Hierarchical reduced graphene oxide supported dealloyed platinum–copper nanoparticles for highly efficient methanol electrooxidation

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Abstract

Exploiting highly efficient electrocatalysts through simple methods is very critical to the development of energy conversion technologies. Herein, we develop a hierarchical reduced graphene oxide supported dealloyed platinum–copper nanoparticle catalyst (Pt–Cu/RGO) by a facile one-step electrodeposition of graphene oxide in the presence of H2PtCl6 and copper ethylenediamine tetraacetate. The nanostructure and composition were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. Meanwhile, the electrocatalytic performance was investigated by cyclic voltammetry and chronoamperometry, showing that the Pt–Cu/RGO catalyst not only equips with an outstanding electrocatalytic activity for the methanol oxidation reaction (2.3 times that of commercial Pt/C catalyst), but also shows a robust durability and superior tolerance to CO poisoning. The excellent electrocatalytic performance could be attributed to the three-dimensional hierarchical structure, porous dealloyed nanoparticles and synergistic effect between each component.

Introduction

Direct methanol fuel cells (DMFCs) have been considered for a long time as promising power conversion devices for portable and mobile applications, owing to their high energy density, low operation temperature and high energy conversion efficiency [1]. However, the commercialization of DMFCs is always hindered by high price and limited abundance of the commonly used Pt/C catalysts. Besides, pure Pt catalyst is readily poisoned by intermediate carbonaceous species (mainly CO) during methanol oxidation reaction (MOR), leading to a sharp decrease in electrocatalytic activity [2]. To solve these problems, one of the most effective methods is to alloy Pt with other less expensive transition metals such as Cu, Ni and Co [3–5], which can not only significantly increase the catalytic performance through modifying the Pt electronic structure, but also remarkably decrease Pt consumption and improve the utilization efficiency of Pt. Among various Pt–M (M = non-noble metal) bimetallic catalysts, Pt–Cu alloy have been identified as a promising candidate because Cu is highly active for the oxidation of poisonous carbonaceous intermediates [6–8]. Until now, many methods have been reported to prepare Pt–Cu alloy nanocrystals, such as hydrothermal process, but additional surface dealloying of the less noble Cu atoms from Pt–Cu alloys is very necessary to the
formation of porous structure with Pt-rich shell [9–11]. To the best of our knowledge, there have been no report on the preparation of dealloyed Pt–Cu nanoparticle electrocatalysts through facile electrodeposition method.

On the other hand, the morphology control using high surface area supporting materials can further expose metal active sites. Graphene has been widely regarded as an excellent catalyst support due to its high surface area, outstanding electrical conductivity, and excellent chemical stability. The abundant functional groups on the surface of graphene oxide can provide many favorable sites for anchoring catalyst nanoparticles [12]. However, due to the irreversible restacking of individual graphene nanosheets, catalyst nanoparticles are often inserted between the graphene layers, causing a decrease of catalytic sites [13–15]. Therefore, three-dimensional hierarchical graphene is highly desirable for catalyst loading to facilitate the mass transfer and maximize the accessibility to the catalyst surfaces [16,17]. Nevertheless, the hierarchical graphene was usually achieved by some complicated and expensive methods, which are also difficult in compatibility with the fabrication process of practical electrochemical devices [18,19]. Thus, the facile preparation of hierarchical graphene as catalyst supports on a large scale from low-cost graphene oxide is very attractive but challenging.

In our work, we successfully design and synthesize a hierarchical reduced graphene oxide supported dealloyed platinum–copper nanoparticle hybrid (Pt–Cu/RGO) by a facile one-step electrodeposition method. Electrodeposition is one of the simple, rapid and green techniques for the fabrication of “clean” binder-free electrode materials [20,21]. The hierarchical Pt–Cu/RGO hybrid was obtained by a direct cyclic voltammetric (CV) electrolysis of graphene oxide (GO) colloidal solution containing the precursors of Pt and Cu. Electrochemical dealloying of the less noble Cu from the Pt–Cu alloy was additionally performed. The resultant Pt–Cu/RGO hybrid was employed as an electrocatalyst for methanol oxidation reaction (MOR), exhibiting high electrocatalytic activity (2.3 times that of commercial Pt/C catalyst) and good durability. To the best of our knowledge, this is the first prototype about dealloyed Pt–Cu nanoparticles supported by hierarchical graphene nanosheets.

Preparation of Pt–Cu/RGO hybrid

Graphite oxide was prepared through the improved method with a minor modification according to our previous work [22,23]. The graphite oxide was exfoliated in a 1/15 M pH 8.0 phosphate buffer by ultrasonication for 3 h in ice water to obtain homogeneous 0.3 g L−1 GO colloidal solution. A certain amount of copper ethylenediamine tetracacetate (Cu–EDTA) (0.5 mM) was added into the mixed dispersion containing 0.3 g L−1 GO and 2.0 mM H2PtCl6, and the solution was used as the precursor for electrochemical preparation of Pt–Cu/RGO hybrid. The electrodeposition was carried out under magnetic stirring using CV technique on a CHI 660C electrochemical workstation (CH Instruments) with a three-electrode system: a GC electrode (0.07 cm2 in geometric area) as the working electrode, a Pt foil (1.0 cm2 in geometric area) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The GC electrode was polished by 0.5 μm Al2O3 powders followed by ultrasonic washing in deionized water. The scan was performed between −1.4 and 0.6 V at a rate of 50 mV s−1 for ten cycles. After electrodeposition, the Pt–Cu/RGO electrode was transferred into 1.0 M H2SO4 solution and conducted between −0.2 and 1.2 V (scan rate: 50 mV s−1) until the CV curves were reproducible. Then the electrode was carefully washed for several times and dried at room temperature.

For comparison, Pt/RGO hybrid was prepared using the similar method without the addition of Cu–EDTA. Pure RGO was obtained through CV electrodeposition of graphene oxide. Pure Pt nanoparticles were achieved from electrodeposition of Pt precursor. The commercial Pt/C catalyst electrode was prepared by ultrasonically dispersing commercial Pt/C powder in ethanol solution containing Nafion (υ:υ = 20:1) to form a 2.0 g L−1 ink, and then casting the 10 μL ink on a newly polished GC electrode.

Characterization

The as-prepared samples were characterized by field emission scanning electron microscopy (SEM, Hitachi, S-4800) equipped with an energy dispersive X-ray spectrometer (EDX), transmission electron microscopy (TEM, JEM-3010 operating at 200 kV), high angle annular dark-field scanning TEM (HAADF-STEM, FEI Tecnai G2 F20S-TWIN), X-ray diffraction (XRD, D-max 2500, Cu Kα radiation, λ = 1.54056 Å), Raman spectroscopy (Labram-010 with a 632.8 nm laser), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Kα 1063 system with a monochromatic Al Kα source, 1486.6 eV, all the binding energies were corrected with reference to the C 1s peak at 284.8 eV). The Pt loading amount in the hybrid electrodeposited on electrodes was evaluated by inductively coupled plasma-atomic emission spectrometry (ICP-AES, PS-6, Baird, USA) after dissolution with aqua regia.

Electrochemical measurements

The electrochemical measurements of the as-prepared catalysts were performed by a conventional three-electrode system. The electrocatalytic activity for the MOR was characterized by CV measurement between 0 V and 1.0 V at a...
scan rate of 50 mV s\(^{-1}\). Several activation scans were performed until reproducible voltammograms were obtained (generally about five cycles). The electrocatalytic durability was performed by CV and chronopotentiometry, and the given potential was 0.65 V for a period of 1500 s. The electrolyte is a 1.0 M H\(_2\)SO\(_4\) solution containing 1.0 M CH\(_3\)OH. Prior to all these experiments, the electrolyte solution was purged with high purity N\(_2\) (>99.99\%) for at least 30 min to remove dissolved oxygen. CO stripping measurements were taken to evaluate the poison resistance of these catalysts through our previous method [23]. All the CV scans were performed at a rate of 50 mV s\(^{-1}\) from 0.2 V to 1.0 V for the CO oxidation, and all the potentials discussed in our work are relative to SCE.

Results and discussion

According to our previous work [24], the RGO film with a few wrinkles (Fig. 1a) was prepared by direct CV electrolysis of GO colloid solution, and obviously, pure RGO nanosheets tend to horizontally stack on substrates. Fig. 1b displays the SEM image of pure Pt nanoparticles, and the particle diameter is about 77 nm (shown in the inset). Using one-step co-electrodeposition method, the Pt/RGO hybrid was achieved (Fig. 1c), which is similar to the preparation of Au/RGO hybrid [25]. Fig. 1d shows the enlarged SEM image, revealing that Pt nanoparticles with average diameter 44 nm disperse uniformly on the RGO sheets. However, the RGO nanosheets still tend to aggregate, thus most of Pt nanoparticles are embedded into the electrolyte, the obtained morphology becomes totally different, displaying a hierarchically three-dimensional nanosheet (Fig. 1e) and the RGO sheets are not observed. The magnified image (Fig. 1f) shows that the Pt–Cu nanoparticles are supported by RGO nanosheets (clearly revealed by the following TEM characterization), forming a sandwich-like structure with the active sites of Pt–Cu nanoparticles fully exposed. In addition, the Pt–Cu particles are thought to be porous because the cyclic electrodeposition of Cu-based noble metal alloys enable the simultaneous anodic dissolution of Cu atoms during the electrodeposition process [26]. (Fig. S1) EDX spectra were also collected. In contrast to the Pt/RGO hybrid (shown in Fig. S2), the Pt–Cu/RGO hybrid (Fig. 1g) has additional Cu atoms except the signals of O, Pd, and Ti (coming from the Ti plate substrate).

In order to further improve the catalytic performance, dealloying experiment was additionally performed on the Pt–Cu particles by CV treatment of the Pt–Cu/RGO electrode in sulfuric acid [27]. The anodic peak current for copper (0.3–0.6 V vs. SCE) decreasing with the dealloying proceeding indicates the dissolution of Cu atoms, and thus more Pt atoms are exposed due to the porosity formation on the Pt–Cu nanoparticles, as evidenced by the increase of hydrogen adsorption/desorption peak current of Pt (−0.2 to 0.05 V vs. SCE) (Fig. 2a). In contrast, there are no changes on the Pt/RGO electrode (Fig. 2b) under the same experimental condition.

The detailed nanostructure and composition of Pt–Cu/RGO hybrid were further characterized by TEM techniques. Fig. 3a shows the TEM image of Pt–Cu/RGO hybrid, revealing that Pt–Cu nanoparticles are anchored on the RGO nanosheets, and distributed on both sides. In other words, RGO sheets act as framework and are sandwiched between the nanoparticle layers. The HR-TEM image (shown in the inset) demonstrates clear lattice fringes with an interfringe distance of approximately 0.19 nm, corresponding to the lattice spacing of the Pt–Cu (200) planes [28,29]. The well alloyed Pt–Cu nanoparticles of Pt–Cu/RGO hybrid were further confirmed by XRD technique (Fig. 3b). Except that these diffraction peaks of Ni foam (marked with ◆, JCPDS no. 04-0850), four typical diffraction peaks locating at 2θ = 40°, 47°, 68° and 83° could be indexed to the (111), (200), (220) and (311) lattice plane of a face centered-cubic (fcc) structure, respectively. All these peaks were located in between the standard patterns of pure Pt and pure Cu, thus confirming the formation of only single phase Pt–Cu alloy [28]. In addition, the peak of C(002) was also observed, indicating the presence of RGO support. The HAADF-STEM technique was also used to analyze the distribution and composition of the elements in the Pt–Cu/RGO hybrid. Fig. 3c shows the HAADF-STEM image of Pt–Cu/RGO hybrid and the corresponding EDX mapping images of Pt (blue, Fig. 3d) and Cu (yellow, Fig. 3e). As is observed, the elemental mapping of Cu was dovetailing uniformly with the even distribution of Pt, which further confirms the successful formation of Pt–Cu alloy. In addition, the elemental mapping also reveals the presence of C and O elements in the hybrid (Fig. S3). Obviously, the carbon element comes from the RGO support, and a certain amount of oxygen element are observed, which is ascribed to that the RGO was partially electrochemically reduced [30] and also Pt/Cu element might be possibly slightly oxidized.

Raman spectroscopy is a useful tool to characterize carbonaceous materials, especially for distinguishing RGO and GO. For the pure RGO film, there were two prominent peaks at about 1296 cm\(^{-1}\) and 1588 cm\(^{-1}\) (Fig. 4), corresponding to the well documented D and G bands. After loading Pt or Pt–Cu nanoparticles, these two peaks can also be obviously observed, indicative of the existence of graphene in the catalysts. Usually, the ratio of the intensities of the D (I\(_D\)) and G (I\(_G\)) bands, I\(_D\)/I\(_G\), is used to be an indicator of the degree of the sp\(^2\) domain. Compared to the Raman spectrum of GO (Fig. S4), all the values of I\(_D\)/I\(_G\) are found to be increased, which further confirms that RGO was obtained from GO suspension through the simple green electrodeposition process.

The amount of available active sites of these Pt-based catalysts, which can be reflected by the electrochemically active surface area (ECSA), are investigated by the CV technique. Fig. 5a shows the cyclic voltammograms for Pt–Cu/RGO, Pt/RGO and commercial Pt/C in N\(_2\) saturated 1.0 M H\(_2\)SO\(_4\) solution at a scan rate of 50 mV s\(^{-1}\). The three voltammetric profiles exhibit similar characteristic peaks of platinum, such as platinum oxide formation (0.6–1.0 V) and reduction (0.2–0.7 V), as well as typical peaks of hydrogen adsorption/desorption (−0.2 to 0.05 V). The hydrogen desorption peaks are used to estimate the ECSA by employing the following equation [31–33]:

\[
\text{ECSA} = \frac{Q}{m_{Pt} \times 210 \mu C \text{ cm}^{-2}} \tag{1}
\]
where \( Q \) represents the total charge concerning the hydrogen desorption (\( \mu \)C), 210 \( \mu \)C cm\(^{-2}\) is the charge density required to oxidize a complete hydrogen monolayer on Pt atom surface, and \( m_{Pt} \) is the mass (g) of Pt on the electrode. Based on the integrated area under the desorption peak between \(-0.2 \) and \(0.05\) V in the cyclic voltammogram, the ECSA of Pt–Cu/RGO hybrid is calculated to be 40.5 m\(^2\) g\(^{-1}\), which is much higher than that of Pt/RGO (33.8 m\(^2\) g\(^{-1}\)) and commercial Pt/C (28.4 m\(^2\) g\(^{-1}\)). The Pt–Cu/RGO hybrid possesses more active sites, and this distinctly higher ECSA is mainly attributed to the unique hierarchical structure and porous dealloyed Pt–Cu nanoparticles.

We therefore examined its application in direct methanol fuel cells, and the electrocatalytic activity and durability...
towards the MOR were investigated. Fig. 5b shows CVs of Pt–Cu/RGO, Pt/RGO and commercial Pt/C catalyst at a scan rate of 50 mV s\(^{-1}\). The electrolyte solution is N\(_2\)-saturated 1.0 M H\(_2\)SO\(_4\) solution containing 1.0 M CH\(_3\)OH. All the CV curves showed a similar methanol oxidation peak in the forward scan (\(I_f\)) and another oxidation peak in the backward scan (\(I_b\)) corresponding to the removal of the residual carbonaceous species formed in the forward scan. Obviously, the mass current density of Pt–Cu/RGO catalyst was 0.42 A mg\(^{-1}\), much higher than that of Pt/RGO (0.27 A mg\(^{-1}\)) and commercial Pt/C catalyst (0.18 A mg\(^{-1}\)), which is consistent with the result of the above ECSA. The ratio of \(I_f/I_b\) can be used to evaluate the tolerance of catalysts towards the poisoning species (especially CO), and a higher \(I_f/I_b\) ratio indicates more effective oxidation of methanol to carbon dioxide during the anodic scan [34]. The ratio value of Pt–Cu/RGO catalyst was calculated to be 1.56, and this result was larger than that of Pt/RGO (1.33) and commercial Pt/C catalyst (1.28), indicating good oxidation ability, which brings a fewer accumulation of carbonaceous residues on the catalyst surface.

![Cyclic voltammograms (CVs) of Pt–Cu/RGO (a) and Pt/RGO (b) in N\(_2\)-saturated 1.0 M H\(_2\)SO\(_4\) solution at a scan rate of 50 mV s\(^{-1}\).](image1)

![TEM images of Pt–Cu/RGO, inset is HR-TEM image of Pt–Cu alloy nanoparticles; XRD patterns of Pt–Cu/RGO on Ni foam, the diffraction peaks marked with \(\bullet\) come from the Ni foam (JCPDS no. 04-0850); HAADF-STEM image of Pt–Cu/RGO and (d, e) corresponding element mapping of Pt (blue) and Cu (yellow).](image2)
The catalytic durability for the MOR was measured by chronopotentiometry and cyclic voltammetry. Fig. 6a shows the current–time curves of different catalysts at a fixed potential of 0.65 V vs. SCE. At this potential, reaction intermediate species such as CO$_{ad}$ would begin to accumulate on the catalyst surface due to the continuous methanol oxidation. All the current density showed decays at the initial stage, but the decay in Pt–Cu/RGO catalyst is the slowest. Then the current gradually reached a steady state, and among the three catalysts, the Pt–Cu/RGO catalyst also maintained the highest limiting currents over the entire duration. Additionally, long-term potential cycling was further used, and the CVs of Pt–Cu/RGO, Pt/RGO and commercial Pt/C catalyst for the MOR at the 1st, 100th, 200th, 300th, and 400th cycles are shown in Fig. S5. Fig. 6b summarizes the forward anodic peak current of the MOR as a function of cycle number. After 400 cycles, the current retention rate of Pt–Cu/RGO catalyst was 64.6%, much higher than that of Pt/RGO (39.2%) and commercial Pt/C (12.8%). All these results indicate that the Pt–Cu/RGO catalyst is an efficient electrocatalyst, which possesses excellent catalytic activity, robust long-term durability and high tolerance against reaction intermediates.

To verify whether Cu promotes the removal of adsorbed CO by the bifunctional mechanism, electrocatalytic oxidation of pure CO molecules was also investigated through the CO stripping experiments (Fig. 7). The peak potential of CO oxidation on the Pt–Cu/RGO electrode is 0.69 V, much lower than that of Pt/RGO (0.75 V). Lower potential values (difference value of 60 mV) on the Pt–Cu/RGO catalyst indicate that less applied electric energy is required to oxidate CO molecules.
Fig. 7 – CO stripping voltammograms of Pt–Cu/RGO, and commercial Pt/C in 1.0 M H2SO4 solution at a scan rate of 50 mV s⁻¹.

[35]. This means that the addition of Cu atoms facilitates the removal of CO out of the catalyst surface, which is in consistence with the higher electrocatalytic activity and better durability demonstrated above.

Conclusions

In conclusion, we have successfully prepared a hierarchical reduced graphene oxide supported dealloyed platinum–copper nanoparticle nanosheet (Pt–Cu/RGO) electrocatalyst. The catalyst was obtained by a simple and green one-step electrodeposition method. The resulting Pt–Cu/RGO electrocatalyst was firstly applied in methanol electro-oxidation, which not only shows an excellent electrocatalytic activity (2.3 times that of commercial Pt/C catalyst), but also has a robust durability and superior tolerance to CO poisoning. This high performance was attributed to the large active surface areas and favorable electron and mass transport pathways endowed by the novel hierarchical nanostructure. This facile and simple electrodeposition method can be extended to prepare other functional nanomaterials for energy-related applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2017.01.133.

References


