

Electrocatalytic oxidation of methanol and other short chain aliphatic alcohols at Ni(II)–quercetin complex modified multi-wall carbon nanotube paste electrode

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Abstract A modified electrode Ni(II)–Qu–MWCNT-PE has been fabricated by electrodepositing nickel(II)–quercetin [Ni(II)–Qu] complex on the surface of multi-wall carbon nanotube paste electrode (MWCNT-PE) in alkaline solution. Ni(II)–Qu–MWCNT-PE exhibits the characteristic of improved reversibility and enhanced current responses of the Ni(III)/Ni(II) couple compared with Ni(II)–MWCNT-PE and Ni(II)–Qu-carbon paste electrode. It also shows electrocatalytic activity toward the oxidation of methanol and other short chain aliphatic alcohols, such as ethanol, 1-propanol, and 1-butanol. The catalytic peak current and peak potential decrease in exponential form with the increase of carbon number of the chains. Kinetic parameters such as the electron transfer coefficient, α , rate constant, k_s , of the electrode reaction, and the catalytic rate constant, k_{cat} , for oxidation of methanol are determined. The stability and reproducibility of the Ni(II)–Qu–MWCNT-PE are good for practical applications.

Keywords Methanol · Nickel · Quercetin · Multi-wall carbon nanotubes · Modified electrode · Electrocatalysis

Introduction

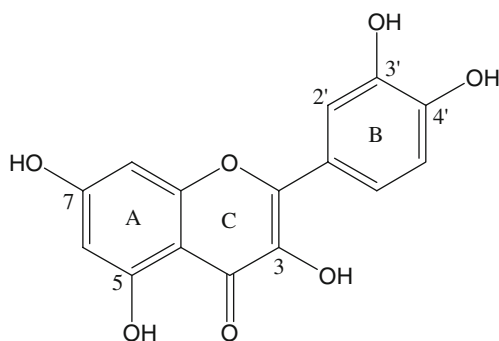
The alcohol fuel cells are of great concern for their several advantages, such as high efficiency, low polluting emissions, a potentially renewable fuel source, and convenient refueling. One problem encountered in the development of alcohol fuel cells is the typically large overpotentials in the direct oxidation of alcohols such as methanol at most unmodified electrode surfaces [1–4]. Thus, a large number of investigations have been carried out to develop modified electrodes to diminish the overpotentials using such modifiers as metal alloys [5–7], nanoparticles [8], polymeric matrixes incorporated metal [9–11], and nickel or cobalt hydroxide [12, 13]. Among others, different nickel(II) complexes such as Ni(II)–tetraazamacrocyclic [14], Ni(II)–curcumin [15], Ni(II) dimethylglyoxime [16], and so on [17–19] have shown interesting catalytic properties toward the electro-oxidation of methanol or other aliphatic short chain alcohols with good stability and low cost. The Ni(III)/Ni(II) redox couple in nickel(II) complexes acts as redox mediators between a substrate and an electrode in electro-oxidation processes. Therefore, it is of practical importance to further investigate such nickel(II) complexes modified electrode.

Quercetin (Qu, structure shown in Scheme 1) belongs to the flavonoid family that widely distributes in fruits and vegetables and has broad pharmacological activities [20]. It can complex with various metal cations such as nickel(II) to form stable complex with demonstrable antibacterial property and anti-tumor activity [21–23]. However, to our knowledge, there is no report about quercetin–metal or other flavonoid–metal complex modified electrode.

Additionally, carbon nanotubes (CNT) have been paid enormous attention due to their exceptional electrical,

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Scheme 1 Structural formula of quercetin

chemical, and mechanical properties. These properties make them extremely attractive as electrode material [24–26]. Recently, CNT composite materials that possess some unique properties and enhance electrocatalytic activity have gained growing interest [27–29].

Thus, in this work, Ni(II)–Qu complex and multi-wall carbon nanotubes (MWCNT) were both employed to fabricate a chemically modified electrode Ni(II)–Qu–MWCNT-PE by electrodepositing Ni(II)–Qu complex on the surface of multi-wall carbon nanotube paste electrode (MWCNT-PE). The electrochemical behavior and the electrocatalytic property to the oxidation of methanol and other aliphatic short chain alcohols of the Ni(II)–Qu–MWCNT-PE were investigated by cyclic voltammetry and chronoamperometry.

Materials and methods

Materials

Quercetin (purity >98.9%) was purchased from Shanghai Reagent Company (Shanghai, China). MWCNT (diameter, 10–20 nm; length, 1–2 μm ; purity, >95%) was purchased from Shenzhen Nanotech Port (Shenzhen, China) and used without further purification. Graphite powder (spectral pure) was purchased from Beijing Chemical Reagent Factory (Beijing, China). Ni(II) ion was prepared via the dissolution of 10 mM NiSO₄ in a 2.5% ammonia solution. All the chemicals used were of analytical-reagent grade. Twice-distilled water was used throughout the experiments.

Apparatus

Electrochemical measurements were carried out on a CHI 650C electrochemical workstation (Chenhua Instrumental Company, Shanghai, China) controlled by a personal computer. A three-electrode system was employed, including a homemade Ni(II)–Qu–MWCNT-PE working elec-

trode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. All the potentials quoted in this work were referred to SCE. All experiments were carried out at room temperature.

Electrode preparation

MWCNT-PE was prepared by mixing MWCNT and paraffin oil in a ratio of 3:2 (*w/w*) in a mortar. The conventional carbon paste electrode (CPE) was prepared in a similar way by mixing graphite powder with paraffin oil. A portion of the resulting paste was packed firmly into the cavity (1.6-mm diameter) of a polytetrafluoroethylene tube. The electric contact was established via a copper wire. The surface of electrode was smoothed on a weighing paper and rinsed with water. The efficient area of the MWCNT-PE was about 1.9 times as large as that of the CPE using K₃Fe(CN)₆ as a probe according to Randles–Sevcik equation.

Ni(II)–Qu–MWCNT-PE was fabricated by the following procedure: MWCNT-PE was placed in 0.1 M NaOH solution containing 0.5 mM Qu and 0.5 mM Ni(II) ion and scanned consecutively between 0.1 and 0.7 V in scan rate of 0.1 V s⁻¹ for 60 cycles. Qu–MWCNT-PE and Ni(II)–MWCNT-PE were fabricated by the same procedure as Ni(II)–Qu–MWCNT-PE in 0.5 mM Qu or 0.5 mM Ni(II) ion, respectively. Also, Ni(II)–Qu–CPE was fabricated by the same procedure as the Ni(II)–Qu–MWCNT-PE, but the substrate electrode was a CPE.

Results and discussion

The preparation and electrochemical behavior of Ni(II)–Qu–MWCNT-PE

Voltammograms of 60 consecutive potential cycles between 0.1 and 0.7 V in 0.1 M NaOH solution containing 0.5 mM Ni(II) ion and 0.5 mM Qu at MWCNT-PE with scan rate of 0.1 V s⁻¹ are shown in Fig. 1. As shown, an anodic peak and a cathodic peak were observed with peak potential at around 0.51 and 0.37 V, respectively. Peak currents increased gradually with continuous scanning, which indicated that poly[Ni(II)–Qu] film was deposited on the surface of MWCNT-PE, and a Ni(II)–Qu–MWCNT-PE was prepared.

To investigate the electrodeposition mechanism, the electrochemical behavior of Ni(II)–Qu–MWCNT-PE was examined and compared with those of Qu–MWCNT-PE, Ni(II)–MWCNT-PE, and Ni(II)–Qu–CPE. Figure 2 shows cyclic voltammograms of Qu–MWCNT-PE (curve a), Ni(II)–Qu–MWCNT-PE (curve b), Ni(II)–MWCNT-PE (curve c), and Ni(II)–Qu–CPE (curve d) in 0.1 M NaOH

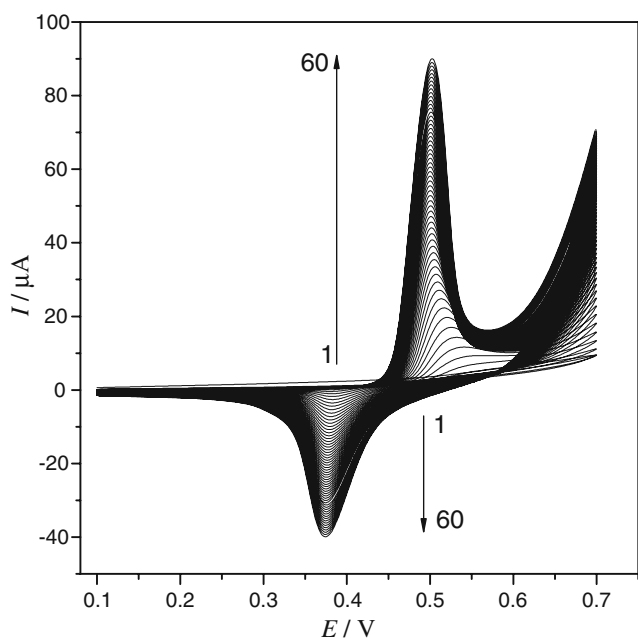
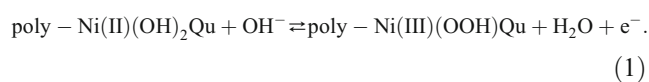


Fig. 1 Multicycle voltamograms of MWCNT-PE in 0.1 M NaOH solution containing 0.5 mM Ni(II) ion and 0.5 mM Qu. Scan rate, 0.1 V s⁻¹; potential range, 0.1–0.7 V

solution at scan rate of 20 mV s⁻¹. At Qu–MWCNT-PE, there was no electrochemical response of Qu, as reported by Xu and Kim [30] that Qu exhibited no oxidation beyond pH 10. At Ni(II)–Qu–MWCNT-PE, a pair of well-defined redox peak with high peak current ($I_{pa}=28.6 \mu\text{A}$) and low peak potential separation ($\Delta E_p=88 \text{ mV}$) were observed. However, at Ni(II)–MWCNT-PE, the peak current of Ni(III)/Ni(II) couple was low ($I_{pa}=0.49 \mu\text{A}$)

and the peak potential separation was high ($\Delta E_p=130 \text{ mV}$). Also, the peak current response was low ($I_{pa}=7.9 \mu\text{A}$) and the peak potential separation was high ($\Delta E_p=94 \text{ mV}$) at Ni(II)–Qu–CPE compared with those at Ni(II)–Qu–MWCNT-PE. The above results indicated that the anodic and cathodic peaks observed were due to the redox reaction of Ni(III)/Ni(II) couple in Ni(II)–Qu–MWCNT-PE. Qu was easy to adsorb at the MWCNT surface [31] and its presence as complexant allowed the Ni(II) ion to adsorb to the MWCNT-PE surface more easily. The presence of MWCNT might supply larger surface area to allow more deposition of poly[Ni(II)–Qu] and might accelerate electron transfer process between poly[Ni(II)–Qu] and the substrate electrode. Thus, the reversibility and electrochemical responses of Ni(III)/Ni(II) couple in Ni(II)–Qu–MWCNT-PE improved. The mechanism of film formation was probably that Qu was first adsorbed at MWCNT-PE surface and then the incorporation of Ni(II) ion into the structure made the film conductive and allowed the growth of a multilayer system. The redox process of the modified electrode was expressed as follows [14–17]:



The influence of scan rate in a wide range of 0.005–2 V s⁻¹ to the electrochemical behavior of Ni(II)–Qu–MWCNT-PE was also investigated (Fig. 3a). As shown, the peak currents increased with the increase of scan rate, ν , and

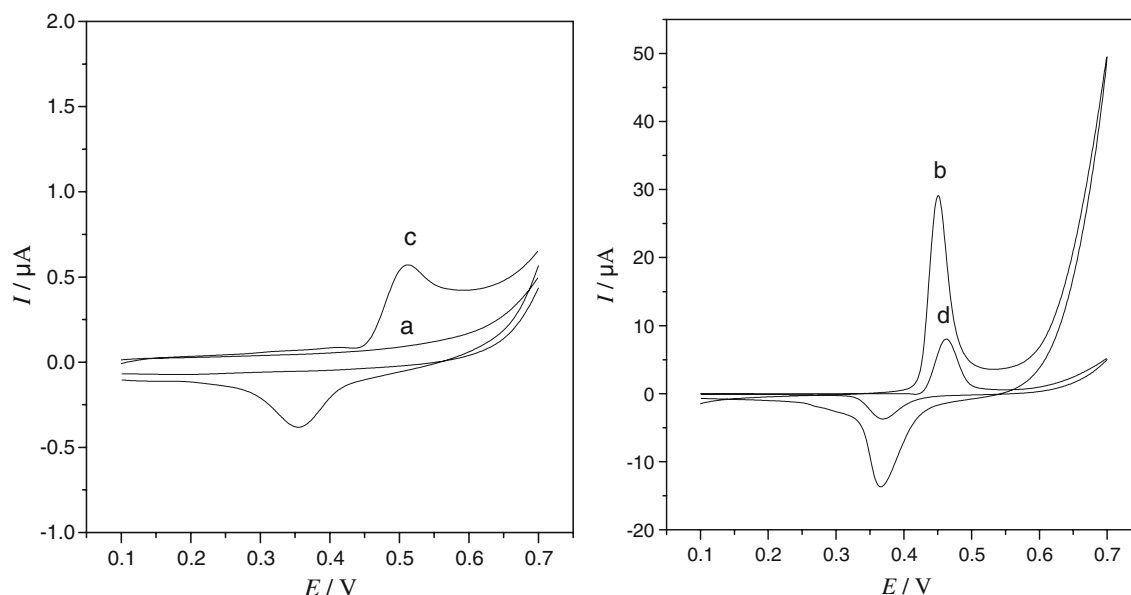


Fig. 2 Cyclic voltammograms of Qu–MWCNT-PE. (a), Ni(II)–Qu–MWCNT-PE (b), Ni(II)–MWCNT-PE (c), and Ni(II)–Qu–CPE (d) in 0.1 M NaOH solution at scan rate of 20 mV s⁻¹

were proportional to scan rate below 0.1 V s^{-1} (Fig. 3b), which indicated a surface-confined redox process. According to the following equation [32]:

$$I_p = \frac{n^2 F^2 v A \Gamma_c}{4RT} \quad (2)$$

where I_p was the peak current, A the electrode surface area, and the other symbols had their usual meanings. The surface coverage concentration (Γ_c) of the redox couple was calculated to be $3.5 \times 10^{-8} \text{ mol cm}^{-2}$ from the slope of I_p versus v relationship ($v \leq 0.1 \text{ V s}^{-1}$). When $v > 0.1 \text{ V s}^{-1}$, the peak currents became proportional to the square root of scan rate (Fig. 3c), signifying the dominance of a diffusion process. This diffusion process was expressed in Eq. 1 and

might be the charge neutralization of the film during the oxidation/reduction process [19].

Moreover, the E_p was proportional to the logarithm of scan rate when $v \geq 0.4 \text{ V s}^{-1}$ (Fig. 3d). Based on the Laviron theory [33], the electron transfer coefficient, α , could be calculated. For cathodic and anodic peak, the slope of E_p versus $\log v$ relationship was -0.098 and 0.149 , respectively. The calculated value of α was 0.60 . According to the following equation:

$$\log k_s = \alpha \log(1 - \alpha) \log \alpha - \log(RT/nFv) - \alpha(1 - \alpha)nF\Delta E/2.3RT \quad (3)$$

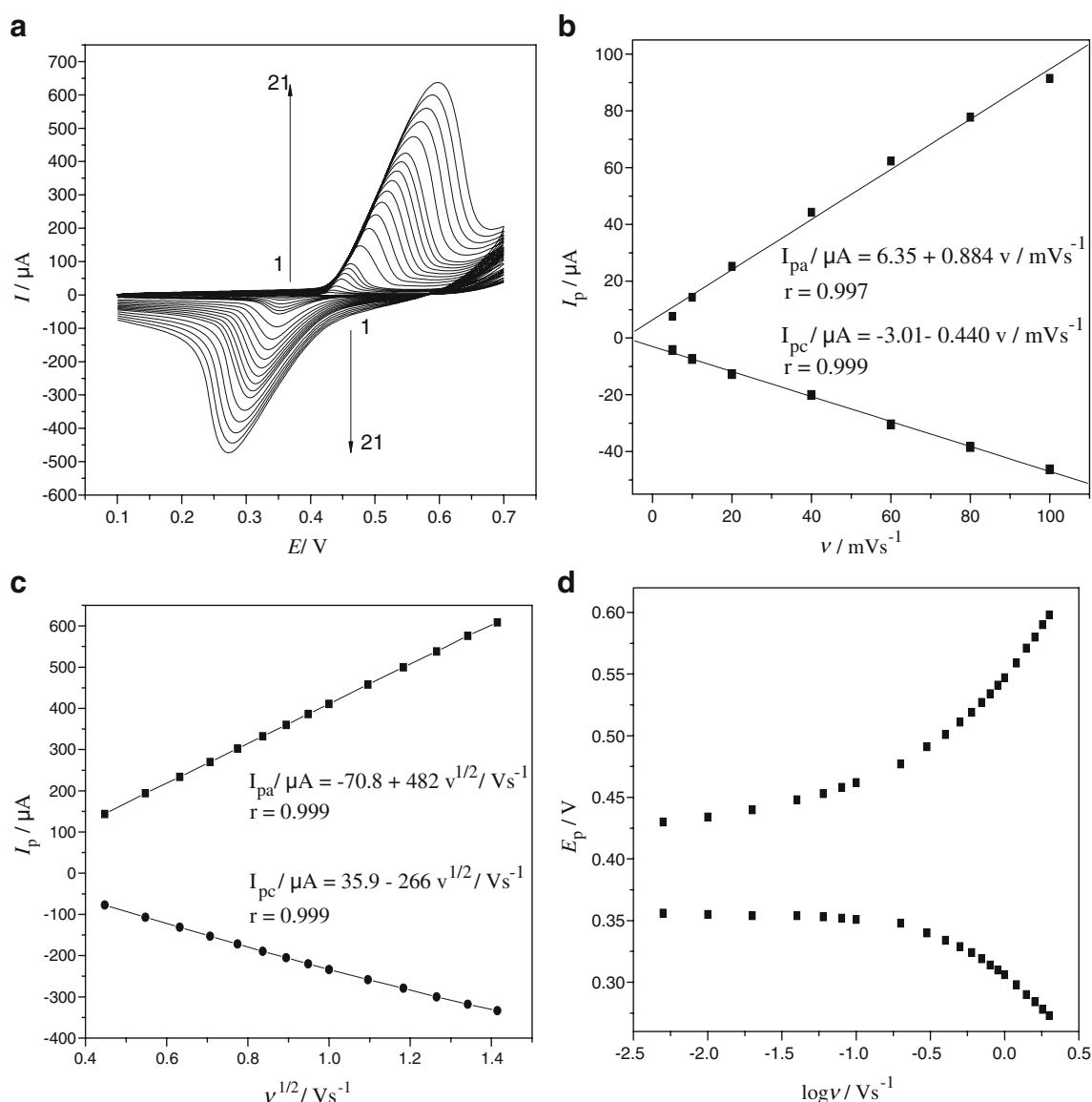


Fig. 3 **a** Cyclic voltammograms of Ni(II)-Qu-MWCNT-PE in 0.1 M NaOH solution at various scan rates (from *inner to outer*): 0.005 to 2 V s^{-1} . **b** Plot of I_p vs. v . **c** Plot of I_p vs. $v^{1/2}$. **d** Plot of E_p vs. $\log v$

where k_s was rate constant of electrode reaction and other symbols had their conventional meanings. k_s was calculated to be 1.04 s^{-1} .

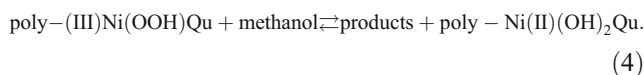
Electrocatalytic oxidation of methanol and other aliphatic short chain alcohols at Ni(II)–Qu–MWCNT-PE

Methanol and other short chain aliphatic alcohols (ethanol, 1-propanol, and 1-butanol) did not undergo oxidation prior to the discharge of the supporting electrolyte at CPE and MWCNT-PE in 0.1 M NaOH solution.

The cyclic voltammograms of Ni(II)–Qu–MWCNT-PE and Ni(II)–Qu–CPE in the absence and the presence of 0.10 M methanol are shown in Fig. 4. As shown, a pair of redox peaks corresponded to the Ni(III)/Ni(II) couple was observed in the absence of methanol (Fig. 4a, c). However, in the presence of 0.10 M methanol (Fig. 4b, d), peak P_{a1} corresponded to the oxidation of Ni(II) to Ni(III) at +0.46 V increased slightly, and a new anodic peak P_{a2} at +0.58 V with a significantly large peak current appeared. Moreover, the peak current of P_{a2} increased linearly with methanol concentration, which indicated that it pertained to the process in which methanol was involved. The appearance of the new large anodic peak P_{a2} at more positive potential could lead to the conclusion that methanol oxidation took place mainly after the oxidation of Ni(II) to Ni(III) and the catalytic role of Ni(III) for methanol oxidation was obvious as proposed previously by Fleischmann et al. [34]. At the reverse scan, an anodic peak appeared at about +0.57 V as methanol was still

oxidized. The cathodic peak P_{c1} corresponding to the reduction of residual Ni(III) to Ni(II) decreased slightly.

Figure 4 also shows that the oxidation peak current of methanol at Ni(II)–Qu–MWCNT-PE was much larger than that at Ni(II)–Qu–CPE, which indicated that the combination of MWCNT and Ni(II)–Qu complex definitely improved the characteristic of methanol oxidation. Thus, the electrocatalytic oxidation of methanol at Ni(II)–Qu–MWCNT-PE might be expressed as follows:



Furthermore, the electrocatalytic oxidation of other short chain aliphatic alcohols such as ethanol, 1-propanol, and 1-butanol at Ni(II)–Qu–MWCNT-PE was also investigated. As in the case of methanol, the electrocatalytic oxidation of the other aliphatic alcohols studied gave rise to two different anodic peaks, indicating the same reaction mechanism as methanol at Ni(II)–Qu–MWCNT-PE. However, with carbon number Z of the aliphatic chain increased, the catalytic peak currents decreased and obeyed the experience equation of $I_{pa}/\mu\text{A} = 384.8e^{-152Z} + 41.9$ ($r = 0.999$) (Fig. 5a); meanwhile, the catalytic peak potential shifted to negative values and obeyed the equation of $E_{pa}/\text{V} = 0.273e^{-154Z} + 0.532$ ($r = 1$) (Fig. 5b).

These results indicated that Ni(II)–Qu–MWCNT-PE was more efficient in the electrocatalytic oxidation methanol. Thus, the electrocatalytic oxidation of methanol was mainly discussed in the following.

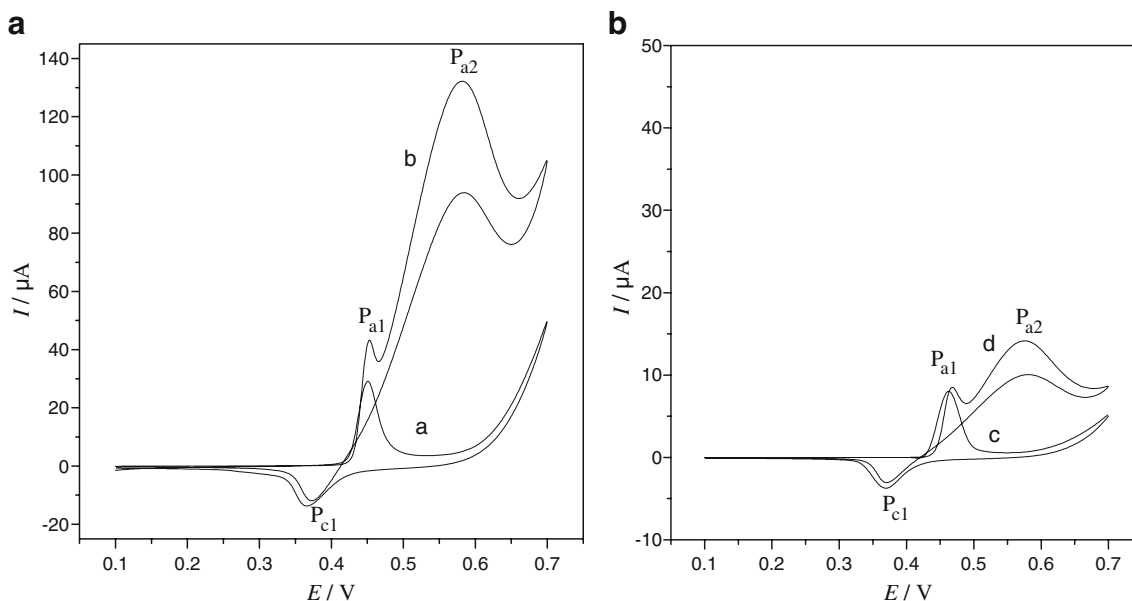


Fig. 4 Cyclic voltammograms of Ni(II)–Qu–MWCNT-PE (**a**) and Ni(II)–Qu–CPE (**b**) in the absence (**a**, **c**) and the presence (**b**, **d**) of 0.10 M methanol in 0.1 M NaOH solution at scan rate of 20 mV s^{-1}

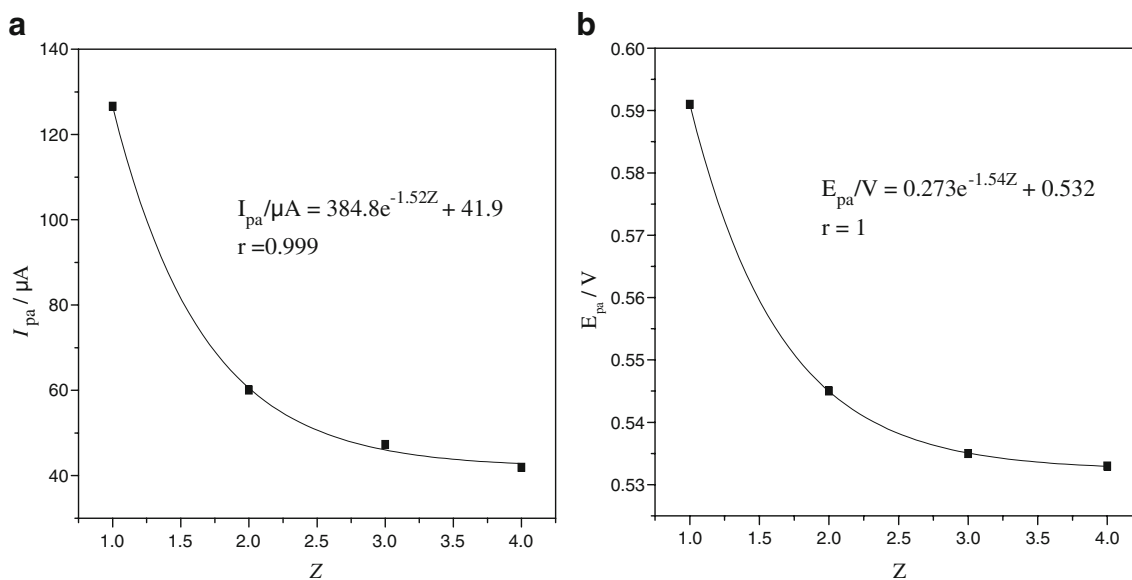


Fig. 5 **a** Plot of the catalytic peak current to the carbon number Z . **b** Plot of the catalytic peak potential to the carbon number Z

To further investigate the kinetic process of the catalytic reaction, linear sweep voltammetry and chronoamperometry were employed. Figure 6a shows the linear sweep voltammograms of 0.10 M methanol at different scan rates. As shown, the peak current of P_{a2} for anodic oxidation of methanol was proportional to the square root of the scan rate (Fig. 6b), which indicated that the electrocatalytic process was controlled by methanol diffusion to the electrode/solution interface and depended on the

methanol concentration in solution, which was an ideal case for quantitative applications. The peak potential for the catalytic oxidation of methanol shifted to more positive values with increasing the scan rate, suggesting that there was a kinetic limitation in the reaction between the redox sites of the modifier and methanol.

By recording chronoamperograms of different concentration of methanol (Fig. 7a), the catalytic rate constant, k_{cat} , was evaluated. At intermediate time, when the current

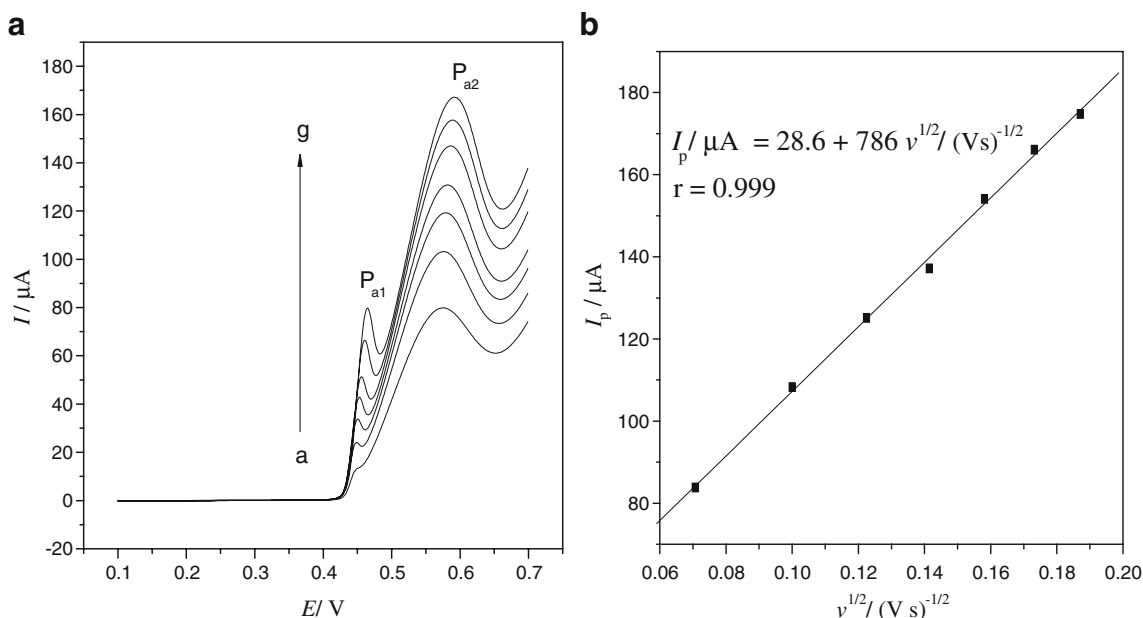


Fig. 6 **a** Linear sweep voltammograms of the Ni(II)-Qu-MWCNT-PE in 0.1 M NaOH solution containing 0.10 M methanol at various scan rates (from **a** to **g**): 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035 V s^{-1} . **b** Plot of E vs. $v^{1/2}$

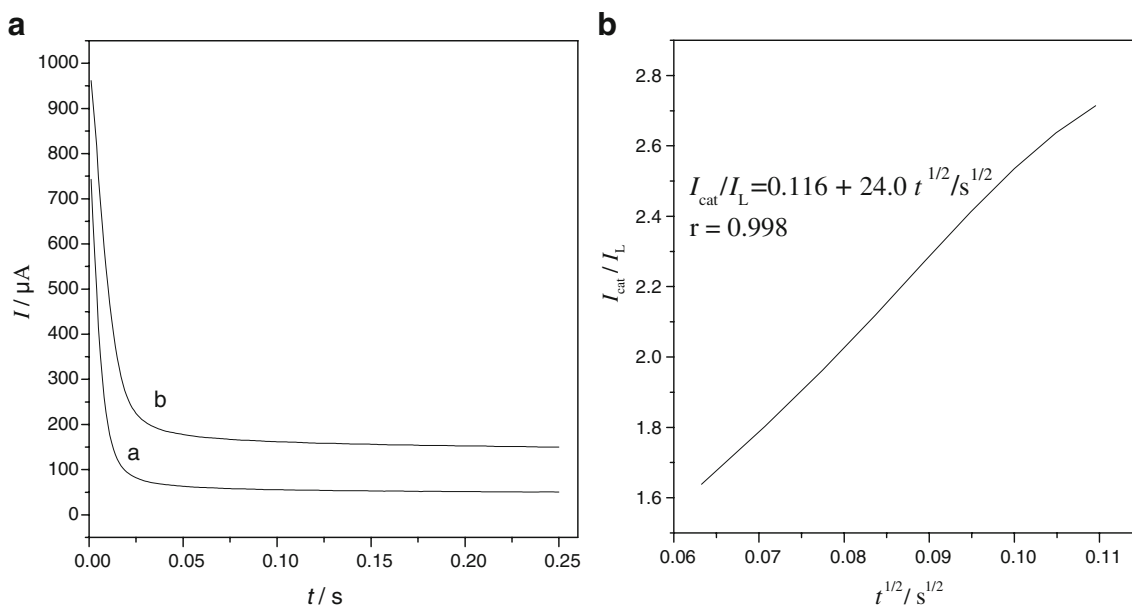


Fig. 7 **a** Chronoamperograms of Ni(II)-Qu-MWCNT-PE in 0.1 M NaOH solution in the absence (**a**) and the presence (**b**) of 0.10 M methanol. **b** Plot of I_{cat}/I_L vs. $t^{1/2}$. Initial potential 0.5 V, final potential 0.7 V

was dominated by the rate of the electrocatalytic reaction of methanol, the catalytic current, I_{cat} , could be written as follows [35]:

$$I_{cat}/I_L = \pi^{1/2}(k_{cat}c_0t)^{1/2} \tag{5}$$

where I_{cat} and I_L were the oxidation currents of the Ni(II)-Qu-MWCNT-PE in the presence and the absence of methanol, respectively. k_{cat} , c_0 , and t were the catalytic rate constants ($M^{-1} s^{-1}$), the bulk concentration (M) of methanol, and time elapsed (s). From the slope of the I_{cat}/I_L versus $t^{1/2}$ relationship (Fig. 7b), the k_{cat} was calculated to be $1.83 \times 10^3 M^{-1} s^{-1}$ when $c_0=0.10$ M.

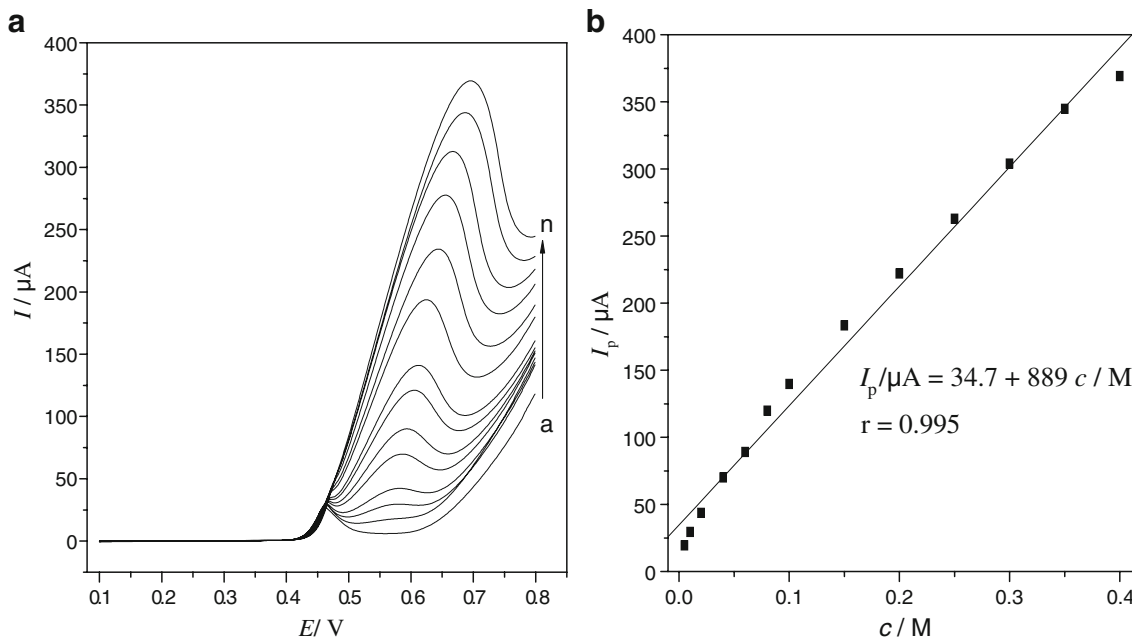


Fig. 8 **a** Linear sweep voltammograms of the Ni(II)-Qu-MWCNT-PE for electrocatalytic oxidation of methanol at scan rate of 20 mV s^{-1} in 0.1 M NaOH solution with different concentrations of methanol, from **a** to **n**: 0.0 to 0.4 M. **b** Dependence of methanol oxidation peak current on the methanol concentration

Relationship between the catalytic currents and the methanol concentration

Figure 8a shows the linear sweep voltammograms of Ni(II)–Qu–MWCNT-PE in 0.1 M NaOH solution with increasing the concentration of methanol in the range of 5.0 mM to 0.4 M. As shown, the catalytic peak current increased linearly with the methanol concentration up to 0.40 M (Fig. 8b). The linear regression equation was $I_{cat}/\mu A = 34.7 + 889c_{methanol}/M$ with the linear relation coefficient of 0.995 ($n=13$).

Stability and reproducibility

The stability and reproducibility of Ni(II)–Qu–MWCNT-PE were studied by cycle voltammetry in a 0.1 M NaOH solution. Investigation indicated that after 500 continuous potential cycles at 20 mV s^{-1} , the peak heights of the cycle voltammogram decreased less than 5%. A set of ten replicate measurements for 0.050 M methanol yielded a relative standard deviation of 2.8%. In addition, after 30 days of storage in dry conditions, no significant change in current response was observed. Thus, the stability and reproducibility of the Ni(II)–Qu–MWCNT-PE were good for practical applications.

Conclusions

A new modified electrode Ni(II)–Qu–MWCNT-PE was fabricated. The reversibility and current responses of Ni(III)/Ni(II) couple at Ni(II)–Qu–MWCNT-PE were improved in comparison with those at Ni(II)–MWCNT-PE and Ni(II)–Qu-CPE. Ni(II)–Qu–MWCNT-PE also exhibited electrocatalytic activity for the oxidation of methanol and other short chain aliphatic alcohols, such as ethanol, 1-propanol, and 1-butanol. The combination of unique properties of MWCNT and Ni(II)–Qu complex resulted in the remarkable synergistic augmentation on the electrochemical responses. Some kinetic parameters were also calculated, and the stability and reproducibility of Ni(II)–Qu–MWCNT-PE were good for applications.

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