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Graphitic carbon nitride nanosheet supported high loading silver nanoparticle catalysts for the oxygen reduction reaction



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ABSTRACT

Ag/graphitic carbon nitride (Ag/g-C₃N₄) catalysts with high loading Ag are prepared using g-C₃N₄ by protonation. Ag⁺ can combine with Cl⁻ on the surface of g-C₃N₄ nanosheet by protonation and further deoxidize by sodium citrate. It contributes to well disperse Ag nanoparticles on the surface of g-C₃N₄. In addition, Ag/g-C₃N₄ catalysts are also used for the oxygen reduction reaction (ORR) in alkaline solution. Compared with g-C₃N₄ and g-C₃N₄-H⁺Cl⁻, the Ag/g-C₃N₄ catalysts with 80 wt% Ag show excellent catalytic activity for ORR. The proposed catalyst is promising, facile and low-cost, and can be a potential candidate for application in alkaline fuel cells.

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1. Introduction

For the fabrication of commercially viable fuel cell devices for future energy applications, it is key to develop highly efficient catalysts for the oxygen reduction reaction (ORR) [1]. Generally, high-efficiency Pt/C catalyst is often limited in ORR due to high cost and low stability [2]. Recently, Ag hybrids can be a candidate for this as it is significantly cheaper, thermodynamically and electrochemically stable at high pH. [3] Among Ag hybrid catalysts, carbon-supported Ag has attracted extensive interest because carbon materials can act as excellent support materials due to their low cost, large surface area, and unique electrical properties [4]. The electrochemical reduction of oxygen has been studied on Ag nanoparticle/multi-walled carbon nanotube nanocomposites in alkaline solution employing the rotating disk electrode (RDE) method [5]. Graphitic carbon nitride (g-C₃N₄) with high nitrogen content, outstanding chemical and thermal stability has been extensively studied for it can strengthen the initial chemical adsorption of oxygen on the surface of catalyst, and it is low-cost material, which makes it potentially suitable for photoelectrochemical energy conversion [6–11]. Liu et al. have developed Co-g-C₃N₄@graphene, a novel nonprecious metal-heterocyclic polymer as an ORR catalyst with high activity and good stability [12].

Herein, Ag/g-C₃N₄ catalysts with high loading Ag were prepared using g-C₃N₄ by protonation. And, Ag nanoparticles with

small size were able to well disperse on the g-C₃N₄ nanosheet. In addition, Ag/g-C₃N₄ catalysts were also explored as ORR catalysts under alkaline conditions. Compared with g-C₃N₄ and g-C₃N₄-H⁺Cl⁻, the Ag/g-C₃N₄ catalysts prepared here displayed a higher ORR activity via a four-electron transfer pathway.

2. Experimental

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (China), without further purification. Graphitic carbon nitride (g-C₃N₄) was synthesized by directly heating dicyandiamide [13]. In a typical process [14], 2 g as-prepared g-C₃N₄ was added into HCl aqueous (12 mol L⁻¹) solution and stirred for 12 h. g-C₃N₄-H⁺Cl⁻ was washed into neutral with distilled water and ethanol, before dried at 50 °C for 8 h.

In a typical reaction, the g-C₃N₄-H⁺Cl⁻ (4 mg) was added into a clean 100 mL flask with distilled water (25 mL). After being added into silver nitrate (0.0255 g) and sodium citrate (0.275 g), the system was refluxed and stirred for 2.5 h, and then cooled to room temperature. The final product was separated by centrifugation, washed with distilled water and absolute ethanol four times, and dried under vacuum at 50 °C for 12 h. According to this method, the Ag/g-C₃N₄ samples with different weight ratios were obtained.

X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity CuKα (λ = 1.54 Å). Thermogravimetric (TG) analysis was done on STA-449C Jupiter

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(NETZSCH Corp., Germany) under a N_2 atmosphere. The testing process was under 23–1000 °C at a heating rate of 10 °C min^{-1} . The field-emission scanning electron microscopy (SEM) measurements were carried out with a field-emission scanning electron microscope (JEOL JSM-7001F) equipped with an energy-dispersive X-ray spectroscope (EDS) operated at an acceleration voltage of 15 kV. Transmission electron microscopy (TEM) micrographs were taken with a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV.

The evaluation of ORR activity of various catalysts was performed in a standard three-electrode glass cell on a CHI 660B workstation (CH Instruments Company). A RDE was used as the working electrode. 20 μL of the electrocatalyst suspension in ethanol (1 mg mL^{-1}) was drop-casted on the surface of the RDE. The electrode was allowed to dry at room temperature and heated at 60 °C for 15 min. After that, 5 μL of 0.05 wt% Nafion was further drop-casted on the surface of the electrode. Finally, the electrode was again dried at room temperature and heated at 60 °C for 15 min. Ag/AgCl and Pt wire were used as reference and counter electrode, respectively. 0.1 M KOH as electrolyte was freshly prepared.

3. Results and discussion

In XRD (Fig. 1 A), $g-C_3N_4-H^+Cl^-$ presents two consistent peaks with $g-C_3N_4$, suggesting that $g-C_3N_4-H^+Cl^-$ basically has the same crystal structure with $g-C_3N_4$. The peak at 13.6° corresponds to in-plane structural packing motif of tri-s-triazine units, which is indexed as (100) peaks. The peak at 27.6° corresponds to interlayer stacking of aromatic segments with a distance of 0.324 nm, which

is indexed as (002) peak of the stacking of the conjugated aromatic system [7]. The characteristic peaks of $g-C_3N_4$ around 13.1° and 27.7° can be clearly identified in XRD pattern of Ag/ $g-C_3N_4$ (80 wt %). Ag nanoparticles are deposited on $g-C_3N_4$ supports without producing noticeable impurity phases in the XRD analysis (Fig. 1A). The chemical composition of the nanocomposites is determined by EDS (Fig. 1B), further confirming the existence of C, N and Ag elements. These results indicate the formation of Ag/ $g-C_3N_4$.

In the TG analysis (Fig. 1C), weight loss of $g-C_3N_4-H^+Cl^-$ and $g-C_3N_4$ occur at two stages. The weight loss at the first stage is caused by the loss of absorbed water, and the maximum weight loss occurs at about 60 °C. At the second stage, the weight loss is caused by thermal degradation of $g-C_3N_4$. Based on the above results, it can be seen from the TG analysis of Ag/ $g-C_3N_4$ that the weight loss of 2.5% and 19.5% are also caused by the loss of absorbed water and thermal degradation of $g-C_3N_4$. Thus, mass ratio of $g-C_3N_4$ to Ag is 1:4 in Ag/ $g-C_3N_4$.

Fig. 2 shows typical SEM and TEM images of Ag/ $g-C_3N_4$ (80 wt%) and $g-C_3N_4-H^+Cl^-$. It has been found that the as-prepared $g-C_3N_4$ is nanosheet in the previous work [15]. As is shown in Fig. 2 (e, f), the $g-C_3N_4-H^+Cl^-$ is also nanosheet. It indicates that morphology of the $g-C_3N_4$ is not changed by protonation. As is shown in Fig. 2 (a, b), Ag nanoparticles disperse on the surface of $g-C_3N_4$. The TEM images (Fig. 2 (c, d)) indicate that the Ag nanoparticles anchoring on the surface of $g-C_3N_4$ look like rivets and have a good dispersion behavior on $g-C_3N_4$ nanosheets. The diameters of Ag nanoparticles are in the range of 5–10 nm, as shown in Fig. 2d. The formation process of Ag/ $g-C_3N_4$ can be expressed by a schematic representation shown in Fig. 2g. $g-C_3N_4-H^+Cl^-$ can be obtained by protonating $g-C_3N_4$. At the subsequent stage, Ag^+ will combine with Cl^- on the surface of

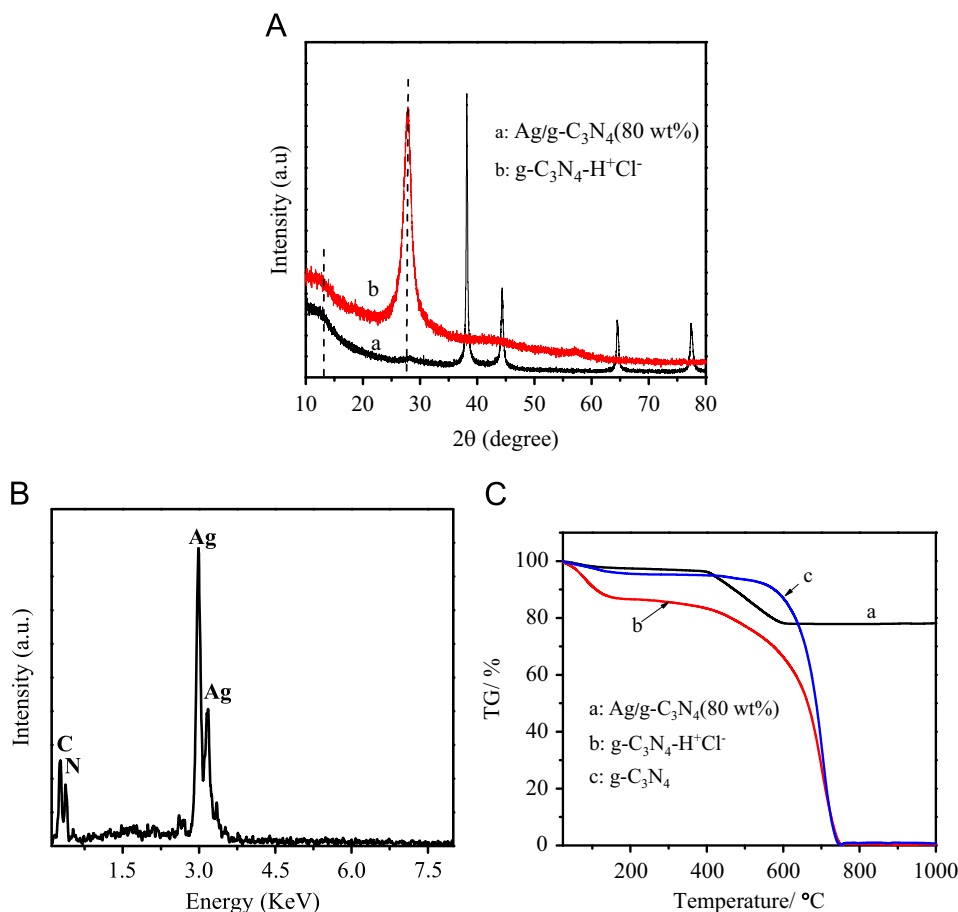


Fig. 1. (A) XRD patterns of Ag/ $g-C_3N_4$ (80 wt%) and $g-C_3N_4-H^+Cl^-$; (B) EDS analysis of Ag/ $g-C_3N_4$ (80 wt%); (C) TG curves of $g-C_3N_4$, $g-C_3N_4-H^+Cl^-$ and Ag/ $g-C_3N_4$ (80 wt%).

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