Facile and green synthesis of a surfactant-free Au clusters/reduced graphene oxide composite as an efficient electrocatalyst for the oxygen reduction reaction†

Shengjie Xu and Peiyi Wu*

In this work, a well-dispersed Au cluster/reduced graphene oxide (RGO) composite was synthesized using citric acid (CA) as a reducing and binding agent. The as-prepared composite was systematically characterized by TEM, XPS, TGA and FTIR. TEM image showed Au clusters uniformly distributed on the RGO sheet with an average size of 1.8 nm. The Au clusters/RGO composite exhibited excellent catalytic performance for the oxygen reduction reaction (ORR). Moreover, the electrocatalytic comparison indicated that the long-term durability and methanol tolerance of this composite was superior to the commercial Pt/C catalyst. Therefore, such a composite might be an alternative and more promising non-Pt electrocatalyst for fuel cells.

A significant amount of work has been reported on several metals and metal oxides, such as Pd, Au, Fe, Co3O4, Fe3O4, etc., which can substitute Pt as efficient catalysts for ORR. Among these, Au has attracted significant increasing attention over the past few years because of its high catalytic activity for both oxidation and reduction reactions in electrochemistry.28–31 Interestingly, the particle size of Au has a significant effect on catalytic activity. As is well-known, Au is one of the most inert metals in its bulk state; however, it exhibits excellent catalytic activity at the nanoscale. Numerous studies have demonstrated that Au nanoparticles with sizes of less than 2 nm (Au clusters) have excellent electrocatalytic activity for ORR. Compared with Pt catalysts, Au is low cost and more stable when carbon monoxide or methanol is mixed in electrolytes during the ORR process. Therefore, Au clusters are widely regarded as a new and promising substitute for Pt.32–34 However, like other metals or metal oxides catalysts, Au clusters frequently undergo aggregation, dissolution, and destruction during catalysis in fuel cells, which seriously reduces the catalytic activity and decreases the lifetime of the catalysts.35 However, as far as we know, nanostructured catalyst supports can efficiently overcome this obstacle. Several nanostructured supports have been utilized in many studies, such as metals, metal oxides, silicas and carbon materials (carbon black, porous carbon, graphene, and carbon nanotubes), etc., and it has been demonstrated that the high specific surface area of these substrates can maximize the electroactive sites of catalysts and improve the catalytic activity and durability. Among these substrates, graphene is regarded as the most promising materials.19,35 Its 2D single-layer C–C sp²-bonded honeycomb structure gives graphene excellent electrical conductivity, which could drastically...

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Laboratory of Advanced Materials, Fudan University, Shanghai, 200433, P. R. China. E-mail: peiyiwu@fudan.edu.cn

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enhance the mobility of charge carriers. Moreover, its high specific surface area and good chemical and environmental stability make it an ideal substrate for growing or anchoring Au clusters. Noticeably, graphene sheets could also tightly immobilize Au clusters and strongly prevent their aggregation through hybridization between the clusters and graphene, which would clearly improve the catalytic activity and stability of Au clusters. Many calculation studies have demonstrated that the metal clusters/reduced graphene oxide (RGO) composites show higher catalytic activity than other clusters composites because of enhanced charge transfer from the clusters to RGO sheets.

Numerous studies focusing on the preparation and catalytic performance of Au clusters or Au nanoparticles/RGO composites have been reported; however, reports on the fabrication of Au clusters/RGO composites with excellent electrocatalysis activity are relatively few because it is not easy to synthesize uniform Au clusters on RGO sheets. Herein, we present a facile and green approach to fabricate a uniformly distributed Au clusters/RGO composite by using citric acid (CA), which not only acts as a reducing agent for GO but also serves as an “adhesive” for binding Au clusters and RGO sheets. This composite exhibits excellent electrocatalytic activity for ORR; moreover, the long-term durability and methanol tolerance is significantly better than Pt/C, implying that it could be a promising catalyst to substitute the commercial Pt/C catalysts. In addition, our work may offer an efficient and versatile route for the preparation of evenly distributed metal clusters/RGO composites.

Experimental section
Materials
Chloroauric acid tetrahydrate (HAuCl₄·4H₂O), N,N-dimethylformamide (DMF), ammonium hydroxide (NH₃·H₂O), hydrazine hydrate (N₂H₄·H₂O), potassium permanganate (KMnO₄), potassium nitrate (KNO₃), concentrated sulfuric acid (H₂SO₄), potassium hydroxide (KOH), and hydrogen peroxide (H₂O₂) were purchased from Sinopharm Chemical Reagent Co. Ltd. Graphite powder (8000 meshes, 99.95%), ascorbic acid (AA), and citric acid (CA) were obtained from Aladdin Reagent Co. Ltd. N₂ and O₂ with a purity of 99.9% were purchased from Shanghai Jifu Gas Co. Ltd. All the other reagents are of analytical grade and used without further purification.

Preparation of GO
Monolayer GO sheets were synthesized according to the modified Hummers method. Typically, 5 g of expandable graphite powders, 15 g of potassium permanganate (KMnO₄) and 2.5 g of potassium nitrate (KNO₃) were added in 115 mL of concentrated sulfuric acid (H₂SO₄) under vigorous stirring for 3 h at 0 °C in an ice-water bath. Afterwards, the temperature was increased to 35 °C and 115 mL of deionized water was rapidly added to the mixture to maintain the temperature under 100 °C for about 30 min. Then, another 700 mL of water was added, followed by the addition of 50 mL H₂O₂ (30 wt%) to reduce excessive KMnO₄. Finally, the resulting suspension was centrifuged and the centrifugate was dialyzed for 2 weeks to remove the residual metal ions, and then freeze-dried before using.

Preparation of Au clusters
Au clusters were synthesized according to the method reported by Kawasaki. In brief, 30 mL DMF was heated to 140 °C, then 300 µL of 0.1 M aqueous HAuCl₄ was added and the mixture was refluxed at 140 °C for 6 h under vigorous stirring. Then, a part of the products were evaporated under vacuum at 90 °C for at least 6 h to remove the excess DMF.

Preparation of Au clusters/RGO composites
Typically, 40 mg of as-prepared Au clusters and 10 mg of GO were dispersed in deionized water with sonication for 2 h, followed by the addition of a certain amount of reducing agent (N₂H₄/NH₃, AA, and CA). After another 10 min sonication, the mixture was heated to 90 °C for 20 h. Finally, the resulting suspension was centrifuged several times at 12 000 rpm for 10 min to remove excess reducing agent and Au clusters which were not adsorbed onto the graphene. The resulting black precipitate was freeze-dried and redispersed in water for further characterization. For Au clusters/RGO composite directly prepared by DMF, a certain amount of GO was dispersed in DMF under sonication for 2 h, then the mixture was added to the as-prepared Au clusters (DMF) solution and heated at 140 °C for another 6 h. Afterwards, the resulting suspension was centrifuged at 12 000 rpm and washed with deionized water several times to remove excess Au clusters which were not adsorbed onto the graphene. The products were freeze-dried and redispersed in water for further characterization.

Electrochemical measurement
1. Cyclic voltammetry (CV). CV was carried out in a standard three-electrode cell using a platinum wire as the counter electrode, Ag/AgCl electrode as the reference electrode and a glassy carbon electrode as the working electrode (CH660D). The preparation of the working electrode was carried out as described in our previous work. Briefly, 10 mg of product was dispersed in 10 mL deionized water, and the mixture was sonicated for 1 h to obtain an homogeneous suspension. Then, 5 µL of suspension was dropped onto the 3 mm glassy carbon electrode. After the suspension was dried, 5 µL of Nafion solution (5 wt%) was dropped to cover the catalyst. The three electrodes were put into 0.1 M KOH solution with a flow of O₂ or N₂ maintained for 40 min to achieve an O₂-saturated or an O₂-free state. The experiment was cycled at least 10 times in the potential range from −1.0 V to 0.2 V at a scanning rate of 5 mV s⁻¹.

2. Rotating disk electrode (RDE) measurement. The working electrode was prepared by the same method as for the CV measurements. The method was carried out at a scanning rate of 5 mV s⁻¹ with various rotating speeds from 400 to 1900 rpm. After the measurements, Koutecky–Levich plots (J⁻¹ vs. ω⁻¹/²) were obtained at different potentials from −0.5 to −0.85 V. The slopes of their best linear fit lines were used to
calculate the number of electrons involved in oxygen reduction. Current density \( J \) was related to angular velocity \( \omega \) according to:

\[
\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{B_0^{1/2}} + \frac{1}{J_k}
\]

where \( J_k \) and \( J_L \) are the kinetic and diffusion-limiting current densities, respectively, and \( \omega \) is the angular velocity. \( B \) is the Levich slope calculated as:

\[
B = 0.62nFCO_2DO_2^{2/3}r^{-1/6}
\]

where \( n \) is the number of electrons transferred in one \( O_2 \) molecule reduction, \( F \) is the Faraday constant (96 485 C mol\(^{-1}\)), \( r \) is the kinematic viscosity for KOH (0.01 cm\(^2\) s\(^{-1}\)), \( C_{O_2} \) is the concentration of \( O_2 \) in solution (1.2 \times 10^{-6} mol cm\(^{-3}\)), and \( D_{O_2} \) is the diffusion coefficient of \( O_2 \) in solution (1.9 \times 10^{-5} cm\(^2\) s\(^{-1}\)).

**Characterization**

The transmission electron microscope (TEM) images of Au clusters/RGO were obtained using a JEOL JEM2011 at 200 KV. Scanning electron microscope (SEM) observations were carried out on a Zeiss Ultra 55 FE-SEM with gold coating. Thermo gravimetric analyses (TGA) were performed at a heating rate of 1.8 °C min\(^{-1}\) on Perkin-Elmer Pyris-1 TGA in nitrogen at a flow rate of 40 cm\(^3\) min\(^{-1}\). UV-vis spectra were recorded on a Hitachi U-2910 spectrophotometer. Raman spectra were measured on a Renishaw inVia Reflex micro-Raman spectrometer with He/Ne laser excitation at 632.8 nm. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 470 spectrometer. X-ray photoelectron spectroscopy (XPS) were obtained on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Ka radiation (\( h\nu = 1253.6 \) eV). Fluorescence spectroscopy was carried out using a Shimadzu RF-5301PC spectrophotometer.

**Results and discussion**

**Characterizations of Au clusters and Au clusters/RGO composite prepared with CA**

Au clusters were homogeneously synthesized in hot DMF without the formation of big gold nanoparticles as by-products.\(^49\)\(^-\)\(^54\) Prior to reduction, the DMF solution containing HAuCl\(_4\) is nonfluorescent and shows a light yellow colour. After the reaction, the solution changes to yellow and exhibits a light blue photoluminescence. The UV-vis spectrum shows no characteristic peak at ~520 nm, which is usually assigned to the surface plasmon resonance (SPR) band of big gold nanoparticles, revealing that the diameter of these Au clusters is less than 2 nm (Fig. 1a), which is confirmed by the TEM image (Fig. S1†).\(^50\)\(^-\)\(^54\) In the photoluminescence (PL) spectra (Fig. 1b), these Au clusters exhibit an emission wavelength maxima of \( \lambda_{em} = 472 \) nm (\( E_{ex} = 385 \) nm), which is consistent with Kawasaki’s work, indicating that the Au clusters have been successfully synthesized.\(^54\)

Citric acid (CA) was employed to reduce GO and synthesize the Au clusters/RGO composite; the detailed preparation process is exhibited in Scheme 1. We have reported that CA is a green and efficient reducing agent for GO in our previous work.\(^49\) In this system, the reduction of GO and the formation of Au clusters/RGO composite are achieved simultaneously in the presence of CA. In the TEM images, monodispersed Au clusters are evenly distributed onto the RGO sheets with an average size of 1.8 nm, and no free clusters can be observed outside the RGO sheets, suggesting that free Au clusters are completely eliminated by centrifugation and that residual Au clusters are tightly adsorbed onto RGO sheets (Fig. 2a and b). The EDS pattern and corresponding N (N element is from DMF that is anchored onto the surface of the Au clusters as a protection agent) with Au elemental-mapping images confirm the uniform distribution of Au clusters on the RGO sheets (Fig. 2c–f). Raman spectra were employed to demonstrate the reduction of GO by CA. The G band of GO at 1588 cm\(^{-1}\) shifts to 1591 cm\(^{-1}\), and also the intensity ratio of D/G increases from 1.01 to 1.13, suggesting a decrease in the size of the sp\(^2\) domains during the reduction of GO. While for the Au clusters/RGO composite, the Raman spectrum is almost the same with RGO, which indicates that the Au clusters do not significantly reduce the size of the in-plane sp\(^2\) domains of RGO, that is, that Au clusters do not destroy RGO sheets during the formation of composite (Fig. S2†). It is not unreasonable that the non-covalent interaction is a key factor for the formation of this composite. Some CA may be anchored on the functional groups of GO sheets by non-covalent interactions during the reduction of GO. On the other hand, CA exhibits strong binding ability to metal nanoparticles, and previous works have demonstrated that CA is easily and strongly adsorbed onto metal nanoparticles and can act as a stabilizing and dispersing agent.\(^55\)\(^-\)\(^57\) Moreover, free Au clusters
are partially covered by protecting DMF molecules; thus, they can also be adsorbed on the functional groups of CA by strong non-covalent interactions. Because of the efficient binding effect of CA, Au clusters should be uniformly and tightly adsorbed onto the RGO sheets.

To investigate whether CA is an essential agent to synthesize Au clusters/RGO composites, other reducing agents have been utilized in our experiments. First, we directly added GO to the as-prepared hot Au cluster DMF solution (140 °C) to synthesize Au clusters/RGO composite; whereby, the brown suspensions turned black after 6 h of reaction. Only a few Au clusters can be found on the edge of the RGO sheets, which is probably caused by the non-covalent interaction between the residual functional groups on the edge of the RGO sheets and DMF, which is tightly adsorbed onto the surface of the Au clusters (Fig. 3a). In addition, two other reducing agents, N2H4/NH3 and ascorbic acid (AA), were also utilized during the preparation. Fig. 3b shows the TEM image of the Au clusters/RGO composite prepared with N2H4/NH3. There are more Au clusters loaded on the RGO sheets than with the composite prepared with DMF; however, they are not uniformly distributed, and indeed some regions of the RGO sheets are still blank. When the reducing agent is AA, the Au clusters are uniformly distributed on RGO sheets and the amount increases (Fig. 3c); however, the Au clusters are distributed more loosely than with the composite prepared with CA, that is, there are several more Au clusters on RGO sheets when CA is utilized to prepare Au clusters/RGO composites; indicating that CA is the most efficient and suitable agent for the preparation of Au clusters/RGO composites. To systematically investigate the binding ability of different agents, EDS patterns were employed to calculate the content of Au clusters in different Au clusters/RGO composites. As shown in Fig. S3,† the content of Au in Au clusters/RGO (CA) composites is 2.10 wt%, which is higher than that in Au clusters/RGO (AA) composites (1.65 wt%), confirming that CA is a better binding agent to adhere Au clusters to RGO sheets than AA. While for Au clusters/RGO (N2H4/NH3) and Au clusters/RGO (DMF) composites, Au clusters can barely anchor onto the RGO sheet (0.01 wt% and 0 wt%), which suggests that the binding ability of these two agents for Au clusters and RGO sheets is very weak. Apart from the content of Au, we are also concerned about the N content on EDS patterns. As we have mentioned before, Au clusters are protected by DMF; thus, the N content can indicate Au content in the RGO composite prepared by CA and AA. The content of N in Au clusters/RGO (CA) composites (6.75 wt%) is higher than that in Au clusters/RGO (AA) composites (5.10 wt%), which is consistent with Au content in these two composites. For Au clusters/RGO (N2H4/NH3) and Au clusters/RGO (DMF) composites because of these two agents containing N elements, it is not appropriate to quantitatively estimate Au content by N content. Noticeably, the content of N in Au clusters/RGO (DMF) composites is close to 0 wt%, indicating that the DMF molecules cannot be directly adsorbed onto RGO sheets, which is the probable reason why Au clusters are rare on RGO sheets in Au clusters/RGO (DMF) composites (Fig. 3a). Furthermore, Fourier transform infrared (FTIR) spectra were also employed to estimate N content by the intensity of the peak at 1651 cm⁻¹, which is assigned to amide I. The stronger intensity of amide I in Au clusters/RGO composites (CA) reveals that the N content of the Au clusters/RGO composite (CA) is higher than that of Au clusters/RGO composite (AA), which is identified by EDS patterns (Fig. S4†) All the results demonstrated that CA is a better reducing and binding agent than AA, N2H4/NH3 and DMF for the preparation of Au clusters/RGO composites.

Although the precise mechanism for the better binding ability of CA is still unclear, the strong interaction between –COOH and the metal ions or charge metal nanoparticles (one CA has three –COOH) is the probable reason. On the other hand, the –COOH and –OH groups of CA can form strong non-covalent interactions with the oxygenic groups on RGO and the by-product of DMF oxidation, which is tightly adsorbed on the surface of the Au clusters such that CA can efficiently bind Au clusters to RGO sheets.32 AA has a similar molecular size and reducing power as citric acid, and is also usually used as a green

Fig. 2 (a and b) TEM images and (c) SEM image of Au clusters/RGO composite prepared with CA. (d–f) corresponding carbon, nitrogen, and gold elemental-mapping images of (c). The ratio of Au clusters : RGO is 5 : 1.

Fig. 3 (a) TEM image of Au clusters/RGO composite directly prepared in DMF solution at 140 °C; (b) and (c) TEM images of Au clusters/RGO composites prepared with N2H4/NH3 and ascorbic acid (AA). All the ratio of Au clusters : RGO are 5 : 1.
reducing agent. Moreover, AA can also be tightly adsorbed onto RGO sheets because of the strong non-covalent interactions between –OH of AA and oxygenic groups on RGO. However, numerous reports have already demonstrated that the binding ability of AA to the metal surface is weaker than CA because the interaction between –OH and metal ions (or the metal surface) is weaker than that between –COOH and metal ions (or the metal surface).58,59 Furthermore, AA does not have –COOH groups, and therefore, the interaction between –OH and DMF is weaker than the interaction between –COOH and DMF because H-bonds can also be formed between the H on DMF and C=O on CA, resulting in non-covalent interactions between AA and DMF being weaker than that between CA and DMF. Both these factors imply that the binding ability of CA is stronger than that of AA for the preparation of Au clusters/RGO composites. For N\textsubscript{2}H\textsubscript{4}/NH\textsubscript{3}, although the interaction of N\textsubscript{2}H\textsubscript{4}/NH\textsubscript{3} and RGO is very strong (Fig. S3 and S4†), the binding ability of N\textsubscript{2}H\textsubscript{4}/NH\textsubscript{3} to Au clusters is very weak; thus, Au clusters are difficult to anchor onto RGO sheets (Fig. 3b). While, for DMF, the binding ability of both Au clusters and RGO sheets is very weak (Fig. S3 and S4†), resulting in few Au clusters being adsorbed onto the RGO sheets (Fig. 3a). Noticeably, we also find several Au clusters anchored onto RGO in Au clusters/RGO (N\textsubscript{2}H\textsubscript{4}/NH\textsubscript{3}) and Au clusters/RGO (DMF) composites (Fig. 3a and b). This is probably caused by the interaction between the by-product of DMF oxidation, which is tightly adsorbed onto the surface of Au clusters and on the residual oxygenic groups on RGO.

The surface composition and elemental analysis of the resultant Au clusters/RGO composite prepared with CA were characterized by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 4. Three distinct peaks at 285.0, 400.0, and 531.4 eV are observed, which are attributed to C\textsubscript{1s}, N\textsubscript{1s}, and O\textsubscript{1s} peaks, respectively (Fig. 4a). Another small peak at 85.2 eV, which might be attributed to the binding energy of the surface of Au clusters, can also be observed. In general, bulk Au metal has a binding energy of 84 eV (Au\textsubscript{0}); however, numerous studies have demonstrated that the binding energy of metal clusters increases with the decrease in cluster size.56,57 Therefore, this peak should be assigned to the characteristic peak of Au clusters in our systems.54–56 As we know, GO and CA do not contain N, and thus N must come from DMF. This verifies that the dried Au clusters are still protected by DMF. The high-resolution C\textsubscript{1s} spectrum shows four peaks at 284.7, 285.9, 288.2 and 289.7 eV, which are assigned to C=O, C-N/C-O, C=N/C=O and C=O, respectively (Fig. 4b).27 In the N\textsubscript{1s} spectrum, the two peaks at 399.9 and 401.2 eV are attributed to pyrolysis-like N and N=H, respectively, which indicates that some N is doped into the RGO sheets during the synthesis process (Fig. 4c). The O\textsubscript{1s} spectrum exhibits two peaks at 531.2 and 531.8 eV, corresponding to O=C-N and O=C-O, respectively, which also confirms that some DMF is residual in the composite (Fig. 4d).59

Fig. 4 XPS spectra of Au clusters/RGO composite prepared with CA: (a) survey spectrum; (b) high resolution C\textsubscript{1s}; (c) high resolution N\textsubscript{1s}; (d) high resolution O\textsubscript{1s}.

Electro-catalysis application of Au clusters/RGO composites

The electrochemical activity of the Au clusters/RGO composites toward ORR was first characterized by cyclic voltammetry (CV)
in O₂ or N₂ saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹. Four composites prepared with different ratios of Au clusters : RGO were examined. Featureless voltammetric currents within the potential range from −1.0 and 0.2 V are observed in the N₂-saturated solution (dotted curve). In contrast, a well-defined cathodic oxygen reduction peak can be clearly observed when the electrolyte is saturated with O₂ (Fig. 6). When the ratio of Au clusters : RGO is 5 : 1, the value of the onset potential and peak potential of the Au clusters/RGO composite are −0.14 V and −0.28 V against the Ag/AgCl electrode (Fig. 6a), respectively. Although the peak potential is slightly negatively shifted compared with the commercial Pt/C catalyst, this value is still −150 mV more positive than the RGO sheets without Au clusters (Fig. S5†). Furthermore, the catalytic activity is comparable to, or even better, than several N-containingCNT-based or graphene-based metals, metal oxides, or metal nitrogen-containing complexes electrocatalysts, suggesting that this composite could be used as an efficient electrocatalyst for ORR.¹⁹,³⁴,⁶⁴ When the ratio of Au clusters : RGO decreased to 4 : 1, the peak potential negatively shifts to −0.30 V (Fig. 6b). With a decrease in the Au clusters : RGO ratio to 2.5 : 1 and 1 : 1, the peak potential further negatively shifts to −0.32 and −0.34 V, respectively (Fig. 6c and d). Therefore, it is not unreasonable to suggest that the decline of electrochemical activity results from the decrease in Au clusters anchored on RGO sheets (Fig. S6†). Recently, Sohn et al. successfully prepared uniformly and densely distributed Au nanoparticles on RGO sheets; although the content of Au in such a composite is very high, the ORR catalytic activity is mediocre (−0.45 V vs. Ag/AgCl) because the size of the Au nanoparticles is more than 5 nm.⁴⁰ This indicates that the size of the Au nanoparticles is a key factor for the catalytic activity for ORR. Previous work has demonstrated that the excellent catalytic activity of these Au clusters could be attributed to the high fraction of surface atoms with low coordination numbers. Thus, the oxygen molecules are efficiently captured by the Au atoms on the clusters surface and can then be activated more easily than their close-packed counterparts.³²

To demonstrate that CA is a better agent to prepare Au clusters/RGO composites for ORR, the electro-catalysis activity of Au clusters/RGO composites prepared with other agents was also measured (Fig. S5†). The peak potential of Au clusters/RGO composites prepared with DMF is −0.38 V (Fig. S7a†), and although there are only a few Au clusters on the RGO sheets (Fig. 3a), it still positively shifts by −50 mV compared with the RGO sheets (Fig. S3†), indicating that Au clusters are the key factor for ORR in our experiment. When the composite is generated with NH₃/N₂H₄, the Au clusters anchored on the RGO sheets increase in number, and the peak potential positively shifts to −0.33 V (Fig. S7b†). When AA is employed, the potential further positively shifts to −0.32 V because of the increase in Au clusters on RGO sheets (Fig. S7c†). The potential of all these composites is negative compared with that of the composite prepared with CA, which is consistent with TEM images (Fig. 1b and 2). These results suggest that, in our work, CA is the best reducing and binding agent for preparing well distributed Au clusters/RGO composites as ORR electrocatalysts.

Linear-sweep voltammetry (LSV) curves of oxygen reduction for Au clusters/RGO composites in O₂-saturated 0.1 M KOH solution were also performed on a rotating disk electrode (RDE). Fig. 7a shows the RDE curves of commercial Pt/C catalyst and of Au clusters/RGO composites generated using different reducing agents at a rotation rate of 1300 rpm. The corresponding ORR current density of Au clusters/RGO composites (CA) reaches about 3.5 mA cm⁻² at −1.0 V, which is significantly higher than that of the commercial Pt/C catalyst and other Au clusters/RGO composites, suggesting the excellent ORR activity of this composite. Fig. 7b exhibits the RDE curves of the Au clusters/RGO composites generated with CA at different rotation rates from 400 to 1900 rpm. The ORR current density clearly increases with the improvement in rotation rate, which is probably caused by the enhanced diffusion of electrolytes, indicating that diffusion rate is a key factor for the catalytic process of this catalyst. The Koutecky–Levich plots at various electrode potentials from −0.85 V to −0.50 V are presented in Fig. 7c. The nearly parallel and straight fitting lines reveal that the reduction reaction of dissolved O₂ catalyzed by the Au clusters/RGO composite is a first-order reaction.⁶⁵–⁶⁷ The transferred electron number (n) per oxygen molecule is calculated to be 3.49–3.83, according to the K–L equation, suggesting a direct four-electron transfer pathway for ORR on Au clusters/RGO composite (CA) electrodes (Fig. S8†).

To investigate the electrochemical stability of Au clusters/RGO composite prepared with CA, continuous cyclic voltammetry was performed in O₂-saturated 0.1 M KOH solution. As shown in Fig. S9† after 1000 cycles, the composite experiences an initial loss of ~16%, which is comparable to that reported by Tang et al. for Au clusters/RGO hybrid and much smaller than that of commercial Pt/C catalyst (~27%) and some Fe–N–RGO composites;³⁴,⁶⁴ moreover, the peak potential of the Au clusters/RGO composite (CA) is almost unchanged after 1000 cycles, suggesting stable ORR activity of the Au clusters/RGO (CA) catalyst. On the other hand, because of the possibility that fuel molecules, such as methanol or glucose, in the anode may permeate through the barrier membrane to the cathode and

![Fig. 6](image-url) CV curves of Au clusters/RGO composites (CA) prepared with different ratios of Au clusters : RGO in O₂ and N₂ saturated 0.1 M KOH solution. (a) 5 : 1; (b) 4 : 1; (c) 2.5 : 1; (d) 1 : 1.
seriously influence the performance of the catalysts, the cross-over effect also should be considered to accurately evaluate the properties of the electrocatalyst.\textsuperscript{11} Hence, the electrocatalytic selectivities of the Au clusters/RGO composite (CA) and the Pt/C catalyst against the electrooxidation of methanol were also measured in O\textsubscript{2}-saturated 0.1 M KOH using 3 M CH\textsubscript{3}OH (Fig. 7d). For the Pt/C catalyst, a strong response with a pair of peaks are observed at -0.35 and -0.20 V for methanol oxidation, whereas the cathodic peak for ORR at -0.23 V vanishes (blank line in Fig. 7d). However, no evident change can be observed in the oxygen-reduction current on the Au clusters/RGO (CA) catalyst under the same conditions (red line in Fig. 7d), suggesting methanol-tolerant ORR activity of this electrocatalyst.\textsuperscript{15,68} Undoubtedly, Au clusters/RGO composites (CA) exhibit a high selectivity for ORR with an excellent ability to avoid crossover effects. Thus, this material can be a promising non-Pt electrocatalyst for direct use in methanol and alkaline fuel cells.

Conclusions

A uniformly distributed Au clusters/RGO composite was prepared by CA via a very simple route. In our work, CA not only acted as a reducing agent for GO, but also served as an “adhesive” for binding Au clusters and RGO sheets. Various characterizations were employed to demonstrate that the Au clusters were tightly anchored onto the RGO sheets. Experimental comparisons revealed that CA was most suited and more efficient to bind Au clusters and RGO sheets than other agents, such as AA, N\textsubscript{2}H\textsubscript{4}/NH\textsubscript{3} and DMF. Au clusters/RGO composites (CA) exhibited excellent electrocatalytic performances toward ORR, and the long-term durability and methanol tolerance of this composite was significantly better than that of the commercial Pt/C electrocatalyst. Hence, this could be a promising and alternative non-Pt catalyst to replace Pt/C catalyst in fuel cells. In addition, our work might provide a facile, efficient
and versatile route for the large scale preparation of uniform metal cluster/RGO composites.

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Notes and references