Promotional role of gold in electrochemical methanol oxidation

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ABSTRACT

Polymeric form of graphitic carbon nitride (CN) has attracted much attention in recent years because of their performance as a support material of various reactions. Here, we report the fabrication of CN and gold nanoparticle-decorated CN system for electrochemical methanol oxidation process. The microscopic, optical, thermal, and surface properties of the synthesized materials have been analyzed using different characterization techniques. Both the synthesized materials were successfully used as electrocatalyst for methanol oxidation reaction under the alkaline media. The stability and the tolerance of the synthesized catalysts have been studied, in connection with the title reaction, on the basis of oxophilicity of the gold. The strong coordination between gold nanoparticles and amine groups of CN facilitates the electron transfer from amine to metal, which makes the gold particles more electron rich and consequently makes the Au-CN system more active for electrocatalytic methanol oxidation reaction.

Introduction

Sustainable technology emphasizes on the designing of alternative processes that cause minimal environmental impact and prevent pollution [1]. Recently, significant attention has been paid for the development of alcohol-based fuel cell in the use of mobile and stationary applications, such as onboard electric power sources for advanced propulsion systems, non-polluting electric vehicles, and portable devices, because of the high conversion efficiencies and low pollution [2,3]. The electrochemical performance of fuel cells depends on the activity of the electrode catalyst, and it is well known that platinum is one of the most widely used anode catalysts for alcohol-based fuel cell [4,5]. Though platinum-based catalysts show the best performance for alcohol oxidation [6], the use of platinum as a catalyst is not economically viable and the problem is associated with catalyst poisoning [7]. Serious attention has been paid to replace platinum with palladium as an anode catalyst for the alcohol-based fuel cell application because of its lower cost and greater resistance to carbon monoxide (CO) poisoning [8,9], though the pure form of palladium is not efficient enough as well for fuel cell technology [10,11].

A palladium–cobalt system exhibited a mass activity similar to palladium for electrocatalytic oxidation of ethanol [10], whereas palladium–copper alloy showed much higher mass activity than palladium alone [11]. The incorporation of copper in the palladium system makes the system economically viable. It is also reported that the porous palladium–copper alloy catalyst shows good activity and long-term stability toward the electro-oxidation of formic acid and methanol [12].
Apart from the alloy system of palladium, reports have been published on platinum-based bimetallic (Pt-Ru) electrocatalyst toward methanol oxidation reaction where the particles are uniformly dispersed throughout the porous carbon support [13]. Bimetallic Pt-Ru catalysts are widely used as anode materials in methanol fuel cells where ruthenium dissolution from the anode causes a decrease in activity of the catalyst, which results in a deterioration of the cell performance [14]. The gold nanoparticles have shown potential applications in various systems, such as homogeneous, heterogeneous, photo-, and electrocatalyst [15–18]. Apart from these applications, gold-based nanoparticles have tremendous application in energy [19] and more specifically fuel cell-related reactions [20]. It was reported that gold-based alloy particles were used as electrocatalysts for fuel cell reactions such as methanol oxidation and oxygen reduction reaction [21]. A report has also been published on the superior performance of Pt-Ru/C catalyst on methanol oxidation reaction in combination with gold, with high CO tolerance at lower potential range [22]. Highly dispersed small and uniform gold particles on the graphene-polymer system showed oxygen reduction efficiency due to a high fraction of the surface metal atoms [23].

Nanoparticles have a high surface energy with an intrinsic nature to minimize their energy through agglomeration [24]. To prevent the agglomeration, the nanoparticles are generally capped with various stabilizers [18,25–32], but that seriously limits the catalytic performance of metals by lowering the accessibility of the reactants on the catalyst surface. Various solid materials, such as carbon, clay, and metal oxide, have also been employed as a support system for the metal catalysts where strong metal-support interaction prevents the metal-metal interaction and seizes the agglomeration process. In our earlier studies, we showed the carbon nitride (CN) could also act as a successful support material for the metal catalyst for various heterogeneous reactions [33–36].

These days, several efforts have been made by the scientists in the search of metal-free catalysts with comparable catalytic activity, like metal-based catalysts, for the next-generation electrocatalysis research and development. Metal-free CN shows remarkable catalytic activity for a variety of reactions such as photocatalytic hydrogen production [37,38] and fuel cell-based research [39,40]. In this current study, we demonstrate a stabilizer-free synthetic route of gold nanoparticles supported on CN. Both CN and gold–CN (Au-CN) were employed as anode catalysts for the oxidation of methanol where CN showed the catalytic performance for the title reaction and the gold particles acted as promoters for the reaction.

**Experimental details**

**Materials**

Urea (reagent grade, 98%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.9%), methanol (anhydrous, 99.8%), and potassium hydroxide (reagent grade, 90%, flakes) were purchased from Sigma-Aldrich (South Africa) and used without further purification process. Milli-Q water (>18.2 MΩ cm resistivity) was obtained from a Milli-Q (Advantage A-10) water filter system.

**Material characterization**

Microscopy study was performed using JEOL (JEM-2100) transmission electron microscope (TEM). The sample for TEM analysis was prepared by depositing the material onto a carbon-coated copper grid. The X-ray diffraction (XRD) patterns of the synthesized materials were recorded on a Shimadzu XD-3A X-ray diffractometer. Fourier transform infrared (FTIR) spectroscopy study was performed using a Shimadzu IR Affinity-1. The surface areas were calculated by the Brunauer–Emmett–Teller method, whereas the pore size distribution was calculated from the Barrett–Joyner–Halenda theory using an AutoPore IV 9500 automated mercury porosimeter (Shimadzu, Japan). X-ray photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument. Thermal characterization of the samples was performed using a Shimadzu TGA-51 thermogravimetric analyzer. Electrochemical studies were carried out with a Bio-Logic, SP-200, potentiostat connected to a data controller and attached with an electrochemical impedance spectroscopy (EIS). The electrochemical study was done with a glassy carbon electrode (GCE) as the working electrode. The Ag/AgCl electrode and a Pt electrode were used as the reference and counter electrodes, respectively.

**Synthesis: general procedure for the synthesis of CN and Au-CN**

In a typical experiment, 15 g of urea was kept in a covered crucible at 80°C under ambient pressure for 2 h. After that, the dried urea was transferred into a muffle furnace for 4 h at 500°C. The light-yellow-colored product, graphitic CN, was dispersed in 10 mL of water in a 25-mL round-bottom flask. The Au-CN has been synthesized using a single-step borohydride reduction technique at room temperature [41]. An aqueous solution of tetrachloroauration (10⁻¹ mol.dm⁻³) was added dropwise (10 wt% loading of Au) to the round-bottom flask. After that, 5 mL of NaBH₄ (10⁻² mol.dm⁻³) solution was added slowly for the reduction of the gold salt. Finally, the material
was filtered, washed with water, and dried. The resultant material, Au-gCN, was characterized using optical, microscopic, and surface analysis techniques.

**Result and discussion**

**Figure 1** shows the TEM images of the CN support (A) with a film-like layered morphology. For Au-CN (B) sample, the dark spots are the gold nanoparticles distributed on the CN support with a wide size distribution within the range of 5–15 nm. The phase of the synthesized products was characterized by XRD analysis. For CN sample in the XRD pattern, **Figure 2(a)**, the most intense peak at 27.38° can be indexed as the (002) plane, equivalent to a d-spacing of 0.326 nm. This is usually ascribed to the distance between the layers of the graphitic material [42]. **Figure 2(b)** shows the XRD pattern of the Au-CN; besides the CN peak at 27.23°, the other three peaks at 38.2°, 44.0°, 64.65°, and 77.50° (for 2θ degree axis) can be assigned to the (111), (200), (220), and (311) reflection lines, respectively, which were in agreement with the diffraction standard of metallic gold (JCPDS: 04–0784) [43]. The shifting of the (002) plane (from 27.38° to 27.23°) and the decrease of peak intensity of CN in the XRD pattern correspond to the change of d-spacing in between the layers and also indicate the weakening of the interlayer stacking of CN due to the incorporation of gold nanoparticles [44]. For the identification of the chemical state of gold in the Au-CN sample, XPS measurement was done (**Figure 2(c)**). The peaks at 84.0 and 87.7 eV correspond to the binding energies of Au 4f_{7/2} and Au 4f_{5/2} electrons, respectively, resulting from the spin-orbital splitting of Au 4f spectra and designate the presence of metallic state of the gold in the sample [45].

The FTIR spectra, illustrated in **Figure 3(a)**, spectrum (a): CN and spectrum (b): Au-CN, with the typical stretching modes of C–N heterocycles ranging from 1230 to 1640 cm⁻¹ strongly indicate the formation of CN [34]. The band at 810 cm⁻¹ for both the samples represented the out-of-plane bending vibration and the typical characteristic of heptazine rings. The broad band ranging from 3000 to 3600 cm⁻¹ corresponds to the stretching modes of NH₂ or NH groups. It is also important to mention that for Au-CN sample, some of the vibrational bands are missing and also have shifted toward the higher wavenumber (lower wavelength) direction, in the range of 3000–3600 cm⁻¹, as compared with the CN sample. The above phenomenon indicates that the gold nanoparticles strongly coordinate with the amine groups, and a higher energy was required for the vibration of the functional groups.

The photoluminescence (PL) spectra analysis was performed to study the recombination processes of photogenerated electron–hole pairs of the synthesized materials (CN and Au-CN). **Figure 3(b)** shows the PL spectra of CN, spectrum (a) and Au-CN, spectrum (b), under the excitation wavelength of 300 nm. Both the materials show the PL with the peak value of 465 nm but with different intensities. The typical PL spectra of the CN originate due to the transition between the lone pairs and the π* conduction band [46]. A fairly moderate amount of PL quenching was observed in the sample of Au-CN as compared with CN. The intensity of the PL spectrum is a direct measurement of the recombination rate of electron–hole pairs, where the stronger the PL peak intensity the higher the recombination rate. The gold nanoparticles on CN form a Mott–Schottky heterojunction where during the photon irradiation the conduction band electron of CN migrates to gold nanoparticles.

**Figure 1.** The TEM images of the (a) carbon nitride and (b) Au-CN.
to create a Schottky barrier, which restricts the recombination process between electron–hole pairs and quenches the intensity of the spectra. Figure S1 shows the results of thermogravimetric analysis (TGA) for both CN and Au-CN samples. From the thermograph, it is evident that both the samples are fairly stable up to 500°C and after that, a sharp weight loss was observed. The sharp weight loss feature for both the samples may be due to the oxidation of the CN to form graphite and nitrogen [47]. From the figure, it is evident that CN sample suffered from higher weight loss as compared with Au-CN.

The nitrogen adsorption–desorption isotherms for both the samples follow type IV with an H1 category of hysteresis loop with the surface area values of 58.5 and 63.0 m².g⁻¹ for CN and Au-CN, respectively (Figure 4(a)). The slight improvement of the surface area value of Au-CN could be due to the

![Figure 2. X-ray diffraction (XRD) patterns of (a) CN and (b) Au-CN. (c) High-resolution X-ray photoelectron spectrum with two distinct peaks at 87.7 and 84.0 eV is due to the spin-orbit splitting of the Au 4f5/2 and Au4f7/2 lines, respectively.](image)

![Figure 3. (A) FTIR spectra of (a) CN and (b) Au-CN. (B) The photoluminescence (PL) spectra of (a) CN and (b) Au-CN.](image)
shows the voltammetric responses for (34 mA cm$^{-2}$) and (49.5 mA cm$^{-2}$). Figure 5(a) presents the nitrogen adsorption and desorption isotherms of KOH. The electrochemical impedance spectroscopy was achieved due to the electrolyte in the potential range from −(0.8) to + (0.2) V. Figure 5(b) shows the cyclic voltammetry (CV) responses for the CN-modified GCE in the absence (curve ‘a’) and presence (curve ‘b’) of methanol (1.0 mol dm$^{-3}$) within the potential range from −(0.8) to + (0.2) V. Voltammogram (a) shows a very low current density value (0.2 mA cm$^{-2}$) at 0.2 V, whereas voltammogram (b) shows the improvement of current density (0.57 mA cm$^{-2}$) at 0.2 V. Interestingly, voltammogram (b) shows a prominent peak during the forward scan with the current density value of 0.73 mA cm$^{-2}$ at −0.08 V and a peak during the reverse scan with the current density value of 0.14 mA cm$^{-2}$ at −0.12 V, which is the characteristic feature of electrochemical methanol oxidation [48–52]. In this regard, nitrogen doped carbon materials are of particular interest for their catalytic performance towards the fuel cell reaction and has been confirmed by both experimental studies [53] and quantum-mechanical calculations [54]. Among these nitrogen-containing carbon materials, CN is promising because of its high nitrogen content and easily tailorable structure [55] that makes it potentially suitable as a catalyst for various reactions [37,53,56].

Figure 6(b) shows the voltammetric responses for the Au-CN-modified GCE in the absence (curve ‘c’) and presence (curve ‘d’) of methanol (1.0 mol dm$^{-3}$) within the potential range from −(0.8) to + (0.2) V. Both the voltammograms show improvement of current density values, as compared with CN-modified GCE, which indicate the effect of gold nanoparticles on CN. In the absence of methanol, the Au-CN-modified GCE shows a flat voltammetric feature (curve ‘c’), whereas in the presence of methanol, two prominent peaks with a current density value of 0.99 mA cm$^{-2}$ (49.5 mA cm$^{-2}$/mg of gold) at −0.08 V and 0.68 mA cm$^{-2}$ (34 mA cm$^{-2}$/mg of gold) at −0.2 V, during the forward scan and reverse scan, respectively, were obtained. From the above studies, we have confirmed that a net increment of current density of 0.26 mA cm$^{-2}$ was achieved due to the contribution of gold nanoparticles, which plays the role of a promoter for the title reaction.

The peak appeared during the forward scan is attributed to the oxidation of methanol, while the coordination of gold nanoparticles with the CN network through nitrogen bond as evidenced by the FTIR spectroscopy. The pore diameters for both the samples are within the range between 15 and 45 nm (Figure 4(b)).

The EIS is an effective method for probing the features of surface-modified electrodes and is presented as the sum of the real, $Z'$, and imaginary, $Z''$, components, which originate from the resistance and capacitance of the cell, respectively. Figure 5(a) depicts the Nyquist plots of (a) CN- and (b) Au-CN-modified electrode and were measured within the frequency range from 3 MHz to 10 Hz in KOH (0.5 mol dm$^{-3}$). The magnified impedance spectra at higher frequency region (Figure 5(b)) suggest a low ohmic loss in the presence of KOH electrolyte. Experimental data were also fitted with an equivalent circuit model (Figure 5(c)), where the parameters $R_s$ is the electrolyte resistance in the cell, $R$ is the charge transfer resistance across the electrode–electrolyte interface in parallel combination with a constant phase element (C), and $Z_w$ represents the Warburg impedance diffusion, for both the materials, and modeled as the double-layer capacitor.

In the next step, we have compared the performance of CN and Au-CN as catalyst for the electrochemical oxidation of methanol under a scan rate of 50 mV s$^{-1}$ in alkaline condition (0.5 mol dm$^{-3}$ of KOH). Figure 6(a) shows the cyclic voltammetry (CV) responses for the CN-modified GCE in the absence (curve ‘a’) and presence (curve ‘b’) of methanol (1.0 mol dm$^{-3}$) within the potential range from −(0.8) to + (0.2) V. Voltammogram (a) shows a very low current density value (0.2 mA cm$^{-2}$) at 0.2 V, whereas voltammogram (b) shows the improvement of current density (0.57 mA cm$^{-2}$) at 0.2 V. Interestingly, voltammogram (b) shows a prominent peak during the forward scan with the current density value of 0.73 mA cm$^{-2}$ at −0.08 V and a peak during the reverse scan with the current density value of 0.14 mA cm$^{-2}$ at −0.12 V, which is the characteristic feature of electrochemical methanol oxidation [48–52]. In this regard, nitrogen doped carbon materials are of particular interest for their catalytic performance towards the fuel cell reaction and has been confirmed by both experimental studies [53] and quantum-mechanical calculations [54]. Among these nitrogen-containing carbon materials, CN is promising because of its high nitrogen content and easily tailorable structure [55] that makes it potentially suitable as a catalyst for various reactions [37,53,56].

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The peak appeared during the forward scan is attributed to the oxidation of methanol, while the
peak at the reverse scan is associated with the methanol oxidation intermediates, mainly chemisorbed CO on the catalyst surface [57], and the ratio of the peak current between the forward scan (\(I_F\)) and the reverse scan (\(I_B\)), \(I_F/I_B\), indicates the tolerance of the catalyst to the chemisorption of CO. In this current experiment, we found that the \(I_F/I_B\) ratios for the CN and Au-CN-modified GCE are 5.2 and 1.47, respectively.

Figure 7 shows the progressive increment of current density with the number of scans using Au-CN as an electrocatalyst of the title reaction, and a stable current density value was obtained after 100 cycles. A gradual shifting of the peak positions, as shown by two arrows in Figure 7, toward the higher potential range with the increase of current density for both \(I_F\) and \(I_B\) indicates the retardation of mass transfer process. The current density for the forward peak (\(I_F\)) and the reverse peak (\(I_B\)) reaches at a stable value of 1.14 and 0.82 mA cm\(^{-2}\), respectively, after 100 cycles with a \(I_F/I_B\) ratio of 1.39. The ratio of the forward peak current (\(I_F\)) to the reverse peak current (\(I_B\)) indicates the catalytic performance. In the beginning, the \(I_F/I_B\) ratio for Au-CN catalyst was 1.47 and after the 100 cycles, the ratio was decreased to 1.39, which indicates the deactivation of the catalyst by accumulation of carbonaceous species with the number of cycles.

Different opinions suggest that \(I_F/I_B\) ratio is not related to the degree of CO tolerance of the catalyst but to the degree of oxophilicity [58]. The oxophilicity is a tendency of certain metals, with low electronegativity, to form surface-oxygenated species by complexation with oxygen from organic compounds [59]. Oxygen is highly electronegative, with an electronegativity value of 3.5, and forms a stronger ionic bond with metals of low electronegativity, such as platinum group metals and gold (electronegativity value within the range of 2.4–2.2). The peak intensity during the reverse scan (\(I_B\)) is related to the surface coverage with oxygenated species, and the ratio \(I_F/I_B\) is related to the degree of oxophilicity. [50] The proposal
of oxophilicity (of the metal) concept is also supported in this current study by considering the \( I_f/I_b \) ratio for both CN and Au-CN catalyst.

The stability and durability of the catalysts were further examined by chronoamperometric measurements. To compare the long-term performance of the CN and Au-CN catalysts for the title reaction, the catalysts were biased at potentials at –(0.80) V for 3000 s and the changes in the oxidation current with time were monitored in the presence of methanol (1.0 mol dm\(^{-3}\)) and KOH (0.5 mol dm\(^{-3}\)). In Figure 8, the chronoamperometric curves show an initial sharp decay of current density for both the catalysts, curve (a) for CN and curve (b) for Au-CN, suggesting catalyst poisoning by chemisorbed carbonaceous species, formed during the oxidation of methanol, and after that the current appears to be fairly stable within the rest of the time period. The inset figure indicates that the CN system shows considerable stable performance than the gold-deposited CN system, though the current density for CN is inferior to Au-CN system. In the CN system, improved durability and stability is due to the strong \( \pi \)-bonding within the carbon and nitrogen framework. As mentioned earlier, evidenced by the infrared study, the strong coordination between gold nanoparticles and the amine groups of CN facilitates the electron transfer from amine to metal, which makes the gold particles more electron rich and consequently makes the Au-CN system more active for the electrocatalytic methanol oxidation reaction.

**Conclusion**

In summary, the study indicates that CN is a successful support material for obtaining highly dispersed and active gold nanoparticles. Both CN and gold nanoparticle-decorated CN (Au-CN) acted as catalysts for the electrochemical methanol oxidation reaction, whereas in Au-CN system, the gold particle played the role as a promoter for the title reaction. The presence of nitrogen in the CN support enhances the electron–donor property of the gold particles and consequently improved the catalytic activity for the reaction. It is also important to mention that the 5 wt % of gold on the CN support does not have any considerable impact on the reaction. From the microscopic analysis, it is evident that an irregular size distribution of the gold nanoparticles has been formed on the CN support which could be due to the uncontrolled creation of nucleation centers by the addition of a strong reducing agent (NaBH\(_4\)). In this current method, we are not successful in producing Au-CN composite with a uniform size distribution of the particles to study the reaction effect on the
particle size distribution. Some future studies will be carried out to find the role of particle size, shape, and distribution on the performance of the reaction.

Disclosure statement

No potential conflict of interest was reported by the authors.

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