Au@Gqds@Ptxbi Nano-Dendrites Endows Alkaline Methanol Highly Electro-Catalytic Activity and Stability

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Abstract. In this work, we put forward a simple and green strategy to design and synthetic a highly efficient Au@GQDs@PtBi nano-catalyst with a novel nanostructure composed of an Au@GQDs core and PtBi alloy shell. This material showed outstanding catalytic capability for the oxidation of methanol (MOR) than that of the commercial Pt/C catalyst. The sequence of the mass activity was arranged to be commercial Pt/C (0.29 A mgPt⁻¹) < Au@Pt₃.₅Bi (1.6 A mgPt⁻¹) < Au@GQDs@Pt (1.81 A mgPt⁻¹) < Au@GQDs@Pt₃.₅Bi (17.45 A mgPt⁻¹). The outcomes ascribed to the unique core-shell structure with dendrites, interior electronic and synergistic effect with Bi and Pt. This work enlightens on the delicate proposal of novel core-shell nano-material for improving the electro-catalytic performance of MOR.

Keywords: Core-shell nanostructure, PtBi nano-dendrites, Methanol electro-oxidation, Graphene quantum dots.

1. Introduction

Direct methanol fuel cells (DMFCs), have fascinated a large number of researchers owing to some features such as safe storage and transportation, low environmental impact, high theoretical density (6kWh/kg), and abundant resource [1]. Pt is the most universally hired catalyst for methanol electro-oxidation (MOR). Unfortunately, there are subjected to some difficulties such as low reserves, high price, inevitable to poisoning, and poor stability for MOR, which greatly controlled the industrialization of DMFCs [2].

In order to reduce the loading of Pt on electrode as well as enhance the catalytic activity, two major strategies have been recommended. First of all, numerous nanostructures that hold large surface area or high index facets have been arranged to enhance the catalytic activity. Moreover, open structures are very prevalent nowadays for the accurate creation of PtM shells with ample dendrites and channels. These kinds of framework could not only expand the active surface area but also expose more active sites, and decline diffusion resistance obviously [3]. Although this strategy can reduce the loading, the permanency problem has not been thoroughly settled. Another strategy is to modifying Pt through different materials, as alloys, heterogeneous composite or intermetallic compounds, which is a common method to better tolerance to CO and simultaneously increasing its catalytic properties. It has been approved that these tactics can remarkably improve their catalytic performance, mainly attribute
to the coexisting geometric and electronic structure effects that trace to the lattice mismatch, stretching or compression [4]. Varied Pt-based alloy or structurally ordered intermetallic compounds have been effectively synthesized, such as Pt$_3$Ti, PtSn, PtPb, PtBi [5]. Among them, as for the co-catalytic element Bi, the combination of Bi can facilitate higher patience to CO poisoning and enhance catalytic activity for methanol or alcohol oxidation. The improvement catalytic activity and stability has been mainly ascribed to the increased of OH$_{ads}$ species adsorption on Pt activity sites that benefits to removal of the CO and other reaction intermediates [6].

Encouraged by the systemic investigation, herein, a simple method has been proposed to synthesize a type of Au@GQDs@Pt$_{3.5}$Bi nano-dendrites. Pleasantly, from the electrochemical measurements and comparison experiments, we discovered that the as-arranged Au@GQDs@Pt$_{3.5}$Bi shows excellent electro-catalytic activity for MOR in terms of the specific activity (114mA/cm$^2$), and mass activity (17.45A/mg), as well as the outstanding durability after the measurements of chronoamperometric (CA). Moreover, the next few weeks the potential mechanism of the improved electro-catalytic activity and stability will been comprehensive studied through various characterization methods.

2. Experimental

2.1. Chemicals and materials
Sodium citrate dehydrate (Na$_3$C$_6$H$_5$O$_7$$\cdot$2H$_2$O), Bi (NO$_3$)$_3$ were supplied by Tianjin Kaixin Chemical Reagent Company. Gold chloride trihydrate (HAuCl$_4$$\cdot$3H$_2$O) and Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$$\cdot$6H$_2$O) were ordered from Aladdin Chemistry Co., Ltd (Shanghai, China). Pt/C (20%) was ordered from shanghai Macklin Biochemical Co., Ltd. All of the chemical reagents are of analytical grade and used as received without any further purification. The water in all experiments was prepared in a three-stage Millipore Milli-Q plus 185 purification system and had a resistivity of >18.2 MΩ cm.

2.2. Electrochemical methods
The electrochemically active surface areas (ECSA) and methanol electro-oxidation of the synthesis materials were measured by cyclic voltammetry (CV). CV tests were carried out in 1 M NaOH or 1 M NaOH and 0.5 M methanol with 50 mV s$^{-1}$. The chronoamperometry (CA) were conducted to estimate the stability of the as-prepared materials, it recorded at -0.2V for 3000s.

2.3. Preparation of Au@GQDs@Pt$_{3.5}$Bi nano-dendrites

2.3.1. Synthesis of Au@GQDs@Pt. The production of Au@GQDs@Pt was accepted through a method according to our previous work (have not published). Typically, 120μL H$_2$PtCl$_6$$\cdot$6H$_2$O (19.3mM) was added into the Au@GQDs (10mL), and then incubating for 2 min. Ascorbic acid (AA, 500μL, 0.1M), act as reductant, was put into the mixture at 43℃. Subsequently, the flask was covered and reacting for 55 min to achieved a blue-brown homogeneous solution.

2.3.2. Synthesis of Au@GQDs@Pt$_{3.5}$Bi. The preparation of Au@GQDs@Pt$_{3.5}$Bi is similar to that of Au@GQDs@Pt. A certain quantities of Bi(NO$_3$)$_3$ was injected into the mixed solution of Au@GQDs@Pt and double-distilled water before adding AA solution, then the reaction was sustained for 1h at 55℃. Au@Pt$_{3.5}$Bi used for comparison. It was synthetized by the similar mode as Au@GQDs@Pt$_{3.5}$Bi except for the addition of GQDs.

3. Results and Discussion

3.1. Composition and Morphological Characterization
Electron microscopes, energy dispersive X-ray spectroscopy (EDX) were performed with a FEI-Tecnai G2 TF20 transmission electron microscope operated at 200kV, there were carried out to affirm the structure and composition of the materials. The high-resolution transmission electron microscope
(HRTEM) images and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) (Figure 1a-c) clearly indicate that the as prepared Au@GQDs@Pt3.5Bi materials have the dendrites morphology and the core-shell structure with the size of around 40 nm. The surface crystalline nature of the Au@GQDs@Pt3.5Bi were investigated by the high-resolution TEM (HRTEM) images (Figure 1(a, b)). The lattice distance of the core is about 0.235 nm, being index to that of the (111) plane of Au. However, the crystal lattice constants of the periphery region is measured to be 0.21 nm, 0.22 nm, it can be matched to the (110) and (012) planes of the alloyed PtBi, respectively [7]. The core-shell dendrites structure of Au@GQDs@Pt3.5Bi was also approved by HAADF-STEM, displayed in Figure 1(d-i), which confirmed that the Au@GQDs@Pt3.5Bi was comprised by elements Au (yellow), Pt (red), and Bi (green). The elemental mapping of the Au@GQDs@Pt3.5Bi reveal that most of Au is mainly centered in the core region, whereas Pt and Bi are placed on the shell. All above characterizations verified that successful fabrication of Au@GQDs@Pt3.5Bi material with core-shell nano-dendrites and PtBi alloyed shell.

Figure 1. Representative (a, b) HRTEM images, (c-i) HAADF-STEM image and elemental mappings of the Au@GQDs@Pt3.5Bi nano-dendrites.

3.2. Electrochemical performance of Au@GQDs@Pt3.5Bi nanostructure electro-catalyst
To research the catalytic performance of prefabricate nano-material with different ingredients for MOR in the alkaline electrolyte. First, the cyclic voltammograms (CVs) were employed to investigate the electro-catalysis activities in N2-saturated 1 M NaOH solution and 0.5 M CH3OH. Scans were carried out between -0.8 V and 0.4 V at a scan rate of 50 mV s⁻¹ and at room temperature. As show in figure 2(a), the CVs for MOR have similar peak treads for all as prepared catalytic agents, indicating that their electrochemical reactions likely followed the same pathway. Then, we compare Au@GQDs@Pt3Bi, Au@GQDs@Pt and Au@Pt3Bi to highlight the role of GQDs and Bi element in promoting the electro-catalytic activity. Obviously, the onset potential (forward scan) on Au@GQDs@Pt3.5Bi (-0.6 V) negatively shifts to ca. 0.1 V than Au@GQDs@Pt (-0.5 V), demonstrating
that improved reaction kinetics for MOR with the addition of Bi. Furthermore, the peak current of MOR for Au@GQDs@Pt3.5Bi (114 mA cm\(^{-2}\)) is very higher than those of Au@GQDs@Pt (11.8 mA cm\(^{-2}\)), Au@Pt3.5Bi (10.5 mA cm\(^{-2}\)), and commercial Pt/C (1.88 mA cm\(^{-2}\)), which is 9.6, 10.8 and 60 times than the peak currents on Au@GQDs@Pt, Au@Pt3.5Bi and Pt/C, respectively. The outstanding results are ascribed to the unique core-shell dendrites structures, excellent electron conductivity, synergistic effect and electronic effect between Pt and Bi. This is in agreement with the mass and specific activity histogram consequences of Figure. 2(c). The CV curves of Au@GQDs@Pt3.5Bi, Au@GQDs@Pt, Au@Pt3.5Bi, and Pt/C in 1 M NaOH solution are exhibited in Figure 2(b), where both of Au@GQDs@Pt3.5Bi, and Au@Pt3.5Bi catalysts are not display any obvious hydrogen adsorption or desorption peaks compared with commercial Pt/C or Au@GQDs@Pt. This result once again reveals that the attendance of Bi in the shell would change the electron state of the Pt surface and activity sites on PtBi surface serve for OH\textsubscript{ads} adsorption and Pt sites for methanol dehydrogenation.

The stability of catalyst is regarded as another vital aspect to assessment the electro-catalysts activity of MOR. The chronoamperometric (CA) experiment was surveyed in the electrolyte of 1M NaOH containing 0.5M methanol at -0.2V for 3000s. As shown in Figure 2(d), it was clear that, after tested for 3000s, the Au@GQDs@Pt3.5Bi material had retained a relatively high current density, which was absolutely improved than commercial Pt/C and Au@GQDs@Pt, Au@Pt3.5Bi catalysts. These results verified the better CO anti-poisoning of Au@GQDs@Pt3.5Bi for MOR, which might be ascribed to the synergistic effect of alloying, the modification of Pt electronic state and the single structure of core-shell nano-dendrites. Based on these results, the proposed Au@GQDs@Pt3.5Bi has appropriate potential to be a hopeful candidate for DMFCs applications.

![Figure 2](image-url)

**Figure 2.** (a) Cyclic voltammograms, (c) Mass activity and specific activity histograms, and (d) chronoamperometric curves of Au@GQDs@Pt3.5Bi, Au@GQDs@Pt, Au@Pt3.5Bi, and commercial Pt/C catalysts in 1.0M NaOH solution and 0.5 M methanol with a scan rate of 50 mV s\(^{-1}\); (b) Cyclic voltammograms of Au@GQDs@Pt3.5Bi, Au@GQDs@Pt, Au@Pt3.5Bi, and Pt/C catalysts in 1 M NaOH solution with a scan rate of 50 mV s\(^{-1}\).
4. Conclusion

In conclusion, we have proposed a simple and environmental approach to synthesize Au@GQDs@Pt_{3.5}Bi with Au@GQDs serves as core, and alloy PtBi dendritic acts as shell. The as-prepared Au@GQDs@Pt_{3.5}Bi presented excellent MOR activity (114 mA cm^{-2}), improved stability, and CO-poisoning tolerance compared with Au@GQDs@Pt, Au@Pt_{3.5}Bi, and commercial Pt/C. The dendritic structure is of great importance in supplying a large active surface area and preferring the methanol molecular approachability to the internal active sites of the PtBi shell. In addition, the higher catalytic performance of Au@GQDs@Pt_{3.5}Bi is ascribed to the electronic effect and synergistic effect by alloying Pt with Bi, that could downshift the d-band center of Pt and promote desorption of carbon intermediates, particularly the adsorbed CO. Furthermore, the admirable stability of Au@GQDs@Pt_{3.5}Bi core-shell nano-dendrites is most likely owing to the Au core increasing the Pt oxidation potential, assisting the oxygen adsorption.

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