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Effects of silicotungstic acid on the physical stability and electrocatalytic activity of platinum nanoparticles assembled on graphene

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ABSTRACT

A novel electrocatalyst, Pt@$H_4SiW_{12}O_{40}$/graphene (simplified as Pt@SiW_{12}/GN), was prepared by microwave-assisted reduction method, in which Pt nanoparticles were assembled on reduced graphene and silicotungstic acid was used as a stabilizer to prevent Pt nanoparticles from aggregation. Pt@SiW_{12}/GN was characterized by EDS, XRD, TEM, and XPS analysis. The electrocatalytic activities for methanol oxidation were also investigated. It is found that SiW_{12} facilitates the formation of uniform Pt particles with an average particle size of 7.5 nm. Most importantly, Pt@SiW_{12}/GN catalyst displays higher electrocatalytic activity, higher stability, and better tolerance to CO when it is compared with Pt/GN catalyst prepared by the same method. The enhancement in electrochemical performance of the Pt@SiW_{12}/GN catalyst system can be attributed to the synergistic effect of highly dispersed Pt nanoparticles on the GN and increased oxidation power of SiW_{12} that promotes the removal of the poisonous species on the Pt surface.

1. Introduction

Platinum-based catalysts are of central importance in industrial catalysis and green energy technologies [1–3]. It has been reported that methanol oxidation on a Pt/C catalyst occurs accompanied by the formation of adsorbed CO as intermediate which becomes a poison on the active sites and significantly reduces the cell performance [4]. Pt/C may not be the best catalyst for anode material because of its expensive cost and as well as easy poisoning by CO-like intermediates of methanol electro-oxidation. Thus, improving tolerant ability of the Pt catalyst for CO poisoning is a preferable method for alleviating the deactivation of the Pt catalyst.

Polyoxometalates (POMs) have been applied to various kinds of acid-catalyzed oxidation reactions due to their superior oxidizing abilities [5–7]. Also, it has been demonstrated that Keggin-type $PMo_{12}O_{40}^{3-}$ anions in an aqueous solution could effectively assist the electrochemical oxidation of CO with water molecules into CO_2 over gold catalysts [8,9]. POMs also have been shown to enhance the electrooxidation of methanol in aqueous acidic solution on Pt [10,11], PtRu [12–14], and PtSn [15] modified electrodes. We had previously prepared Pt-{PEI-GNs/$[PMo_{12}O_{40}]^{3-}$}n composite films and found that the synergistic effect of GNs and PMo_{12} remarkably enhanced the electrocatalytic activity and improved tolerance of CO [16]. All these positive studies provide evidence that POMs, in combination with Pt, could act as promoters in the methanol electrooxidation process on fuel cell anode.

Furthermore, to maximize the electrocatalytic activity of Pt nanoparticles (NPs), a suitable carbon support is required to disperse these NPs. Conventional carbon supports used in electrocatalysts include XC-72 carbon black (CB) and carbon nanotubes (CNTs). Recently, graphene (GN) with close-packed conjugated hexagonal lattices has attracted tremendous attention and research interests owing to its exceptional electronic, thermal, and mechanical properties [17,18]. Significantly, its unique structure endows GN with various superior properties such as superior electrical and thermal conductivities, great mechanical strength, inherent flexibility, and huge specific surface area. Many efforts have currently been made to develop GN-based nanomaterials and explore their applications in efficient catalysis [19–21]. It is reasonably expected that GN could construct a three-dimensional structure which is efficient for the diffusion of the fuel while contacting both Pt catalyst and electrolyte materials. However, it is difficult to directly decorate metal nanoparticles on the surface of GN sheets with uniform size and good dispersion. One of the reasons for this is that most of the carbon materials lack sufficient binding sites for anchoring precursor metal ions or metal nanoparticles without surface modification, which usually lead to

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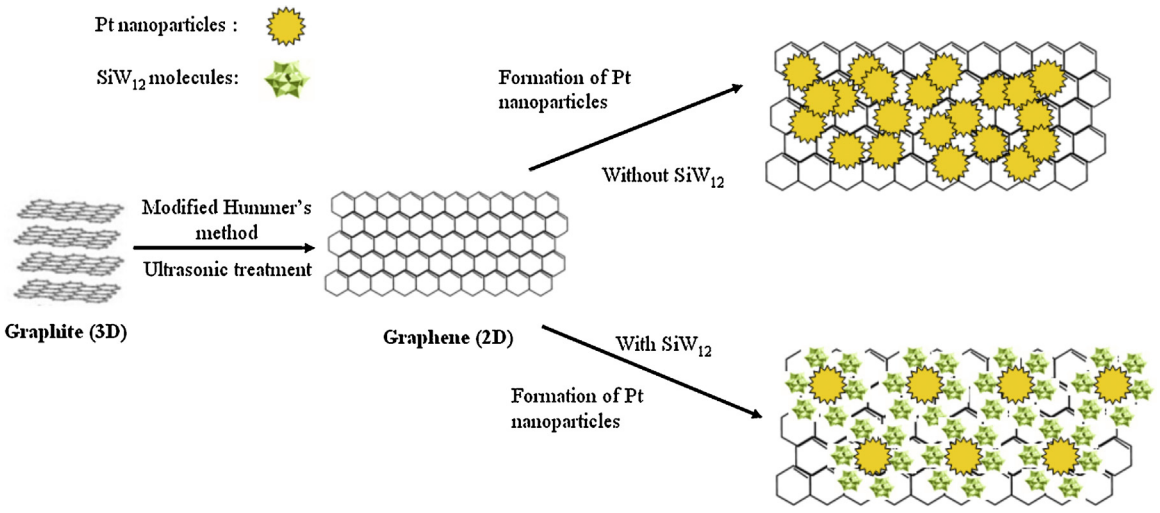

Fig. 1. Schematic illustration of synthesis process.

poor dispersion and aggregation of metal NPs [13,14]. Moreover, the aggregation of GN makes it difficult to demonstrate their superior properties. Therefore, the effective dispersal of metal NPs onto un-oxidized and complete-structure graphene materials remains an important issue. On the other hand, Keggin-type heteropolyacids (HPAs) are known to adsorb irreversibly on carbon and metal surfaces [10,12]. For example, heteropolyanion monolayer-coated electrodes can be formed by simply soaking the electrode in an acidic aqueous solution of heteropolyanion [22,23]. Furthermore, the existence of the strong chemisorption between POMs and carbon materials makes it possible to construct carbon nanostructures [24] and POM-modified multilayered graphene sheets have been obtained through phosphomolybdic acid (a typical POM) solution in a top–down approach to construct graphene–POM composites [25].

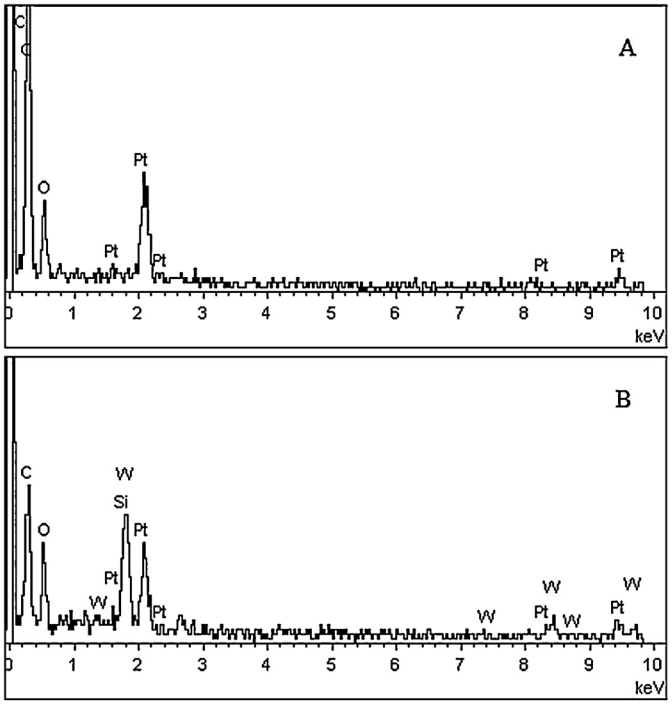

Fig. 2. EDS spectra of the Pt/GN (A) and Pt@SiW_{12}/GN (B).

Microwave-assisted heating has gained importance due to its operational simplicity, efficiency, and reduced preparation time [26,27]. This method promotes rapid reduction of the metallic precursors and is responsible for the achievement of nanometric particle size [28]. In this study, silicotungstic acid (SiW_{12}), a Keggin-type polyoxometalate, was used to stabilize the formation of Pt NPs assembled on reduced graphene by microwave-assisted heating method (Fig. 1). The significative observation was that agglomeration of Pt NPs had been effectively prevented in the presence of silicotungstic acid. The as-obtained composite was used as an electrocatalyst for methanol oxidation, showing enhanced catalytic activity.

2. Experimental

2.1. Synthesis of Pt@SiW_{12}/GN and Pt/GN

The graphene oxide (GO) was synthesized from natural graphite powder by a modification of Hummer's method [29,30]. The

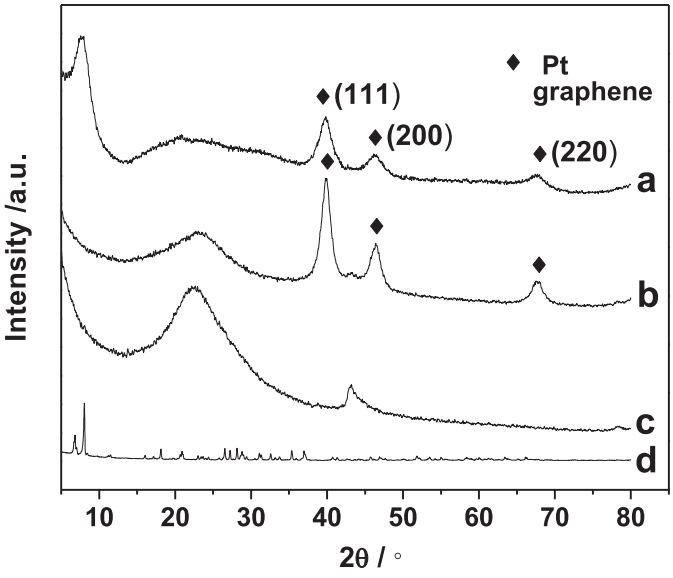

Fig. 3. XRD patterns of compounds (a)Pt@SiW_{12}/GN, (b) Pt/GN, (c) GN, and (d) SiW_{12}.