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Enhanced electrocatalytic performance of cobalt oxide nanocubes incorporated reduced graphene oxide modified platinum electrode for methanol oxidation

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Graphical Abstract

Cobalt oxide nanocubes incorporated reduced graphene oxide prepared by hydrothermal method and used for the electrocatalytic oxidation of methanol.
Enhanced electrocatalytic performance of cobalt oxide nanocubes incorporated reduced graphene oxide modified platinum electrode for methanol oxidation†

Muhammad Shahid Mehmood¹, Alagarsamy Pandikumar²*, Amir Moradi Golsheikh¹, Huang Nay Ming¹*, Lim Hong Ngee²,³*

¹ Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
² Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
³ Functional Device Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Corresponding author’s: huangnayming@um.edu.my (Huang N.M.), pandikumarinbox@gmail.com (Pandikumar. A), and janet_limhn@science.upm.edu.my (Lim H.N.)

Abstract

Herein, we report a facile hydrothermal method for the preparation of cobalt oxide nanocubes incorporated reduced graphene oxide (rGO-Co₃O₄ nanocubes) for electrocatalytic oxidation of methanol. The synthesized rGO-Co₃O₄ nanocubes were characterized using transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Raman techniques. The electrochemical behavior of rGO-Co₃O₄ nanocubes modified electrode was studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The electrocatalytic performances of rGO-Co₃O₄ nanocube-modified electrodes with different wt. % of GO were investigated in relation to methanol oxidation in an alkaline medium. The rGO-Co₃O₄ nanocubes modified electrode showed enhanced current density due to oxidation of methanol when compared to the bare Pt, rGO, and Co₃O₄ nanocubes modified electrodes. The optimal GO content for an rGO-Co₃O₄ nanocube-modified electrode to achieve a high electrocatalytic oxidation of methanol was 2 wt. %, and it showed an anodic peak current density of 362 μA/cm².
Introduction

The constantly increasing energy demand due to the depletion of conventional fossil fuel reserves and the rapid growth of environmental issues have led to search for alternative power sources.\textsuperscript{1,2} These include direct methanol fuel cells (DMFCs) as alternative green, environmentally friendly, and sustainable power sources that can directly convert the chemical energy of methanol into electrical energy.\textsuperscript{3,4} A polycrystalline Pt electrode is the most commonly used electrode material in DMFCs. However, its high cost, rarity, low power density, and poor CO-poisoning tolerance significantly hinder their commercialization and practical application.\textsuperscript{5,6} In order to reach a high power density and low production cost for DMFCs, well-designed and fabricated high-performance electrocatalysts with controlled compositions and morphologies have been emerged as a key point for realizing high device performance.\textsuperscript{5,6}

In this area, carbon-based nanomaterials, including activated carbon, carbon nanotubes (SWCNT, DWCNT, MWCNT), GO, and rGO have enormous potential to boost the performance of DMFCs.\textsuperscript{3,7,8} Among these, graphene plays a crucial role in the fabrication of advanced composite/hybrid electrocatalysts for high performance DMFCs because of its unique physicochemical properties, including a high specific surface area, superior electronic conductivity, and excellent stability.\textsuperscript{8-13} Several attempts have been made to apply metal and metal oxide nanomaterials incorporated graphene modified electrodes in DMFC applications to attain a high power density.\textsuperscript{14,15}

Metal oxide incorporated graphene composite gained tremendous attention because of their low-cost, facile synthesis, high electrocatalytic activity, and durability in DMFC applications.\textsuperscript{4,8,11,14,15} Currently, cobalt oxide (Co$_3$O$_4$) nanomaterials are more attractive due
to their simple preparation method, diverse morphology, high catalytic activity, and applicability in electrocatalysis.\textsuperscript{16} Recently, \( \text{Co}_3\text{O}_4 \) nanomaterials combined with graphene have shown excellent electrocatalytic activities. Hence, these have been applied in the field of electrochemical energy conversion and storage.\textsuperscript{17} Xiao et al. reported the influence of the surface structure on the electrocatalytic activity of \( \text{Co}_3\text{O}_4 \) anchored graphene sheets toward an oxygen reduction reaction for a fuel cell application.\textsuperscript{18}

In the present investigation, cobalt oxide nanocubes incorporated reduced graphene oxide (rGO-\( \text{Co}_3\text{O}_4 \) nanocubes) were prepared using GO (simplified Hummer’s method\textsuperscript{19}) with Co(II) ions by a simple hydrothermal method and used for electrocatalytic methanol oxidation. The as-prepared rGO-\( \text{Co}_3\text{O}_4 \) nanocubes were characterized using TEM, FESEM, XRD, and Raman techniques. The electrochemical behavior of rGO-\( \text{Co}_3\text{O}_4 \) nanocubes modified electrode was investigated using the CV and EIS techniques with a \([\text{Fe}_3(\text{CN})_6]\) redox couple as an electrochemical probe. The electrocatalytic performance toward methanol oxidation was investigated in an alkaline medium for rGO-\( \text{Co}_3\text{O}_4 \) nanocubes modified electrodes with different wt. % of GO content and the optimized GO content for high performance was found to be 2 wt. %, with a high peak current density of 362 \( \mu \text{A/cm}^2 \) during a forward scan. The high electrochemical performance, low-cost, and ease of fabrication make these rGO-\( \text{Co}_3\text{O}_4 \) nanocubes modified electrode a potential candidate for direct methanol fuel cell applications.

**Experimental Methods**

**Materials**

Graphite flakes were purchased from Asbury Inc. (USA). Sulfuric acid (\( \text{H}_2\text{SO}_4 \), 98\%), potassium permanganate (\( \text{KMnO}_4 \), >99\%), hydrochloric acid (\( \text{HCl} \), 35\%), and ammonia
solution (NH₃, 25%) were purchased from R & M Chemicals. Cobalt acetate tetrahydrate (Co(CH₃COO)₂·4H₂O) was purchased from Sigma Aldrich. Hydrogen peroxide (H₂O₂, 35%) and methanol (CH₃OH) were obtained from System, Malaysia. Distilled water was used throughout the experimental work.

Synthesis of rGO-Co₃O₄ nanocubes

In the typical process for the preparation of rGO-Co₃O₄ nanocubes, the graphene oxide (GO) was prepared by using a simplified Hummer’s method.¹⁹ A 12 mL of Co(CH₃COO)₂·4H₂O (83 mM) was mixed with different wt. % of GO (1, 2, 4, 8, and 12 wt. %) and stirred for 2 h to obtain a homogeneous solution. After that, 15 mL of 6 % ammonia was slowly added drop-wise into the above reaction mixture under vigorous stirring. Then, 75 mL of the reaction mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 180 °C for 12 h. Finally, the obtained precipitate of rGO-Co₃O₄ nanocubes was washed five times with DI water and ethanol and dried in a hot air oven at 60 °C. For comparison, Co₃O₄ and rGO were prepared using a similar method without using GO and (Co(CH₃COO)₂·4H₂O), respectively.

Preparation of modified electrode

An rGO-Co₃O₄ nanocubes modified electrode was fabricated by dispersing 1 mg of the synthesized rGO-Co₃O₄ nanocubes in 1 mL of deionized water and then sonicating it for 30 min to ensure a homogeneous dispersion. A 5 µL of the colloidal rGO-Co₃O₄ nanocubes solution was cast on a polycrystalline Pt electrode and then dried in a hot air oven at 65 °C for 1 h. This Pt/rGO-Co₃O₄ nanocubes modified electrode was used for the electrocatalytic oxidation of methanol.
**Characterization techniques**

The size and shape of the rGO-Co$_3$O$_4$ nanocubes were studied using a JEOL JEM-2100F high-resolution transmission electron microscope. The surface morphology and elemental composition were examined using a JEOL JSM-7600F field emission scanning electron microscope. Raman spectra were acquired from a Renishaw inVia 2000 system with a green laser emitting at 532 nm. The crystalline nature and phase identification of the rGO-Co$_3$O$_4$ nanocubes were recorded using a Philips X’pert X-ray diffractometer with copper K$_\alpha$ radiation (\(\lambda = 1.5418 \ \text{Å}\)) at a scan rate of 0.02 degree/sec. All the electrochemical measurements were carried out using a VersaSTAT-3 electrochemical analyzer (Princeton Applied Research, USA) with a conventional three-electrode system under a nitrogen atmosphere at room temperature (27 °C). The rGO-Co$_3$O$_4$ nanocubes modified electrode was used as a working electrode, a platinum wire served as a counter electrode, and a Ag/AgCl electrode was the reference electrode. The supporting electrolyte and target substrate were composed of 0.1 M KOH and 0.1 M CH$_3$OH, respectively. All the potentials are quoted against the Ag/AgCl electrode unless otherwise mentioned.

**Results and Discussion**

**Formation of rGO-Co$_3$O$_4$ nanocubes**

Fig. 1 shows a schematic illustration of the formation of Co$_3$O$_4$ nanocubes incorporated rGO sheets fabricated using a hydrothermal method. In this typical synthetic process, a Co(II) precursor was added to the preformed GO solution, and the medium was changed to basic with the help of an NH$_3$·H$_2$O solution. Upon the hydrothermal process, the GO-Co(OH)$_2$ transformed into rGO-Co$_3$O$_4$ nanocubes. The Co$_3$O$_4$ nanocubes were incorporated like spacers between the disorderedly stacked graphene sheets.
Morphological studies of rGO-Co$_3$O$_4$ nanocubes

The FESEM images of the rGO-Co$_3$O$_4$ nanocubes show that the Co$_3$O$_4$ nanocubes are incorporated onto the surfaces of graphene sheets. As can clearly be seen in Fig. 2(c), the rGO-Co$_3$O$_4$ nanocubes with 2 wt. % of GO lacked sufficient graphene sheet surfaces to anchor the Co$_3$O$_4$ nanocubes, which resulted in a large number of Co$_3$O$_4$ nanocubes being exposed on the surface. When the GO content was increased to 12 wt. % in the rGO-Co$_3$O$_4$ nanocubes (Fig. 2(c)) many of the Co$_3$O$_4$ nanocubes were sandwiched between the disorderly stacked graphene sheets, and few of the Co$_3$O$_4$ nanocubes were exposed on the surface. For comparison, the disorderly stacked graphene sheets and Co$_3$O$_4$ nanocubes prepared using the hydrothermal method are shown in Fig. 2(a and b).

TEM images of the Co$_3$O$_4$ nanocubes and rGO-Co$_3$O$_4$ nanocubes are shown in Fig. 3. There is a clear distinction between the bare and graphene-supported Co$_3$O$_4$ nanocubes. Fig. 3(a) shows the Co$_3$O$_4$ nanocubes without any graphene sheets. As seen, the obtained materials had irregular shapes. It should be emphasized that the absence of graphene affected the Co$_3$O$_4$ nanocubes formation. The Co$_3$O$_4$ nanocubes incorporated graphene is shown in Fig. 3(b). It can be seen that the Co$_3$O$_4$ nanocubes are anchored on the transparent graphene sheet surfaces. This result clearly reveals that the graphene plays a role in the formation of Co$_3$O$_4$ nanocubes.

X-Ray diffraction analysis of rGO-Co$_3$O$_4$ nanocubes

The crystalline natures of the prepared GO, rGO, Co$_3$O$_4$ nanocubes, and rGO-Co$_3$O$_4$ nanocubes were studied by recording the XRD patterns, and their results are shown in Fig. S1†. The GO (Fig. S1(a)†) shows a strong and sharp diffraction peak at the 2θ value of 10° due to the (001) plane. After the hydrothermal process for GO, an intense sharp peak
disappears at the 2θ value of 10°, and two new broad peaks appear at the 2θ values of 26.8° and 42.7°, which can be attributed to the (002) and (100) planes for rGO, respectively (Fig. S1(b)†). The two observed diffraction peaks originate from the disorderedly stacked graphene sheets, which confirms the successful reduction of GO into rGO.20,21 The Co$_3$O$_4$ nanocubes and rGO-Co$_3$O$_4$ nanocubes (Fig. S1(c-d)†) show a characteristic diffraction pattern at the 2θ values around 31.2°, 36.8°, 44.7°, 55.5°, 59.2°, and 65.1°, which were readily indexed to the respective (220), (311), (222), (400), (422), (511), and (440) planes of face centered cubic Co$_3$O$_4$ (JCPDS card No. 42-1467).21,22 For the rGO-Co$_3$O$_4$ nanocubes (Fig. S1(d)†), the diffraction peak of rGO is undistinguishable, which clearly indicates that the face-to-face stacking of the rGO sheets is absent because of the formation of Co$_3$O$_4$ nanocubes on both sides of the rGO sheets.22

**Raman studies of rGO-Co$_3$O$_4$ nanocubes**

Raman analysis is more suitable tool and most commonly employed to differentiate the graphene (graphene oxide and reduced graphene oxide) from the very thin graphite sheets. It is known from the previous reports23-26, the graphite sheets has in-phase vibration of the highly ordered graphite lattice (G band) at 1575 cm$^{-1}$ and a very weak D band at 1355 cm$^{-1}$ due to the disorder graphite edges. In contrast, the graphene oxide and reduced graphene oxide has well defined D and G band at 1355 and 1595 cm$^{-1}$ in comparison with graphite23-26. The Raman spectra of the GO, rGO, Co$_3$O$_4$ nanocubes, and rGO-Co$_3$O$_4$ nanocubes were recorded and are shown in Fig. 4. The Raman spectrum for GO shows D and G band peaks at 1355 and 1595 cm$^{-1}$ due to the $sp^3$ defects and in-plane vibrations of $sp^2$ carbon atoms, respectively.27,28 A small bump in Fig. 4(a,b) was observed related to the band 2D for GO (2680 cm$^{-1}$) and rGO (2694 cm$^{-1}$) respectively. This shows the multilayer GO and rGO, also a shift to higher wavelengths in the 2D band of rGO was observed after reduction from GO
which indicates the restacking of graphene sheets due to the removal of functional group from GO which may prevent restacking of GO sheets after it was reduced.\textsuperscript{28} It was observed that 2D band of rGO in Fig. 4 (d) retain the same position as for GO showing no stacking of graphene layers. It may because of Co\textsubscript{3}O\textsubscript{4} nanocubes behave like spacer in between the graphene sheets as confirmed by FESEM image. It was also demonstrated that D band remained unchanged, while the G band of rGO was shifted to 1610 cm\textsuperscript{-1} because of the “self-healing” characteristics of the rGO, which recovers the hexagonal network of carbon atoms with defects. In addition D/G band intensity ratio for rGO greater than that of GO suggesting decrease in sp\textsuperscript{2} domain of GO after reduction.\textsuperscript{27,29} This observation clearly indicates the successful transformation of GO to rGO (Fig. 4(a-b)). The Raman spectrum of the rGO-Co\textsubscript{3}O\textsubscript{4} nanocubes (Fig. 4(d)) shows four peaks at approximately 482, 525, 615, and 686 cm\textsuperscript{-1}, which correspond to the $E_{\text{g}}$, $F_{2g}$, $F_{2g}$, and $A_{1g}$ modes of Co\textsubscript{3}O\textsubscript{4}, along with the D and G bands for rGO.\textsuperscript{30-32}

**Electrochemical behavior of rGO-Co\textsubscript{3}O\textsubscript{4} nanocubes modified electrode**

The rGO, Co\textsubscript{3}O\textsubscript{4} nanocubes and rGO-Co\textsubscript{3}O\textsubscript{4} nanocubes modified electrodes were electrochemically characterized by recording the cyclic voltammograms in 0.1 M KOH at a scan rate of 50 mVs\textsuperscript{-1} and their results are shown in Fig. 5(A). All the cyclic voltammograms show a clear peak at -0.2 V and a small peak at -0.1 V due to the hydrogen adsorption/desorption processes in this potential region. The anodic peaks observed for Co\textsubscript{3}O\textsubscript{4} nanocubes and rGO-Co\textsubscript{3}O\textsubscript{4} nanocubes modified electrodes around 50 mV were due to the adsorption of oxygen containing species such as, H\textsubscript{2}O and OH\textsuperscript{-}\textsuperscript{33,34}, and another peak observed between 200–300 mV was attributed to the formation of higher valence oxides or hydroxides of cobalt in the alkaline medium.\textsuperscript{34,351} The observed cathodic peaks at 70 and 480 mV for the Co\textsubscript{3}O\textsubscript{4} nanocubes and rGO-Co\textsubscript{3}O\textsubscript{4} nanocubes modified electrodes are related to
the regeneration of Co(II) species. The overall electrochemical processes during the anodic and cathodic scans are given in Eqn. (1) and (2) below:

\[
\begin{align*}
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \rightleftharpoons 3\text{CoOOH} + e^- \quad \ldots (1) \\
\text{CoOOH} + \text{OH}^- & \rightleftharpoons \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad \ldots (2)
\end{align*}
\]

The cyclic voltammograms for an rGO-Co$_3$O$_4$ nanocubes modified electrode in the presence of 1 mM K$_3$[Fe(CN)$_6$] in 0.1 M KCl at a scan rate of 50 mVs$^{-1}$ shows a smaller peak potential separation ($\Delta$Ep) and larger peak current than those of a bare Pt electrode (Fig. 5(B)), indicating a rapid electron transfer and larger electroactive surface area for the rGO-Co$_3$O$_4$ nanocubes. After modification with rGO, Co$_3$O$_4$ nanocubes, and rGO-Co$_3$O$_4$ nanocubes, the $\Delta$Ep values decreased by 76, 67, and 60 mV, respectively, when compared to the bare Pt (80 mV), and the peak current increased on the order of rGO-Co$_3$O$_4$ nanocubes > Co$_3$O$_4$ nanocubes > rGO when compared to the bare Pt electrode (Fig. 5(B)). The noticeable increase in the anodic and cathodic peak current of the rGO-Co$_3$O$_4$ nanocubes compared to the rGO confirmed the contribution of the Co$_3$O$_4$ nanocubes to an increase in the electroactive surface area and the promotion of electron transfer. Notably, the rGO-Co$_3$O$_4$ nanocubes modified electrode showed a $\Delta$Ep value that was very similar to the ideal kinetics (59 mV) of a one-electron reversible process, suggesting the excellent conductivity and ideal reversibility of the redox reaction.

The scan rate was varied in the range of 10–500 mVs$^{-1}$ for the rGO-Co$_3$O$_4$ nanocubes modified electrode with $1 \times 10^{-3}$ M of K$_3$[Fe(CN)$_6$] in 0.1 M KCl, and the results are shown in Fig. S2(A)†. It can be seen that the redox peak current for the anodic and cathodic scan increased linearly with the increasing scan rate, and no obvious shift is observed for the
anodic and cathodic peak potentials. This clearly suggests that the electrochemical redox reaction that occurs for the rGO-Co$_3$O$_4$ nanocubes modified electrode is reversible. A plot of the anodic and cathodic peak current vs. square root of the scan rate is shown in Fig. S2(B)$\dagger$, which shows the linear relation for the rGO-Co$_3$O$_4$ nanocubes modified electrode ($R^2 = 0.9938$ and 0.9942), indicating an adsorption controlled redox process.$^{40}$

In order to investigate the electrochemical behavior of bare Pt, rGO, Co$_3$O$_4$ nanocubes and rGO-Co$_3$O$_4$ nanocubes modified electrode, electrochemical impedance spectroscopic (EIS) analyses were performed by dipping the electrodes into a solution containing $1 \times 10^{-3}$ M K$_3$[Fe(CN)$_6$] in 0.1 M KCl at a scanning frequency range of 0.01–120,000 Hz. The Nyquist plots for the bare Pt, rGO, Co$_3$O$_4$ nanocubes and rGO-Co$_3$O$_4$ nanocubes modified electrodes show a line in the low-frequency region and an arc in the high frequency region (Fig. 6(A) and Fig. S3). The bare Pt electrode shows a large semicircle compared to the other modified electrodes, which is a result of the large charge-transfer resistance ($R_{ct}$) at the electrode/electrolyte interface due to the sluggish electron transfer kinetics. It can obviously be seen that $R_{ct}$ decreased for the rGO, Co$_3$O$_4$ nanocubes and rGO-Co$_3$O$_4$ nanocubes modified electrodes, which can be attributed to the presence of high conductive rGO sheets and catalytically active Co$_3$O$_4$ nanocubes on the electrode surface. Fig. 6(B) shows the Bode-phase plots of various modified electrodes in the frequency range of 0.1–10000 Hz. A higher phase peak intensity can be seen at a frequency range of 100–1000 Hz, which is attributed to the charge-transfer resistance of the modified electrode.$^{41,42}$ Interestingly, the phase peaks in the Bode plots for the rGO, Co$_3$O$_4$ nanocubes and rGO-Co$_3$O$_4$ nanocubes modified electrode are shifted to a low frequency region of 0.1–100 Hz as a result of the high electron transfer behavior of the highly conductive rGO sheets and the catalytically active Co$_3$O$_4$ nanocubes based modified electrodes.
Electrocatalytic oxidation of methanol at rGO-Co$_3$O$_4$ nanocubes modified electrode

The schematic representation of methanol oxidation at the Pt/rGO-Co$_3$O$_4$ modified electrode is shown in Fig. 7. During the electrooxidation of methanol, the anodic oxidation peak current is obtained due to the oxidation of freshly chemisorbed species coming from the adsorption of methanol and the formation of intermediate carbonaceous species in the forward scan and further it reacts with adsorbed CO on the electrode to produce CO$_2$, H$_2$O, electron (e$^-$). In the reverse scan, the oxidation peak is primarily associated with removal/oxidation of carbonaceous species not completely oxidized in the forward scan, rather than caused by freshly chemisorbed species. In order to investigate the electrocatalytic activity of the prepared rGO-Co$_3$O$_4$ nanocubes modified Pt electrode, a cyclic voltammogram was recorded in the presence of 0.1 M CH$_3$OH and 0.1 M KOH at a scan rate of 50 mVs$^{-1}$, and its results is shown in Fig. 8(d). For comparison purposes, cyclic voltammograms were also recorded for polycrystalline Pt, rGO and Co$_3$O$_4$ nanocubes modified electrodes under the same conditions (Fig. 8(a-c)). Interestingly the rGO-Co$_3$O$_4$ nanocubes modified electrode showed a higher electrocatalytic oxidation current density during forward (358 $\mu$A/cm$^2$) and backward (196 $\mu$A/cm$^2$) scans compared to the other modified electrodes (poly crystalline Pt, rGO, and Co$_3$O$_4$ nanocubes). The peak currents observed during the forward and reverse scans were due to the methanol oxidation and removal of the residual carbonaceous species formed in the forward scan, respectively.$^{43,44}$ The higher electrocatalytic activity of the rGO-Co$_3$O$_4$ nanocubes modified electrode was mainly due to the combination of the cubic Co$_3$O$_4$ structure and highly conductive reduced graphene oxide (Fig. 2 and 4) and this catalytic activity is good in agreement with the FESEM and Raman results (Fig. 2 and 4). The enhanced structural features of Co$_3$O$_4$ nanocubes incorporated rGO resulted in the efficient electron transport to the active sites on the catalyst than the bare Co$_3$O$_4$ nanocubes. Hence,
the FESEM images (Fig. 2) supported the fact that the high dispersion of Co$_3$O$_4$ nanocubes into the rGO matrix leads to significantly enhanced the electrocatalytic performance. Xiao et al. reported that the electrocatalytic activity was significantly influenced by the graphene when it was incorporated into different Co$_3$O$_4$ nanostructures.$^{18}$

**Optimization of rGO content in rGO-Co$_3$O$_4$ nanocubes modified electrode for efficient methanol oxidation**

Optimizing the weight percentage of the GO in the rGO-Co$_3$O$_4$ nanocubes is very important to attain a high electrocatalytic performance toward methanol oxidation. In this regard, the wt. % of the GO content in the rGO-Co$_3$O$_4$ nanocubes was varied and the obtained results are shown in Fig. S4(A)†. The observed results clearly suggest that the oxidation current density was increased during the forward and reverse scans with the increasing of the GO content until it reached a maximum of 2 wt. % of GO in composite of rGO-Co$_3$O$_4$. After this, a further increase in the GO content of the rGO-Co$_3$O$_4$ nanocubes led to a decrease in the current density during the forward and reverse scans (Fig. S4(A)†). The observed current densities for methanol oxidation during the forward and reverse scan for rGO-Co$_3$O$_4$ nanocubes with different GO contents are summarized in Fig. S4(B)†. The decrease in the current density with increasing GO content, which was due to the decrease in the anodic peak current that resulted from the restacking of the graphene nanosheets, substantially decreased the active catalytic sites on the electrocatalysts.$^{45,46}$

**Influence of scan rate and methanol concentration on electrocatalytic activity of rGO-Co$_3$O$_4$ nanocubes modified electrode**

The effect of the scan rate on the electrocatalytic oxidation of methanol was investigated for the rGO-Co$_3$O$_4$ nanocubes modified electrode in the presence of 0.1 M
CH$_3$OH and 0.1 M KOH at different scan rates in the range of 10–200 mVs$^{-1}$, and the results are shown in Fig. 9(A). It can be seen that the oxidation peak current density increased with increasing scan rate. The observed anodic peak current density is plotted against the scan rate for the rGO-Co$_3$O$_4$ nanocubes modified electrode and is shown in the inset of Fig. 9(A). An increase in the scan rate likely enhanced the electron movement. The rGO-Co$_3$O$_4$ nanocubes modified electrode showed a linear relationship between the anodic peak current density obtained from the forward scans and the square root of the scan rate toward methanol oxidation. This suggests that the oxidation of methanol at the rGO-Co$_3$O$_4$ nanocubes modified electrode is a diffusion-controlled process.

The methanol concentration is a crucial factor in the practical application of direct methanol fuel cells. The influence of the methanol concentration was studied by varying the methanol content in an rGO-Co$_3$O$_4$ nanocubes modified electrode at a scan rate of 50 mVs$^{-1}$ in the presence of 0.1 M KOH and the results are shown in Fig. 9(B). It can be observed that the anodic peak current density increases and the anodic peak potential have a slightly positive shift with an increase in the methanol concentration. The positive shift in the anodic peak potential with increasing methanol concentration is due to the saturation of active sites at the surface of the rGO-Co$_3$O$_4$ nanocubes modified electrode.

**Reversibility and stability of the rGO-Co$_3$O$_4$ nanocubes modified electrode towards methanol oxidation**

The reliability of the Pt electrode modified with the rGO-Co$_3$O$_4$ nanocubes towards the electrocatalytic oxidation of methanol was investigated by repeating the CV measurements continually up to 100 cycles. Fig. 10(A) shows the CV curves for the proposed Pt/rGO-Co$_3$O$_4$ modified electrode electrode in 0.1 M KOH and 0.1 M CH$_3$OH. It can be
clearly seen that the CV curves are stable and the current density at -150 mV (vs. Ag/AgCl) shows 108 % retention (increased from 350 to 380 µA/cm²) after 100 cycles. Thus, the proposed Pt/rGO-Co₃O₄ modified electrode shows good sensitivity and better stability towards the electrocatalytic oxidation of methanol.

The electrocatalytic stability of the Pt/rGO-Co₃O₄ modified electrode was studied using chronoamperometry. Fig. 10(B) showed the chronoamperometric curve of 1 mM CH₃OH in 0.1 KOH for the Pt/rGO-Co₃O₄ modified electrode at an applied potential of -150 mV and the electrode shows the rapid decrease in the potentiostatic current at the initial stage during the oxidation of methanol due to the formation of intermediate species, such as CO_ads and CHO_ads etc., 47,48. Then, the current was gradually decayed and achieved the pseudo-steady state. Similar observation also reported to illustrate the stability of the modified electrode for the electrocatalytic oxidation of methanol with the Pt/graphene 48, Pt/Vulcan 48, Pt/C–MoC–Gl 49.

Conclusions

The Co₃O₄ nanocubes incorporated in reduced graphene oxide successfully synthesized using a simple hydrothermal method. The as-prepared rGO-Co₃O₄ nanocubes combined the unique properties of graphene with the effects of Co₃O₄ nanocubes and showed a superior electrocatalytic activity and high poisoning tolerance for methanol electro-oxidation compared with bare Pt, rGO and Co₃O₄ nanocubes modified electrodes. In particular, the best electrocatalytic activity for the rGO-Co₃O₄ nanocubes modified electrode in an alkaline environment could be achieved with an optimized GO content of 2 wt. %, and it showed an anodic peak current density of 362 µA/cm² during the forward scan. Further, the modified electrode showed good reversibility with the retention of 108 % and stability.
towards methanol oxidation. Considering the low-cost, facile, and controllable method for the preparation of rGO-Co$_3$O$_4$ nanocubes and the improved electrocatalytic activity toward methanol oxidation, this direct strategy can applied to the development of metal oxide-graphene composites as new electrode materials for high performance direct methanol fuel cells.

Acknowledgements

This work was financially supported by a University of Malaya Research Grant UMRG Programme (RP007C-13AFR) Science Fund from the Ministry of Science, Technology and Innovation (06-01-04-SF1513); and a High Impact Research Grant from the Ministry of Higher Education of Malaysia (UM.C/625/1/HIR/MOHE/SC/21).

†Electronic supplementary information (ESI) available: XRD analysis, electrochemical properties and electrocatalytic methanol oxidation are available in ESI.

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Figures and Caption

Fig. 1 Schematic representation for the preparation of rGO-Co$_3$O$_4$ nanocubes.

Fig. 2 FESEM images of (a) rGO, (b) Co$_3$O$_4$ nanocubes, and (c and d) rGO-Co$_3$O$_4$ nanocubes with 2 and 12 wt. % of GO.
Fig. 3 TEM images of (a) Co$_3$O$_4$ nanocubes and (b) rGO-Co$_3$O$_4$ nanocubes.

Fig. 4 Raman spectra obtained for the (a) GO, (b) rGO, (c) Co$_3$O$_4$ nanocubes, and (d) rGO-Co$_3$O$_4$ nanocubes.
Fig. 5 (A) CVs obtained for the (a) rGO, (b) Co$_3$O$_4$ nanocubes and (c) rGO-Co$_3$O$_4$ nanocubes modified Pt electrodes in the presence of 0.1 M KOH at scan rate of 50 mVs$^{-1}$. (B) CVs recorded at (a) bare Pt, (b) rGO, (c) Co$_3$O$_4$ nanocubes and (d) rGO-Co$_3$O$_4$ nanocubes modified electrodes for $1 \times 10^{-3}$ M K$_3$[Fe(CN)$_6$] in 0.1 M KCl at a scan rate of 50 mVs$^{-1}$. 
Fig. 6 (A) Nyquist plots and (B) Bode phase plots obtained for (a) bare Pt, (b) rGO, (c) Co$_3$O$_4$ nanocubes and (d) rGO-Co$_3$O$_4$ nanocubes modified Pt electrodes for $1 \times 10^{-3}$ M K$_3$[Fe(CN)$_6$] in 0.1 M KCl.
Fig. 7. Schematic mechanism for the electrocatalytic oxidation of methanol at Pt/rGO-Co$_3$O$_4$ modified electrode.

Fig. 8 CVs obtained for the (a) bare Pt, (b) rGO, (c) Co$_3$O$_4$ nanocubes and (d) rGO-Co$_3$O$_4$ nanocubes modified Pt electrodes in the presence of 0.1 M CH$_3$OH and 0.1 M KOH at a scan rate of 50 mVs$^{-1}$. 
Fig. 9 (A) CV recorded for rGO-Co$_3$O$_4$ nanocubes modified Pt electrode in presence of 0.1 M CH$_3$OH and 0.1 M KOH at different scan rates in range of 10–200 mVs$^{-1}$. (Inset) Plot of scan rate versus anodic peak current density obtained from the CV measurements. (B) CV recorded for rGO-Co$_3$O$_4$ nanocubes modified electrode at scan rate 50 mVs$^{-1}$ in presence of 0.1 M KOH and various concentrations of CH$_3$OH. (Inset) Plot of methanol concentration versus anodic peak current density for rGO-Co$_3$O$_4$ nanocubes modified Pt electrode.
Fig. 10. (A) Cyclic voltammograms obtained for the rGO-Co$_3$O$_4$ nanocubes modified Pt electrode in the presence of 0.1 M CH$_3$OH and 0.1 M KOH at a scan rate of 50 mVs$^{-1}$ with 1 to 100 cycles. (B) Chronoamperometric curve obtained for the Pt/rGO-CO$_3$O$_4$ modified electrode in the presence of 1 μM CH$_3$OH and 0.1 M KOH at a scan rate of 50 mVs$^{-1}$ at a fixed potential of -150 mV vs. Ag/AgCl.