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# Enhanced electro-oxidation of urea based on nickel nanoparticle decorated reduced graphene oxide/PEDOT:PSS composite

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## KEYWORDS

Poly(3,4-ethylenedioxythiophene);  
Reduced graphene oxide;  
Nickel nanoparticles;  
Electro-oxidation;  
Urea.

**Abstract.** A facile two-step systematic plan of action was used to prepare nanocomposite of Reduced Graphene Oxide (RGO) doped poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) decorated with nickel nanoparticles (Ni NPs) onto a Glassy Carbon Electrode (GCE). Composites of PEDOT:PSS and RGO were prepared by mixing each component solution and were fabricated as a beneficial substrate for Ni NPs. Ni NPs were electrodeposited on the PEDOT-RGO support by applying constant potential into nickel ions solutions. Then, Ni/PEDOT-RGO/GCE was employed as an efficient electrocatalyst for electrooxidation of urea. The electrocatalytic properties of Ni NPs/PEDOT-RGO modified glassy carbon electrode toward the oxidation of urea were analyzed by Cyclic Voltammetry (CV) and chronoamperometry (CA). Such studies evidenced the high electrocatalytic activity of Ni NPs and mixed PEDOT-RGO, which is mainly ascribed to the good electrochemical activity of PEDOT-RGO composites and the well-dispersed Ni NPs on the surface of PEDOT-RGO composite.

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## 1. Introduction

To date, the development of clean power sources and the reduction of the emission of greenhouse gases (e.g., carbon dioxide) have led to many investigations into generation of pure hydrogen [1]. Urea is a major product of the metabolism of many nitrogen containing compounds in the human body [2,3]. Also, urea with 0.33 molar concentration in human urine is the major constituent of it, which results in large concentrations of urea in wastewater sewage systems [4,5]. Urea is not directly poison, but it can go through a natural conversion to ammonia, and

then be released to the atmosphere. Ammonia in the atmosphere can be oxidized; therefore, it generates environmental pollutants, such as nitrate and nitric oxides. The ammonia can dissolve into the rain drops and form nitric acid. Ammonia poses risks to the soil and water and causes health problems [6–8]. Thus, treatment of urea has become as important environmental problems [9]. Various methods, such as chemical and biological decomposition and thermolysis, have been utilized for urea dissociation [10–12]. But, urea electrolysis has proven to be an effective technology to cure urea-rich wastewater with the simultaneous pure hydrogen generation [13–15]. Hence, urea can act as a stable, accessible, non-toxic, non-flammable, renewable and cheap hydrogen carrier [16,17]. However, an efficient catalyst for urea electro-oxidation is usually required to achieve high current densities at low overpotential.

Graphene (GR) is a monolayer of carbon atoms

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with  $SP^2$  hybrid that are fastened and pressed together into a two-dimensional, honeycomb solid formed structure [18]. GR-based materials possess superabundant unanticipated properties, such as extraordinary electronic transport properties, extent surface area, and strong mechanical strength [19], which have been investigated in electrochemical sensors, super capacitors, and fabricated field-effect transistors [20,21]. Another important category of novel materials for various electrochemical applications is Conductive Polymers (CPs). CPs have emerged as intelligent materials that can be applied for the development of various devices such as sensors due to their radically distinctive properties, such as high conductivity, light weight, and excellent processability [22,23]. In recent years, interest in the preparation of nanocomposites of conducting polymers and graphene has been put on notice intensively due to cooperating for enhanced effects resulting from the combination of these two classes of compounds [24–26]. Graphene-based polymer nanocomposite has exhibited several fold increases in electrical conductivity. The remarkable improvement in electrical conductivity is due to the formation of a conducting network by graphene sheets in the polymer matrix. In such a nanocomposite, the maximum electrical conductivity is obtained using a very low graphene loading in different polymer matrices compared to other carbon fillers [26].

Among various CPs, Poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS) should be one of the best choices to incorporate into graphene due to its high electrical conductivity and extremely skillful stability compared to other CPs [27,28]. It is known that PEDOT has low-band gap, high environmental stability, and high optical transparency in the oxidized, conductive state [29]. Thus, combination of graphene and conductive polymers as catalyst support materials may increase catalytic activity of NPs. The excellent electric properties of graphene and the unique advantages of PEDOT have attracted great research interests in preparing graphene-PEDOT composites as support materials [30]. Therefore, the synthesis of hybrid materials consisting of graphene with PEDOT matrix as support materials for metal NPs catalysts is an interesting approach to improve the catalytic behavior of metal NPs, because this composite structure is a more conductive support material than other carbon materials and leads to the formation of mono dispersive metal NPs on the surface of the hybrid materials based on the strong coordination interaction between PEDOT and metal NPs [30,31].

In this work, we used RGO-PEDOT nanocomposite as a substrate for Ni NPs effective immobilization. The Ni NPs were directly electrodeposited onto the support. Catalysts with different PEDOT composi-

tions were investigated. The results demonstrate that Ni/PEDOT-RGO/GCE with large active surface area exhibits great catalytic activity and good durability for urea oxidation.

## 2. Experimental

### 2.1. Chemicals

All solutions were freshly prepared with dionized water. Urea, PEDOT:PSS, graphite powder,  $NH_3$ ,  $H_3PO_4$ ,  $H_2O_2$ , ethanol, HCl,  $KMnO_4$ , hydrazine ( $N_2H_4$ , 98%), sulfuric acid,  $Ni(NO_3)_2$ , NaOH, and  $CH_3COOH$  were purchased from Merck.

### 2.2. Electrochemical measurements

The electrochemical oxidation of urea performed in a conventional three-electrode cell was used at  $25 \pm 1^\circ C$ . A saturated calomel electrode, a platinum wire, and a Ni/RGO-PEDOT/GCE were used as a reference, an auxiliary, and working electrodes, respectively. The electrolyte for urea electro-oxidation was dissolved in 1 M NaOH aqueous solution. Electrochemical experiments were performed using a computerized potentiostat/galvanostat (SAMA 500, electroanalyzer, system, I.R. Iran).

### 2.3. Preparation of the PEDOT-RGO composite

For this purpose, firstly, Graphene Oxide (GO) was obtained by oxidizing graphite using an improved method [32]. In brief, a 9:1 mixture of concentrated  $H_2SO_4/H_3PO_4$  (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and  $KMnO_4$  (18.0 g). The reaction was then heated to  $\sim 50^\circ C$  and stirred for 12 h. Then, the reaction pot was cooled to room temperature and poured onto deionized ice (400 mL) with 30%  $H_2O_2$  (3 mL). The obtained solution was filtered. The solid material was then washed with water until pH became neutral, and subsequently washed with 30% HCl, and finally twice with 200 mL of ethanol. The solid obtained on the filter was vacuum-dried for 24 h at  $40^\circ C$  [20]. The graphite oxide was obtained as a light brown powder. Reduced graphene oxide was produced using hydrazine together with ammonia solution. A colloidal suspension of GO in purified water (100 mg/100 mL) was prepared by sonication for 2 h. Subsequently, 150  $\mu L$  of hydrazine solution (98%) was added. Then, it was refluxed at  $80^\circ C$  for 12 h in a heating mantle and cooled down to room temperature. Finally, solutions were centrifuged, and RGO precipitates were washed with distilled water, and then dried at  $60^\circ C$  in vacuum for 12 h. Then, in a simple procedure, 2 mg of RGO powder was added into 1 mL dionized water for the synthesis of PEDOT-RGO composites, followed by sonication for 30 min. Then, the above solution was added into 1 mL PEDOT:PSS solution in dionized

water (1% W/W) and followed by sonication for 30 min.

#### 2.4. Preparation of Ni/RGO-PEDOT/GC electrode

Modified electrodes were prepared by a simple casting method. Prior to the surface coating, Glassy Carbon (GC) electrode polished with alumina was used as substrates for the supported catalysts. The PEDOT-RGO mixture was treated for 30 min with ultrasonication for uniform dispersion. A volume ( $2\ \mu\text{L}$ ) of this mixture was dropped by a microsampler onto the top surface of the GC electrode and dried under room temperature. Then, the as-prepared modified electrodes were treated with nickel ions solution. Nickel NPs were electrodeposited onto the surface of PEDOT-RGO/GCE from 5 mM nickel nitrate solution, applying constant potential at  $-1.1\ \text{V}$  for 12 sec using chronoamperometry method. Modified electrode was eventually washed with double distilled water in order to remove the electrolytes, large and agglomerated NPs. The as-obtained catalyst-modified GC electrode was employed as the working electrode in our experiments.

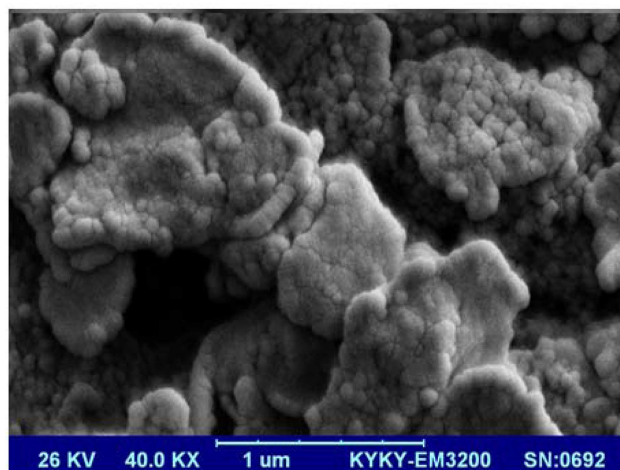
In order to gain the best conditions in the preparation of the Ni/PEDOT-RGO/GCE for catalyst performance, we optimized the concentration and volume of RGO suspensions, PEDOT solution volume, and electrodeposition time of nickel nanoparticles. For comparison, PEDOT-RGO/GCE without Ni, Ni/PEDOT modified without RGO, and unmodified GCE were also prepared in the same way.

### 3. Results and discussion

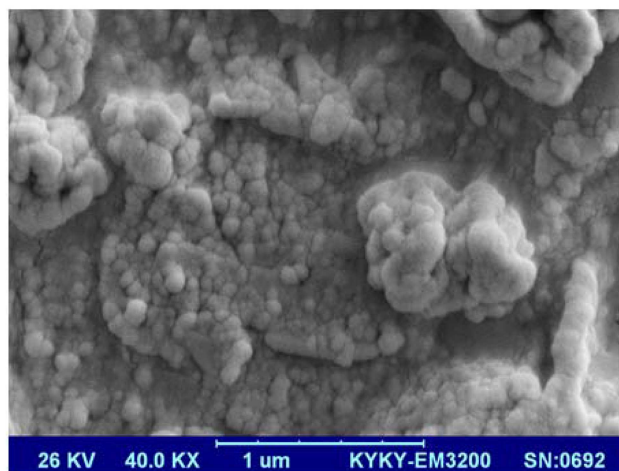
#### 3.1. Morphologies of Ni/PEDOT-RGO nanocomposites

The morphologies of Ni/RGO and Ni/PEDOT-RGO composites were investigated by Scanning Electron Microscopy (SEM). In Ni-RGO composite, Ni NPs were spread on the graphene nanosheets (Figure 1(a)), with the average particle size being equal to 50 nm. On the other hand, Ni/PEDOT-RGO composite has a homogeneous sheet-like structure with granular PEDOT distributed on the RGO surfaces, and Ni nanoparticles deposited on PEDOT-RGO support were observable (Figure 1(b)). This image clearly shows RGO, PEDOT, and Ni NPs that resulted in the formation of a nanocomposite film. When PEDOT was introduced into Ni/RGO nanocomposite, the film becomes more uniform and even, most likely due to the binding and blanketing effects of polymer.

The weight of deposited Ni nanoparticles can be evaluated from chronoamperometry experiments by using the total mols of electrons, according to the Faraday's law. The evaluated value for the weight of deposited Ni nanoparticles is  $1 \times 10^{-7}\ \text{gr}$ .



(a)

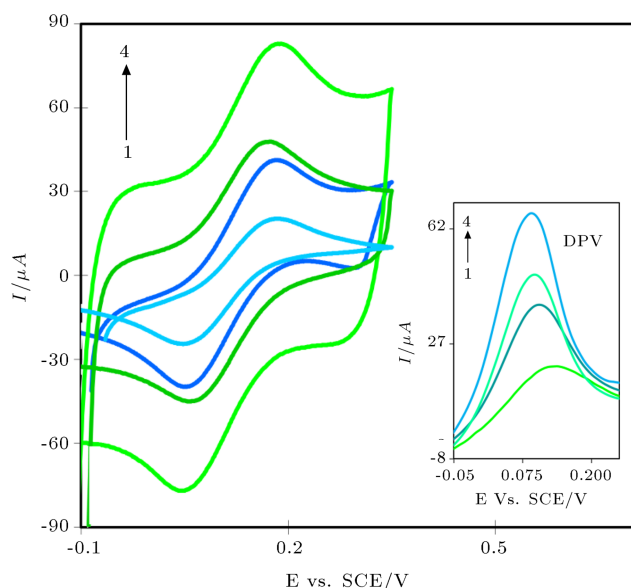


(b)

Figure 1. SEM images of (a) Ni/RGO and (b) Ni/PEDOT-RGO.

#### 3.2. Electrochemical behavior of Ni/PEDOT-RGO/GCE

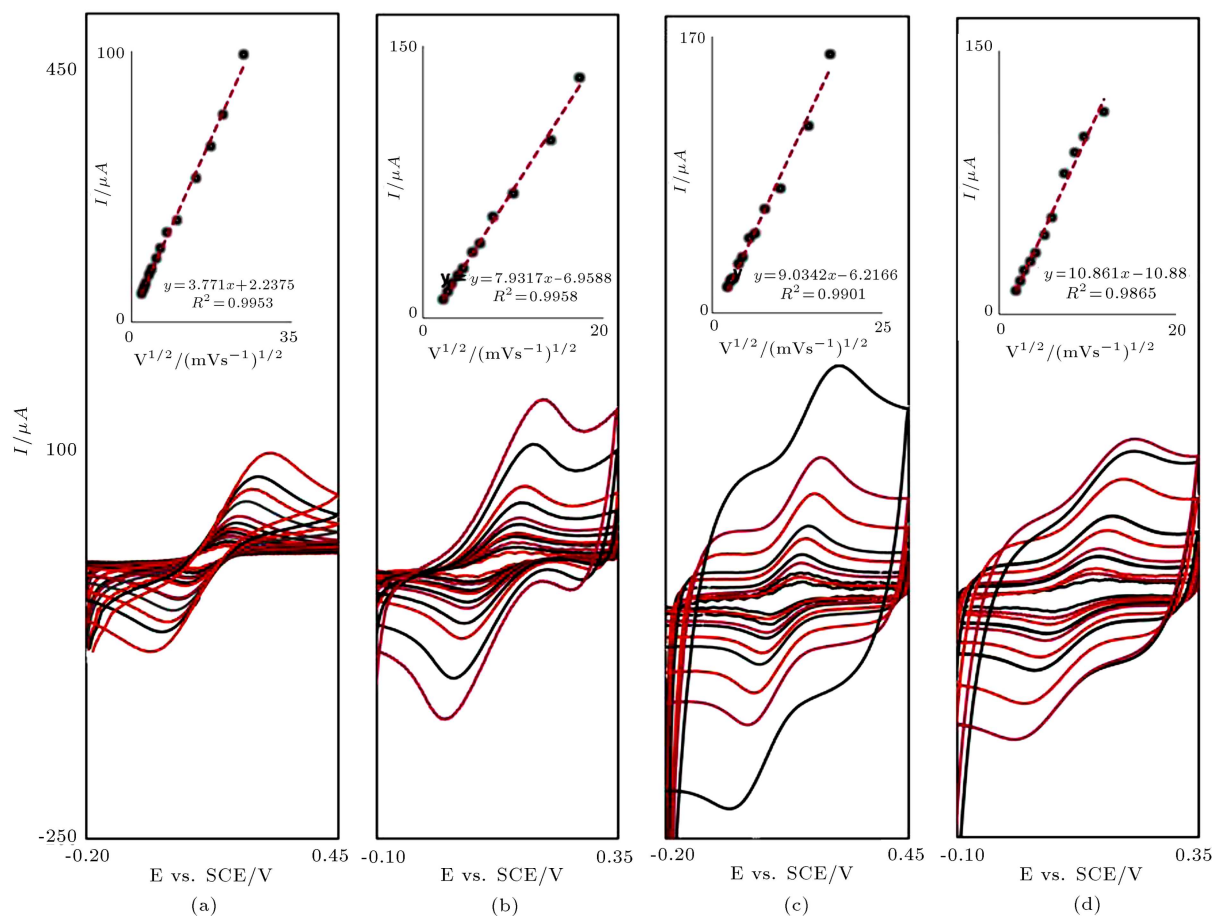
It is well known that  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple can be used as a proof to characterize the electron transfer properties of the electrodes. Figure 2 shows the electrochemical behavior of electrodes in 5.0 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution containing 0.1 M KCl. Typical CVs of  $\text{Fe}(\text{CN})_6^{3-/4-}$  at bare GCE, Ni/RGO/GCE, PEDOT-RGO/GCE, and Ni/PEDOT-RGO/GCE with a scan rate of  $40\ \text{mVs}^{-1}$  were used to evaluate the electron transfer ability of the modified GCE as a redox probe. It can be seen that Ni/PEDOT-RGO/GCE showed higher oxidation peak current ( $51\ \mu\text{A}$ ) than that of the bare GCE ( $16\ \mu\text{A}$ ), Ni/RGO/GCE ( $30\ \mu\text{A}$ ), and PEDOT-RGO/GCE ( $38\ \mu\text{A}$ ). This result indicated that the RGO and PEDOT facilitated the electron transfer. DPV was used for further characterization of the modified electrode. Inset of Figure 2 demonstrates DPVs of various electrodes in 5.0 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$ .



**Figure 2.** Cyclic voltammograms of bare GC, Ni/RGO/GC, PEDOT-RGO, and Ni/PEDOT-RGO/GC electrodes in the electrolyte solution containing 5.0 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  and 0.1 M KCl. Scan rate:  $40 \text{ mVs}^{-1}$ , Inset: DPV for various electrodes.

solution containing 0.1 M KCl. It was observed that the Ni/PEDOT-RGO/GCE electrode produces a higher peak current in comparison with that of the other electrode. This could be attributed to the higher electrochemically active surface area of the Ni/PEDOT-RGO/GCE which is in agreement with the results of cyclic voltammetry [33].

Figure 3 displays a series of cyclic voltammograms on the modified electrodes in different scan rates and the dependence of the peak current ( $I_p$ ) on the square root of the scan rate ( $\nu^{1/2}$ ) for the demonstrated electrodes (insets of Figure 3) in 5.0 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution containing 0.1 M KCl. A, B, C, and D corresponded to the bare GCE, Ni/PEDOT/GCE, RGO-PEDOT/GCE, and Ni/RGO-PEDOT/GCE, respectively. As can be observed in Figure 3, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation on the electrochemical reaction; moreover, the anodic and cathodic peaks of electrodes were found to move into opposite directions, suggesting the redox process to be quasi-reversible [34]. Also, the linearity of  $I_p$  versus  $\nu^{1/2}$  indicates that the electrochemical reaction



**Figure 3.** Cyclic voltammograms: (a) bare GCE, (b) Ni/RGO/GCE, (c) RGO-PEDOT/GCE, and (d) Ni/RGO-PEDOT/GCE in different scan rates. Insets show the plot of the anodic current vs. the square root of the scan rate. Electrolyte solution: 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  and 0.1 M KCl.

is controlled by semi-infinite linear diffusion from the electrolyte to the electrode surface [34].

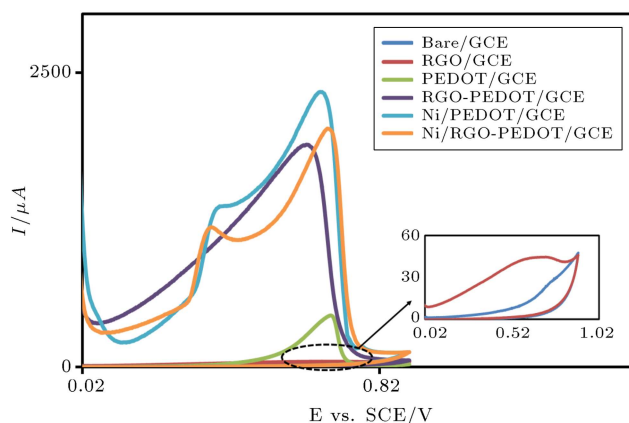
The electrochemical active surface areas of four modes of electrode, including the Ni/RGO-PEDOT/GCE, Ni/RGO/GCE, PEDOT-RGO/GCE, and bare GCE, were calculated by cyclic voltammetry using 5.0 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox probe prepared in 0.1 M KCl. The electrochemically active surface area can estimate the access of a conductive path available to transfer electrons to and from the electrode surface and also assign the number of catalytically active sites available to an electrochemical reaction [35,36].

Based on the slopes of the curves of  $I_p$  versus  $\nu^{1/2}$  and by using Randles-Sevcik equation, for Ni/RGO-PEDOT/GCE, RGO-PEDOT/GCE, Ni/RGO/GCE, and bare GCE, active surface areas were calculated as 0.098, 0.081, 0.071, and 0.03  $\text{cm}^2$ , respectively.

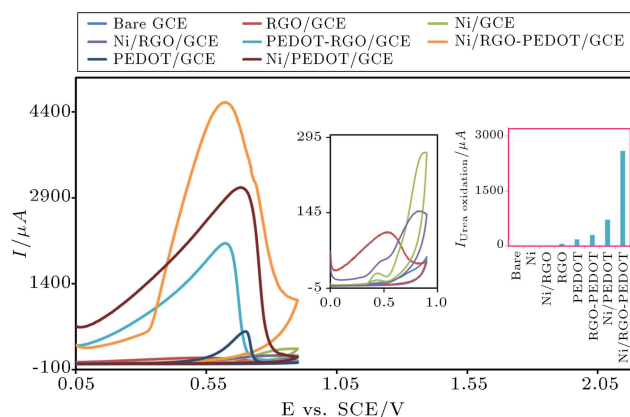
The comparison of the active surface area of different electrodes shows an enhancement (2.3, 2.7, and 3.3 times for Ni/RGO/GCE, RGO-PEDOT/GCE, and Ni/RGO-PEDOT/GCE, respectively, compared to the bare GCE), which indicates that the presence of RGO nanosheet can enhance the active surface area of electrode. The advantages of Ni/PEDOT-RGO/GCE were elucidated with higher conductivity, fast electron transfer rate, good anti-agglomerate properties, and inherent catalytic ability of RGO and PEDOT [24–26].

### 3.3. Electrocatalytic oxidation of urea at Ni/RGO-PEDOT/GCE

Prior to evaluation of the electrocatalytic activity of the as-prepared catalysts toward urea oxidation, one cycle of potential sweeps between 0 V and 0.9 V at  $100 \text{ mVs}^{-1}$  was applied onto the GC electrode modified with catalysts in 1 M sodium hydroxide solution in the absence of urea. As shown in Figure 4, for the Ni/PEDOT-RGO/GCE, Ni/PEDOT/GCE, PEDOT/GCE, PEDOT-RGO/GCE, and RGO/GCE,



**Figure 4.** CVs of Ni/PEDOT-RGO/GCE, Ni/PEDOT/GCE, PEDOT/GCE, PEDOT-RGO/GCE, and RGO/GCE in 1.0 M NaOH solution at the scan rate of  $100 \text{ mVs}^{-1}$ .



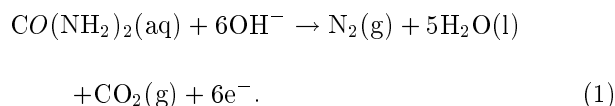
**Figure 5.** CVs for bare GCE, RGO/GCE, Ni/GCE, PEDOT/GCE, PEDOT-RGO/GCE, Ni/PEDOT/GCE, and Ni/PEDOT-RGO/GCE in 0.3 M urea and 1.0 M NaOH solution at a scan rate of  $100 \text{ mV s}^{-1}$ .

an oxidation peak was observed that can be attributed to the over-oxidation reaction onto the surface of PEDOT [37]. Another peak for Ni/PEDOT-RGO/GCE was also detected in 0.4 V ascribed as nickel nanoparticles oxidation [38].

Figure 5 shows the cyclic voltammograms for bare, RGO, Ni, PEDOT, PEDOT-RGO, Ni/PEDOT/GCE, and Ni/PEDOT-RGO/GCE as different catalyst-coated electrodes in 0.3 M urea and 1 M NaOH solution at a scan rate of  $100 \text{ mV s}^{-1}$ . The highest peak currents were observed on Ni/PEDOT-RGO/GCE, indicating the highest catalytic activity for urea oxidation, nearly 6, 2.4, and 1.5 times that on PEDOT/GCE, PEDOT-RGO/GCE, and Ni/PEDOT/GCE electrode catalysts, respectively, indicating that Ni/PEDOT-RGO/GCE might provide much more electroactive sites than other modified electrodes for urea. The synergistic effect could also be observed in this case. As shown in Figure 5, there were no obvious oxidation peaks on the bare GCE, indicating that the bare electrode unfit to urea oxidation and the electrocatalytic performance of bare GCE can be neglected in the presence of urea. To investigate the role of PEDOT on RGO surface in the electrochemical oxidation of urea, the cyclic response of the RGO/GC and PEDOT-RGO/GC electrodes was also recorded. The results indicated that the presence of PEDOT on graphene matrix exhibited 6 times improvement on the oxidation peak current for urea at PEDOT-RGO composite. The higher electrocatalytic current response of the PEDOT-RGO composite than that of the RGO film was presumably caused by a more favorable electrochemical environment for urea on the electrode [39]. PEDOT:PSS chains can be assembled onto the surfaces of RGO sheets through  $\pi$ -stacking interactions between both components [40,41]. The close interaction between PEDOT and RGO in the PEDOT-RGO composite allows the PEDOT to accumulate more electrons in PEDOT-RGO composite

than in RGO without PEDOT. Moreover, due to the nanometer size, large accessible surface per volume, high conductivity, and well dispersion, the PEDOT-RGO nanocomposite offers a favorite microenvironment for electron transfer between urea and the underlying electrode, which results in the improvement on the electrochemical response [42].

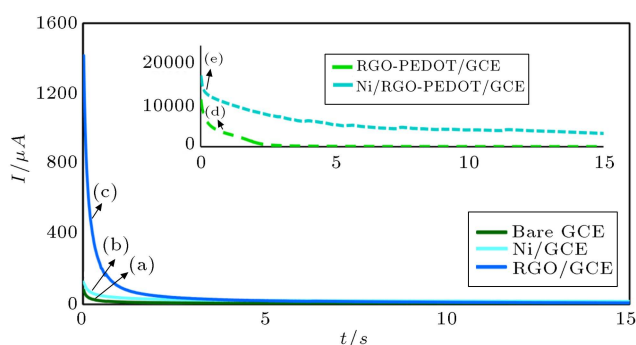
The urea electrochemical decomposition process in alkaline media is described below:



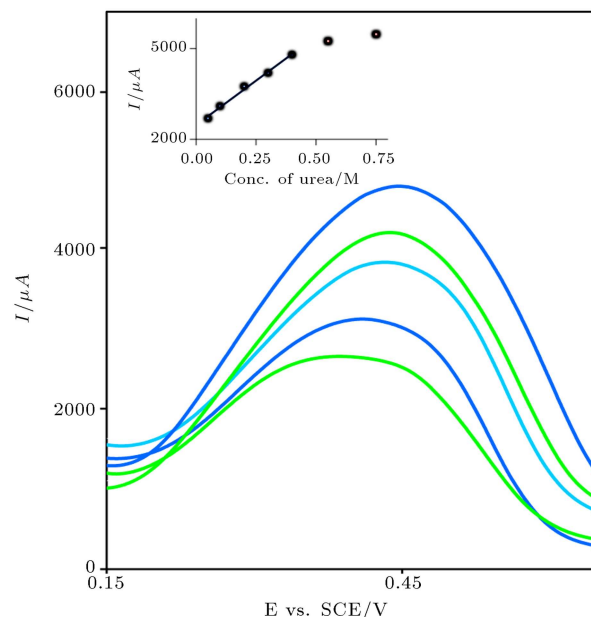
Hence, Ni NPs/PEDOT-RGO catalyst is promising material for urea removal or decomposition from urea-rich wastewater.

The results indicated that the presence of RGO in the polymer matrix surface had great improvement on the electrochemical response (an enhancement of the peak current). The superior performance of Ni/PEDOT-RGO/GCE catalysts may arise from utilization of heterogeneous nucleation sites for NPs and the greatly increased electronic conductivity of the supports.

The steady-state behavior of urea oxidation on the surface of nanocomposite was studied by chronoamperometric measurement. Figure 6 indicates the results of chronoamperometric measurements of bare GCE (a), Ni/GCE (b), RGO/GCE (c), PEDOT-RGO/GCE (d), Ni/PEDOT-RGO/GCE (e) electrodes in the presence of urea. All electrodes reach a steady-state Faradic current response within 15 sec approximately. It was observed that Ni/PEDOT-RGO/GCE electrode produces a higher steady-state current density in comparison with that of the other electrode during the whole measurements. This could be attributed to the higher electrochemically active surface area of Ni/PEDOT-RGO/GCE which is in agreement with the results of cyclic voltammetry of urea oxidation.



**Figure 6.** Chronoamperograms of bare GCE (a), Ni/GCE (b), RGO/GCE (c), PEDOT-RGO/GCE (d), and Ni/PEDOT-RGO/GCE (e) electrodes in the presence of 0.3 M urea and 1 M NaOH at constant potential of 0.7 V.



**Figure 7.** Linear sweep voltammograms of solutions containing 0.05, 0.1, 0.2, 0.3, 0.55, 0.65, and 0.75 M urea in 1 M NaOH.

Figure 7 shows the effect of urea concentration on the anodic peak current at Ni/PEDOT-RGO/GCE in 1 M NaOH. It is clearly observed that as the urea concentration increases, the peak height increases linearly with urea concentration up to 0.40 M. It could be assumed that the increase is due to the presence of a diffusion controlled process that appears to play an important role at low urea concentrations. While the urea concentration exceeds this limit, the rate of the whole oxidation process seems to be limited by that of the catalytic process in origin and its rate depends on the reaction among urea and composite species.

#### 4. Conclusion

Nanocomposite of Ni/RGO-PEDOT:PSS was prepared by a facile two-step method; first, mixing solution of RGO and PEDOT:PSS was performed, and then Ni NPs were electrodeposited on the composite film through electrochemical deposition. Electrochemical studies, such as cyclic voltammetry and chronoamperometry, were performed. Owing to the synergistic effect of PEDOT-RGO and Ni NPs, Ni NPs/PEDOT-RGO modified electrode exhibited excellent electrocatalytic activity toward urea oxidation, and it could be developed into a highly desirable urea decomposer and hydrogen producer.

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