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## Facile Synthesis of Silver@Carbon Nanocable-Supported Platinum Nanoparticles as High-Performing Electrocatalyst for Glycerol Oxidation in Direct Glycerol Fuel Cells

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Zhengyu Bai<sup>a</sup>, Min Shi<sup>a</sup>, Yanxing Zhang<sup>b</sup>, Qing Zhang<sup>a</sup>, Lin Yang<sup>a\*</sup>, Zongxian Yang<sup>b</sup>, Jiujuun Zhang<sup>a,c\*</sup>

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Novel Ag@C nanocables are successfully synthesized through a hydrothermal self-assembled process, and employed as the support material to fabricate uniformly distributed Pt nanoparticle electrocatalyst (Pt/Ag@C) for glycerol oxidation reaction (GOR). Electrochemical measurements demonstrate that this Pt/Ag@C catalyst can have both superior electrocatalytic GOR activity and stability, confirming that Ag@C nanocables should be a great material for supporting catalyst. Theoretical calculation is also carried out for fundamental understanding of the enhanced catalytic performance of this Pt/Ag@C catalyst. The results show that this Pt/Ag@C catalyst should be a great candidate for anode catalyst for direct glycerol fuel cells.

As one type of the important electrochemical energy technologies, fuel cells have been demonstrated and recognized to be feasible for energy conversion to produce clean electric power due to their high energy efficiency and zero/low emissions.<sup>1,2</sup> Among different kinds of fuel cells, direct fuel fuel cells (DFFCs) are considered to be the promising systems for automotive and portable electronic applications, owing to their high energy density, low operating temperature, and liquid fuel feeding operation.<sup>3,4</sup> However, the commercial application of these DFFC is still hindered by several performance issues mainly induced by the slow anode fuel oxidation reaction and cathode oxygen reduction reaction (the catalysts' activities are insufficient) and fast reaction degradation (the catalysts' stabilities are insufficient) besides low fuel utilization, and high catalyst cost.<sup>5,6</sup> To address these challenges, high active and stable fuel oxidation catalysts besides those for oxygen reduction reaction are highly desired.

In general, Pt-based catalysts are the most popular ones for the oxidation of fuels including methanol, ethanol, formic acid, dimethyl ether, tetramethyl orthocarbonate, glycerol, *etc.* However, the morphologies and compositions of the Pt-based catalysts have strong effects on both their catalytic activity and stability.<sup>7,8</sup> Therefore, developing DFFC catalysts with both favorite morphologies and compositions is the major effort in current technological approaches.

On the other hand, there is an urgent need to seek renewable cheap fuels in order to realize DFFCs as the sustainable, economical and energy-efficient technologies.<sup>9</sup> Among different fuels, glycerol has been largely produced as a co-product of the blooming biodiesel production (in normal, if producing 10 kg of biodiesel, 1 kg of glycerol would be co-produced).<sup>10</sup> One of the possibilities is to use crude glycerol as a non-toxic fuel in direct glycerol fuel cells (DGFCs) for cogeneration of electricity, chemicals and heat.<sup>11-13</sup> Hopefully, this utilization of glycerol would not only lower fuel cost of fuel cells but also achieve higher fuel efficiency.

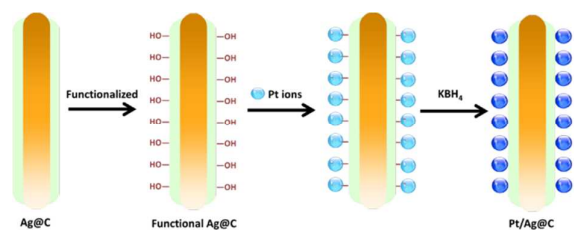
Regarding the improvement of catalyst performance, nature of the catalyst support material and the uniformity of catalyst particle dispersion on the support play important roles in enhancing both catalytic activity and stability.<sup>14,15</sup> At the current state of technology, different carbon materials such as active carbon (Vulcan XC-72 carbon), carbon nanotubes (CNTs) and mesoporous carbon particles, graphene-based nanomaterials are the mostly explored support materials.<sup>16,17</sup> However, the kinetics of fuel oxidation reaction is still insufficient partly due to low platinum utilization when using these carbon support materials. Therefore, design and synthesis of new catalyst support materials should be the necessary approaches to effectively improve the catalyst performance and utilization of platinum catalysts. With respect to this, a new type of nanomaterial, nanocables, has been explored recently and attracted some intensive investigations as catalyst support materials. This can be attributed to their unique physical properties.<sup>18,19</sup> In this regard, many nanocable materials, such as ZnO@ZnS, SnSb@C,

<sup>a</sup> School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Fine Chemicals Green Manufacturing, Henan Normal University, Xinxiang 453007, China. Email: yanglin1819@163.com  
Tel: +86-373-3326058 / fax: +86-373-3328507.

<sup>b</sup> College of Physics and Electronic Engineering, Henan Normal University, Xinxiang 453007, China

<sup>c</sup> Energy, Mining & Environment, National Research Council of Canada, Vancouver, BC, Canada. Email: jiujuun.zhang@nrc.gc.ca

† Electronic Supplementary Information (ESI) available. See



Scheme 1. Proposed formation mechanism of Pt/Ag@C electrocatalyst.

Ni@Si, PANI@Ag, etc., have been prepared by various methods.<sup>20-22</sup>

In our continuing effort to explore new catalysts for fuel cells, we have explored silver-based nanocable materials, such as Ag@C nanocables, for catalyst supports. As believed, the novel nanocable structure could offer several advantages: (1) Ag plays an important role in co-catalyst due to the surface adsorption effect, which is believed to play an important role in the process of catalytic reaction; and (2) when a Ag nanowire is mounted by an inertial carbon sheath, it could be protected from being oxidized or eroded, leading to an improved stability, and meanwhile, the carbon shell could provide channels for efficient charge transport and ionic interchange to enhance the electrocatalytic activities. Therefore, Ag@C nanocable material should be a new candidate for catalyst support.

In this work, an Ag@C nanocable material was successfully synthesized through a hydrothermal self-assembled process, and explored as the support for Pt electrocatalyst which was found to have a uniform dispersion on the support. In the synthesis, silver nitrate was selected to act as the silver source, and the glycerol as the carbon source and also the reducing agent to form the Ag@C nanocables. The formation mechanism of Pt/Ag@C electrocatalyst was proposed in Scheme 1. As shown, first, Ag@C nanocable is synthesized and functionalized with hydroxy in alkaline liquor; second, chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) is added into the system to coordinate with hydroxyl on the surface of Ag@C nanocable; and then a freshly prepared  $\text{KBH}_4$  solution is used as the reducing agent for the preparation of Pt nanoparticles; finally, the product is collected by filtration and washed several times, then dried at  $40^\circ\text{C}$  under vacuum condition to obtain the final product.

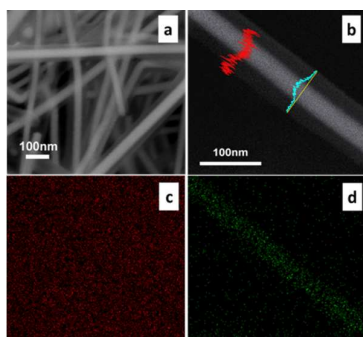


Fig. 1. FESEM images with different magnifications of the as-prepared Ag@C nanocables (a, b) and the corresponding EDS line scan (b), and chemical mapping (c, d).

The morphology and composition of the synthesized Ag@C nanocable support material was determined by the field-emission scanning electron microscopy image (FESEM) and corresponding energy dispersive X-ray spectroscopy (EDS). Fig. 1a shows the FESEM image of Ag@C. It can be seen that the Ag@C nanocables formed through hydrothermal process are well-dispersed with a relatively narrow particle size distribution. The nanocable diameters vary from 100 to 220 nm, and the average thickness of the shell is about 30 nm. Fig. 1b shows the amplificatory FESEM image and the corresponding EDS line scan. In the scanning across the Ag@C, the C content rises on both sides of the nanostructure and the Ag content reaches the highest in the center section. Fig. 1b and Fig. 1c are the corresponding elemental mapping of C and Ag, respectively. From the mapping images, a homogeneous distribution of Ag nanowire can be clearly observed, while C element is uniformly distributed through the entire mapping zone. These results confirm that the obtained nanocable is composed of an inner silver nanowire and an outer carbonaceous layer.

In addition, the result from EDS demonstrates that C:Ag:O atomic ratio within Ag@C nanocable sample is 75.29:17.15:7.56 (Fig. s1). Fig. s2 shows a typical XRD pattern of the Ag@C nanocable sample. It can be observed from the XRD pattern that the five peaks at  $38.3^\circ$ ,  $44.1^\circ$ ,  $64.4^\circ$ ,  $77.5^\circ$  and  $81.5^\circ$ , are characteristics of face-centered-cubic (fcc) crystalline Ag (JCPDS No. 4-783), which correspond to the facets (111), (200), (220), (311), and (222), respectively. It is notable that there is no obvious diffraction peak corresponding to silver oxides, despite the easiness of oxidation of the elemental silver. This may suggest the protecting effect of a carbon nanoshell formed on the surface of silver nanowire.

Fig. 2 shows the TEM images with different magnifications and the size frequency curves of different catalyst samples. From Fig. 2a, it can be seen that the small Pt nanoparticles are evenly deposited on the surface of Ag@C nanocables. The nanoparticles diameters can be determined from the amplificatory TEM image (Fig. 2b), which range from 2.5 to 6.4 nm with a mean size of 4.4 nm calculated by the lognormal distribution (Fig. 2c). To investigate the influence of Ag core on the formation of Pt nanoparticles, a control experiment was

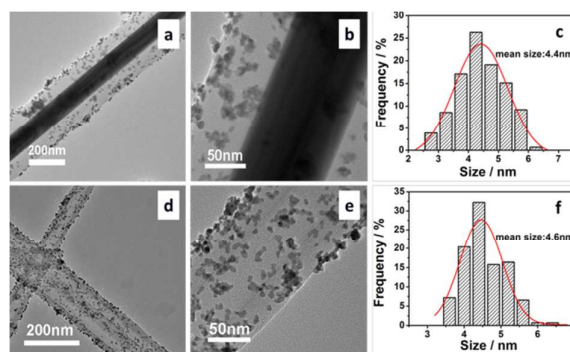
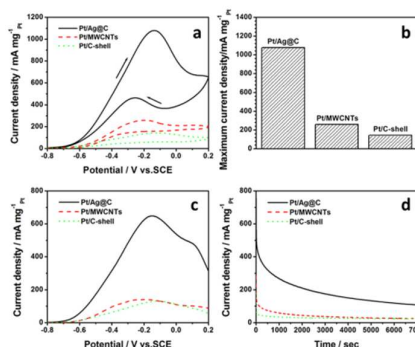


Fig. 2. TEM images with different magnifications and the corresponding size frequency curves of the resulting (a-c) Pt/Ag@C and (d-f) Pt/C-shell samples.

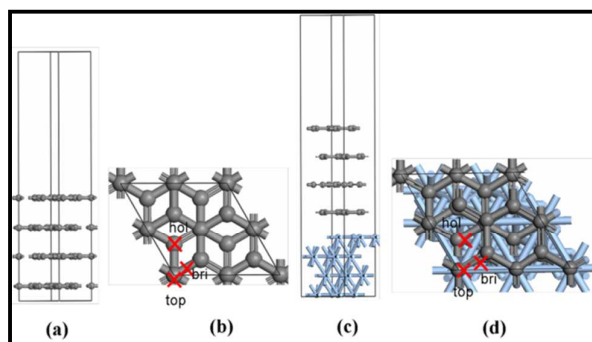
also carried out under the same conditions described in the typical experiment. In this case, the Ag core was removed by soaking and corroding in 1M HCl aqueous solution to produce Pt/C-shell. Fig. 2(d-f) shows the TEM images and the size distribution histogram of the sample produced by the control experiment. As can be seen in Fig. 2(d-f), Ag core is removed completely and only C-shell is left. Pt nanoparticles formed are also well-dispersed on C-shell, with a relatively narrow particle size distribution of about 4.6 nm in diameter. However, it's important to note that the content of <4 nm of Pt nanoparticles is about 28% in Pt/Ag@C, which is much higher than that in Pt/C-shell (16%), and this might attribute to the disappearance of the Ag core. TEM images of the Pt/Ag@C and Pt/C-shell were measured again after durability tests (shown in Fig. s6). The results demonstrate that this Pt/Ag@C catalyst has a higher stability than that of Pt/C-shell under the same conditions.

In order to evaluate the activity and stability of the electrocatalysts, three typical catalysts, such as Pt/Ag@C, Pt/MWCNTs and Pt/C-shell, were tested using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry in a half-cell containing N<sub>2</sub>-saturated in 1 M glycerol + 1 M KOH aqueous solution. In these experiments, both Pt/C-shell and Pt/MWCNTs catalysts were used for comparison. The CV curves recorded at three different catalyst electrodes are displayed in Fig. 3a. It can be seen that a peak for glycerol oxidation appears in both positive and negative directions at all three electrodes. Obviously, the peak current density of Pt/Ag@C catalyst is much higher than both of Pt/MWCNTs and Pt/C-shell catalysts. For a more clear comparison, Fig. 3b shows the histogram of peak current densities of three different catalysts. It can be seen that the peak current density of Pt/Ag@C can be as high as 1079 mA/mg<sub>Pt</sub>, which is much higher than those of Pt/MWCNTs (260 mA/mg<sub>Pt</sub>) and Pt/C-shell (142 mA/mg<sub>Pt</sub>, respectively), further demonstrating that Pt/Ag@C is the most active catalyst among three catalysts tested for glycerol electro-oxidation. It is believed the ratio of the forward anodic peak current (*I<sub>f</sub>*) to the backward anodic peak current (*I<sub>b</sub>*), *I<sub>f</sub>*/*I<sub>b</sub>*, is an indication of Pt surface stability during the potential scanning. Particularly, the peak-like currents for small alcohol electro-oxidation (AEO) at both forward and backward potential scanning directions can be explained as follows: As generally recognized, only pure Pt surface has the AEO catalytic activity, while PtOx has no AEO activity. In this case in Fig. 3a and c, when the Pt-based electrode is positively potential scanning, the Pt surface is oxidized into PtOx after a certain potential value, the Pt's AEO catalytic activity will be lost, then the AEO current starts to fall, resulting in a peak-like current curve. When the potential is scanned back to a certain potential, the PtOx is reduced to pure Pt, and the catalyst activity will be recovered, giving catalytic AEO current. When the potential is further reduced, the Pt losses its catalytic activity, resulting in a peak-like current curve. From this explanation above, CO or COH adsorption is not the main cause for the back peak-like current. From this explanation, The larger *I<sub>f</sub>*/*I<sub>b</sub>* ratio of the Pt/Ag@C (2.32) when compared to that of Pt/C-shell (1.63)

may suggest that Pt in Pt/Ag@C has a better catalyst stability than that in Pt/C-shell. The results reveal that Pt/Ag@C hybrid enhances the performance of glycerol oxidation reaction when compared to Pt/C-shell.



**Fig. 3** Cyclic voltammograms (CVs) (a), peak current densities (b), linear sweep voltammetric curves (LSVs) (c), and chronoamperometric curves (d) of the glassy carbon electrodes coated by three as-prepared catalysts separately, measured in N<sub>2</sub>-saturated 1M glycerol + 1 M KOH aqueous solution. Potential scan rates for both CVs and LSVs are 50 mV s<sup>-1</sup>.



**Fig. 4** Side view (a, c) and top view (b, d) of graphite and graphite/Ag systems.

Another important indicator for catalytic activity is the onset potential of the catalyzed oxidation. To determine the onset potentials for glycerol electro-oxidation catalyzed by these three catalysts, the LSV measurements were carried out, and the results are shown in Fig. 3c. It can be clearly seen that the onset potentials for glycerol oxidation on Pt/Ag@C catalyst (-0.72V) is much more negative than those of Pt/MWCNTs (-0.6V) and Pt/C-shell (-0.54V). Both the lower onset potential and higher peak current density indicate that Pt/Ag@C is indeed the most active catalyst among three catalysts tested for glycerol oxidation. Furthermore, in order to compare the electrochemical stability of the as-prepared catalysts for glycerol oxidation, chronoamperometric tests were carried out at -0.3 V for 7000 s (shown in Fig. 3d). It can be seen that Pt/Ag@C catalyst shows a much higher anodic current and also a much slower degradation in currents, demonstrating that this Pt/Ag@C catalyst has not only a better catalytic activity but also a higher stability than those of others under the same conditions. The electrochemically active surface area (ECSA) value of the Pt/Ag@C catalyst (48.1 m<sup>2</sup> g<sup>-1</sup>) is much larger than that of the Pt/C-shell catalyst (35.7 m<sup>2</sup> g<sup>-1</sup>), suggesting that the

former has a much higher electrocatalytic activity and stability than the latter (shown in Fig. S5). Based on the facts described above, we believe that this high active Pt/Ag@C catalyst toward glycerol oxidation should be a good candidate for anode catalysts for direct glycerol fuel cells.

To understand the outstanding catalytic performance of Pt/Ag@C catalyst for glycerol oxidation, a theoretical calculation was also carried out in this work. In this effort, the influence of Ag core was studied from both aspects of reaction thermodynamics and surface adsorption which is believed to play an important role in the process of catalytic reaction.<sup>23,24</sup> Here, we first studied the adsorption of Pt atom on graphite and graphite/Ag systems, respectively. Three high symmetric sites (top, bridge and hollow) are shown in Fig. 4. It was found that the most stable adsorption site of Pt atom on graphite or graphite/Ag was the bridge site. For the graphite/Ag, the Pt atom adsorption energy at the bridge site was found to be much higher than that on graphite (1.59 vs 0.02 eV), suggesting that the interaction between Pt and graphite/Ag is much stronger than that between Pt and graphite, leading to better catalytic activity. In order to explain the enhanced stability, we also calculated Pt atom adsorption on a free standing graphite with the parameter expanded to 5.78 Å from that of ideal surface (4.92 Å). It was found that the energy of Pt adsorption on the bridge site was almost equal to that on the graphite/Ag system (1.58 vs 1.59 eV). So the enhanced stability of Pt adsorption on the graphite/Ag system could be mainly attributed to the expanded parameter of graphite. Once the Pt adsorption on graphite surface is enhanced, its surface movement would be much more difficult, and the Pt adatoms would not easily grow up to large Pt particles. This may explain the experimental observations about the existence of much smaller radius Pt nanoparticles on the graphite/Ag than on graphite, leading to larger electrochemistry area. Next, we studied the CO adsorption on both Pt/graphite and Pt/graphite/Ag systems. It was found that on the Pt/graphite/Ag, the CO adsorption energy could be decreased by 0.7 eV (2.74 vs 2.00 eV) when compared to that on Pt/graphite system, indicating that Pt/graphite/Ag was more tolerant to CO poisoning than the Pt/graphite system. Compared with Pt/graphite system, the increased electrochemistry area, and Pt stability, and the enhanced tolerance to CO poisoning of Pt/graphite/Ag can contribute to the large catalytic activity enhancement towards fuel oxidation.

## Conclusions

In this work, the novel Ag@C nanocables are successfully synthesized through a hydrothermal self-assembled process, and employed as the catalyst support material for the first time. The as-prepared Pt nanoparticles supported on this Ag@C nanocable material show small particle sizes and uniform dispersion, which could be attributed to the synergy between carbon shell and Ag core of support. Electrochemical measurements demonstrate that this Pt/Ag@C catalyst could have both superior electrocatalytic activity and stability for

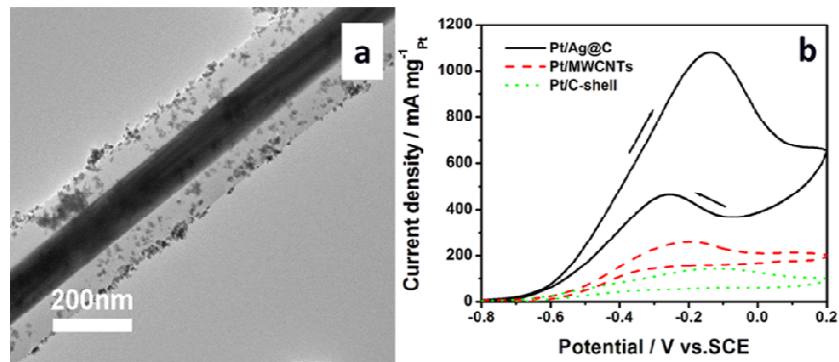
glycerol oxidation, confirming that Ag@C nanocables should be a good material for supporting catalyst. Theoretical calculation is also carried out for fundamental understanding of the enhanced catalytic performance of this Pt/Ag@C catalyst. It is strongly believed that this Pt/Ag@C catalyst should be a great candidate for anode catalyst in direct glycerol fuel cells.

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