{31}$, p. 503

$$\frac{I_{\text{catal}}}{I_d} = \lambda^{1/2} \left( \exp(-\lambda) + \lambda^{1/2} \right)$$

(3)

where $I_{\text{catal}}$ is the catalytic current in the presence of l-Cys, $I_d$ the limiting current in the absence of l-Cys and $\lambda = kC_m t$ ($k$, $C_m$, and $t$ are the catalytic rate constant, bulk concentration of l-Cys and the elapsed time, respectively) is the argument of the error function. For $\lambda > 1.5$, $\text{erf}(\lambda^{1/2})$ almost equals unity and Eq. (3) reduces to:

$$\frac{I_{\text{catal}}}{I_d} = \lambda^{1/2} e^{\lambda^{1/2}} = \pi^{1/2}(kC_m t)^{1/2}$$

(4)

From the slope of the $I_{\text{catal}}/I_d$ plot, the value of $k$ at a given concentration of l-Cys can be derived (Figure 5(C)). The mean value of $k$ in the concentration range of 0.05–0.46 M l-Cys was found to be $8.8 \times 10^{-4}$ cm$^2$ mol$^{-1}$ s$^{-1}$.

In order to develop a voltammetric method for determining of l-Cys, we selected the DPV mode, because the peaks are sharper and better defined at lower concentrations of l-Cys than those obtained by CV, with a lower background current, resulting in improved resolution. According to the obtained results, it was possible to apply this technique to the quantitative analysis of l-Cys. As mentioned previously, the PBS of pH 7.4 was selected as the supporting electrolyte for the quantification of l-Cys. The linear range for the determination of l-Cys was investigated under optimal conditions. The analytical parameters for the detection of l-Cys using β-CD-GQD-modified GCE have been investigated by measuring the CVs of l-Cys with different concentrations (Figure 6). A plot between l-Cys concentration and peak current shows a linear relationship (the inset in the upper-right part of Figure 6). The linear range is observed from 0.01 to 2 mM. The results demonstrate that the β-CD-GQD possess good electrocatalytic activity to the oxidation of l-Cys which may due to the large surface area and good catalytic activity providing abundant active sites for l-Cys oxidation.

The stability of the β-CD-GQD-modified GCE electrode under the storage conditions (exposure to air, ambient temperature) was also examined using the same PBS containing 2 mM l-Cys. During the repeating amperometric detection process, a decrease in response current can be observed and 10% of the response current will be lost after 10 repeated detections. This may result from the adsorption of the intermediate species during l-Cys oxidation. Fortunately, β-CD-GQD-modified GCE electrode can be recovered very well (about 98%) by electrochemical activation in PBS (pH 7.4). The long-term storage stability of the β-CD-GQD-modified GCE electrode was also investigated. The electrocatalytic property of β-CD-GQD-modified GCE electrode to l-Cys oxidation remains satisfactory; only 6% current loss after 6 days and 20% current loss after 1 month are observed.

**Conclusion**

The β-CD-GQD film was formed electrochemically in a regime of CV on a GCE and checked for electrooxidation of l-Cys at physiological pH. It is concluded that the electrooxidation of formaldehyde that starts around 0.2 V vs. Ag/AgCl occurs through a mediated electron transfer mechanism catalyzed by β-CD-GQD species which form in on the surface of GCE. The results show that the β-CD-GQD-GCE exhibit high electrocatalytic activity toward l-Cys oxidation at around 0.6 V. Therefore, β-CD-GQD can promote l-Cys electron-transfer, thus β-CD-GQD/GCE provides higher electroactive surface area and lower charger transfer resistance compared with GQD-GCE. Using CV and chronoamperometry measurements, the kinetic parameters, such as charge transfer coefficient $(\alpha)$ and the catalytically reaction rate constant $(k)$ for oxidation of l-Cys were determined. It is expected that this work opens new horizons on the design of new nanocatalysts for the electrooxidation studies.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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