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Facile synthesis of three-dimensional platinum nanoflowers on reduced graphene oxide – Tin oxide composite: An ultra-high performance catalyst for methanol electro-oxidation

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ABSTRACT

Herein, we report platinum (Pt) nanoflowers decorated reduced graphene oxide (rGO)–tin oxide (SnO_2) composite as an efficient electro-catalyst for direct methanol fuel cells (DMFCs). rGO-SnO_2 composite is synthesized by a novel, eco-friendly hydrothermal method using lemon extract followed by electro-deposition of Pt to yield high density Pt nanoflowers uniformly distributed over rGO-SnO_2 for superior catalytic performance and optimal utilization of Pt nanostructures. Whilst Pt nanoparticles (NPs)-rGO-SnO_2 composite exhibits higher CO tolerance ability ($I_f/I_b = 3$) and poor catalytic stability, Pt nanoflowers-rGO-SnO_2 composite shows comparable CO tolerance ability ($I_f/I_b = 1.81$) with excellent stability. At 3000 s, the current density of Pt nanoflowers-rGO-SnO_2 has been found to be 2.1 folds higher than Pt NPs-rGO-SnO_2 composite. Excellent durability of Pt nanoflowers-rGO-SnO_2 is attributed to the high surface area of Pt nanoflowers which provides more active sites during methanol oxidation without any agglomeration, thus, facilitating diffusion of methanol to Pt for catalytic activity. As per our knowledge, this is the first report on Pt nanoflowers-rGO-SnO_2 composite based electro-catalyst for DMFCs that yields superior performances in terms of catalytic efficiency, CO tolerance activity and stability. The composite shows enormous potential to be used as binder free, cost-effective, efficient and durable electro-catalyst for DMFCs applications.

1. Introduction

Recently, direct methanol fuel cells (DMFCs) have gained wide attention as promising green power sources for portable electronic devices and electric vehicles owing to its theoretically high energy efficiency, easy handling or storage of liquid fuel, low pollution emission, relatively low operating temperature and minimal corrosion problems [1–3]. Nonetheless, several technical barriers are still present for the commercialization of DMFCs such as relatively low catalytic activity, stability and high cost of electrode catalysts for the methanol oxidation reaction (MOR) [4,5]. Therefore, development of new electrode catalyst with excellent catalytic efficiency and stability is of prime importance in DMFCs applications.

Platinum (Pt) has been extensively used as an electro-catalyst in DMFCs as it is very effective in oxidizing methanol in the anodes. The working principle of DMFCs is mainly based on the electro-oxidation of methanol on the surface of catalyst to form carbon dioxide [6]. However, the widespread use of pristine Pt as an electro-catalyst is seriously hindered by high costs, poor utilization efficiency, limited availability of Pt. Furthermore, difficulty associated with Pt in MOR is poisoning generated from the strong interaction of intermediate carbonaceous species with catalyst active sites instead of forming carbon dioxide [6–8]. Hence, considerable efforts must be made to the improvement of poison tolerance ability and efficient utilization of Pt in MOR.

To improve the electro-catalytic activity and durability of the Pt catalyst towards MOR, alloying Pt with other metals, such as Ru, Pd etc., has been considered as an interesting and efficient strategy for DMFCs applications [9,10]. Among bimetallic Pt catalysts, Pt–Ru alloy exhibited outstanding performance in MOR which could be ascribed to a bi-functional mechanism. At room temperature methanol cannot be oxidized on the Ru surface but Ru promotes the oxidation of intermediate carbonaceous species on Pt at more negative potentials [11,12]. However, slow oxidation kinetics and the high price of Pt-Ru catalyst remains a major drawback towards the deployment of DMFCs for practical applications [9,13,14].

The electro-activity, stability and high utilization of Pt catalysts can be further enhanced by loading Pt catalyst into a suitable supporting material. In this regard, graphene (Gr) and related materials like GO or reduced GO (rGO) have gained significant attention as high performance supporting materials in DMFCs applications owing to their

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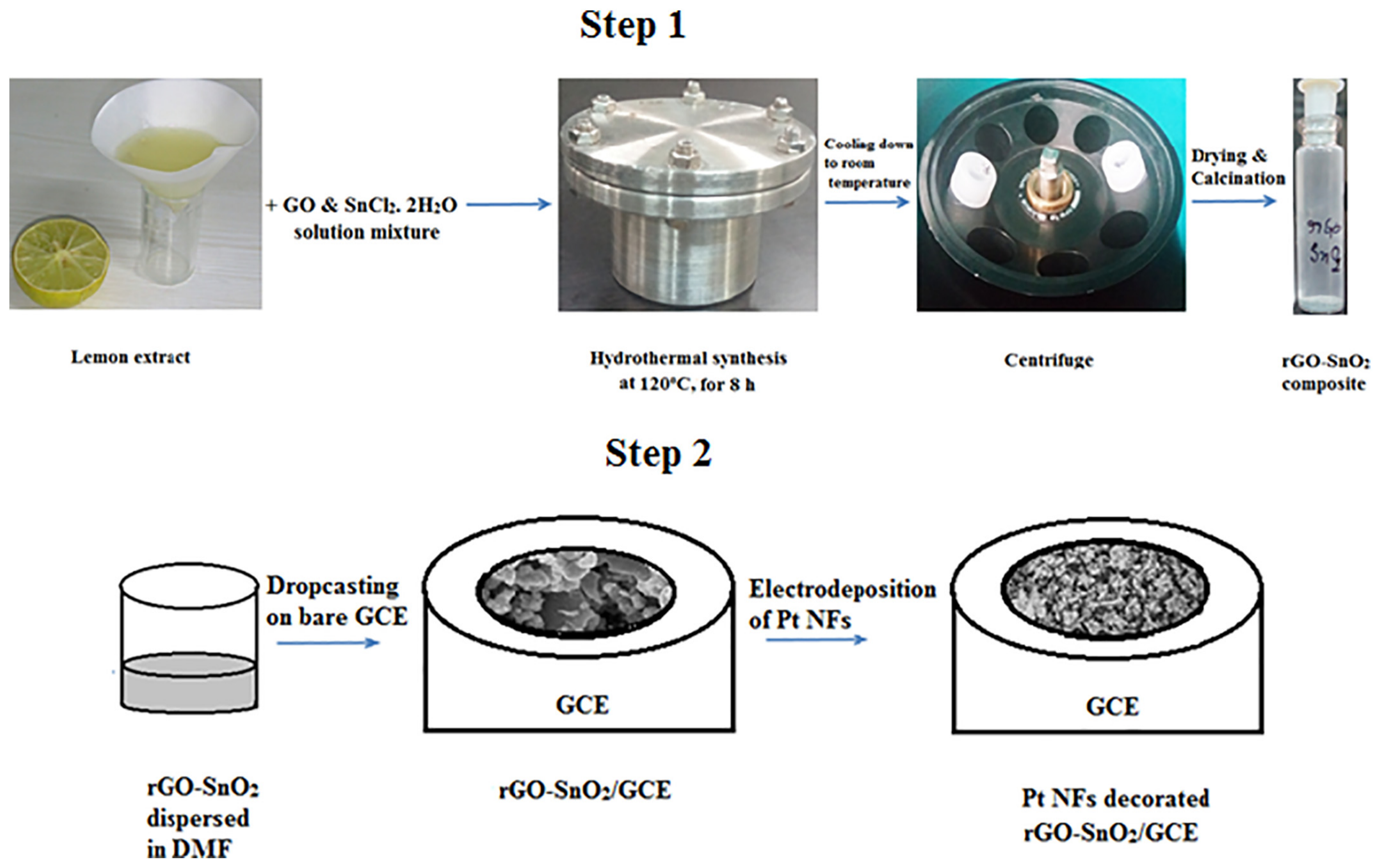

Fig. 1. Schematic demonstrating the two-step synthesis procedure of Pt decorated rGO-SnO_2 composites; step 1: the green synthesis process of rGO-SnO_2 composite and step 2: synthesis of Pt decorated rGO-SnO_2 composite via electro-deposition method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

excellent electrical conductivity, tunable surface chemistry, large specific surface area, high chemical stability and relatively low-cost and ability to improve the catalytic performance [15,16]. Zhou et al. [16] demonstrated Gr supported Pt catalyst while Ensafi et al. [17] reported 3-D Pt nanoparticles decorated rGO for methanol oxidation. Similarly, SnO_2, a well-known, n type metal oxide semiconductor has been used widely in DMFCs applications because of its properties such as low cost, high chemical stability, electro-catalytic activity, wide band gap (~3.5 eV) and ease of synthesis. Fan et al. [18] synthesized hierarchical structure SnO_2 supported Pt nanoparticles and Zhang, et al. presented [19] Pt-SnO_2 flower for methanol oxidation. However, SnO_2, in comparison to carbon support typically suffers from the lower specific surface area and electrical conductivity [18]. Hence, to achieve higher specific surface area with improved electro-catalytic activity, the composites of Gr and SnO_2 have attracted wide attention as supporting materials in DMFCs, combining the synergistic effect of both. Herein, we demonstrate a facile, low cost and environmental friendly hydrothermal process for the synthesis of the rGO-SnO_2 composite using lemon extract and subsequently, Pt decorated rGO-SnO_2 composites were prepared by electro-deposition of Pt on the surface of rGO-SnO_2 composites. Gong et al. [20] reported the green synthesis of 3D SnO_2-Gr composite using two steps wherein SnO_2 nanoparticles were prepared separately and then decorated on and between Gr sheets. Here, rGO-SnO_2 composite was synthesized in one step where rGO and SnO_2 were formed in situ based on the oxidation–reduction reaction between GO and $SnCl_2$. $2H_2O$ without using any surfactant or template. To decorate Pt nanostructures on the surface of rGO-SnO_2 composite modified electrode, electro-deposition method was chosen owing to its several benefits such as (a) simple, one-step, low cost and (b) controlled approach of preparing nano-composite with unique morphology and distribution by tuning the deposition parameters at room temperature [21]. Moreover, it eliminates the difficulties associated with other techniques such as high precursor loading, template removal etc. Here, the effect of electro-deposition cycles on the morphology of Pt nanostructures on rGO-SnO_2 composite surface was explored. The as-prepared Pt decorated rGO-SnO_2 composites were employed as electrocatalysts for methanol oxidation reaction in 0.5 M H_2SO_4 electrolytic solution and their performances were also compared. The catalytic efficiency and CO tolerance activity of Pt decorated rGO-SnO_2 composites were also compared with Pt-SnO_2 catalyst and commercially available Pt-C black.

2. Experimental

2.1. Materials

Tin (II) chloride dehydrate ($SnCl_2$. $2H_2O$), graphite flake, methanol (CH_3OH), chloro-platinic acid hexahydrate (H_2PtCl_6, $6H_2O$), hydrochloric acid (HCl), *N*, *N*-dimethylformamide (DMF) [$(CH_3)_2NC(O)H$],sulfuric acid (H_2SO_4), commercially available platinum-carbon black, Pt-C (10 wt% loading of Pt on carbon support) were procured from Sigma Aldrich and used in the experiments as received. DI water from a Millipore system (~18.2 MΩ cm) was used throughout the experiments.

2.2. Apparatus

Electrochemical measurements were carried out on CHI 660E electrochemical workstation at room temperature at the scan rate of 50 mV/s. A three electrode cell configuration in which Pt decorated