Research Progress of Preparation Methods of Graphene Nanocomposites for Low-Temperature Fuel Cells and Lithium-Ion Batteries

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‖ **Abstract**

Because of its unique two-dimensional structure, huge specific surface area, high electrical conductivity, and other excellent performances, graphene has shown great potential for application in catalysis, electronics, sensors, energy storage, and other areas. Especially, graphene nanocomposites have been found to be promising catalyst support for low-temperature fuel cells, and as anode nanomaterials for high reversible capacity and excellent rate capability for lithium-ion batteries, which has triggered a new round of research hotspot. Preparation methods of graphene nanocomposites mainly for low-temperature fuel cells are reviewed. Particularly, the research progress and principles of physical preparation methods (molecular beam epitaxy), chemical preparation methods (chemical reduction, electrochemical deposition and hydrothermal/solvothermal methods, *etc.*) and high-energy ball milling are summarized. Research outlook of graphene nanocomposites for low-temperature fuel cells are prospected.

‖ **Keywords**

Graphene nanocomposites, preparation methods, low-temperature fuel cells, electrocatalysts, anode materials

1. Introduction

In 2004, *Geim et al.*[1] used the micro-mechanical exfoliation method to obtain graphene with a two-dimensional structure. Graphene has a very high specific surface area (2630 m^{2}g^{-1}), an electron mobility exceeding 15 000 cm^{2}V^{-1}S^{-1} at room temperature, and a thermal conductivity of about 5000 W m^{-1}K^{-1}. Moreover, graphene has an ambipolar field-effect and quantum Hall ferromagnetic characteristics.[2–5] Benefiting from the above superior properties, graphene has been highly attractive both in industrial and fundamental research. For example, in lithium-ion batteries, many metal oxide anode materials have used graphene sheets as an ideal matrix material. Similar to carbon nanotubes, graphene is difficult to produce as a single material, and it is mainly used to produce a new type of composite material with excellent properties. Therefore, graphene composite materials find their application in the fields of catalysis, electrochemistry, and biomedical.[6–8] Accordingly, preparation of graphene nanocomposites using diverse methods from a variety of precursors has been intensively studied.

In recent years, the development of clean, efficient, and new energy sources has become a hot topic. Fuel cells are widely applied in the automobile, stationary power generation, aerospace and other fields[9–13] due to their high energy conversion efficiency and battery device reliability. The widely used catalyst supports are Vulcan XC-72, carbon nanofibers, and carbon nanotubes,[14–17] which partly relieve the problems of high cost and anode catalyst poisoning. However, these materials still cannot meet the requirements as an ideal electrocatalyst of stable performance under repeated start-stop cycles or high-potential conditions. Due to the uniform distribution of electrochemically active sites, catalyst particles supported on the surface of graphene can decrease the over potential of catalytic reactions obviously.[18] In lithium-ion batteries, the demand for research of anode materials with enhanced energy capacity and cycle life has increased a great deal. Consequently, in order to utilize the advantages of graphene, it is desirable to prepare highly efficient graphene-supported metal electrocatalysts to improve the performance of fuel cells, and as effective anode materials for lithium-ion batteries.

2. Preparation methods of graphene nanocomposites

2.1 Physical preparation methods

Physical preparation methods usually use light, electricity, and other forms of energy to evaporate materials in a vacuum or inert atmosphere and deposit the gaseous atoms or molecules to form nanoparticles. Reported methods include molecular beam epitaxy, thermal evaporation and spray technology.[19,20]

Molecular beam epitaxy (MBE) is a method for growth of thin films crystallized in high quality on crystal substrates. In a high vacuum, the vapour generated by heating the furnace containing various components, formed a single crystal layer on the substrate through spray from a small hole of the furnace directly. While controlling the molecular beam and the substrate at the same time, the molecules or atoms could arrange in a layer-by-layer manner.

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Hernández-Rodríguez et al.[21] used a MBE growth method to obtain graphene on Pt and Au using evaporation of carbon atoms from a carbon solid-source in ultra-high vacuum conditions. This method opens up new possibilities for the formation of graphene on many different substrates.

However, due to the high cost of MBE and high vacuum degree, it needs to avoid impurity contamination in the evaporator. MBE requires strict control of smoothness, stability, and purity of the crystal growth parameters. Therefore, how to control the crystal growth parameters is one of the technical problems to be solved.

2.2 Chemical preparation methods

2.2.1 Chemical reduction method

Chemical reduction is a common method for preparation of nanocomposites. Typical procedures include stirring the aqueous mixture of noble metal precursors (*e.g.* $HAuCl_4$, K_2PtCl_4 and H_2PdCl_6 *et al.*) and catalyst carriers in order to make them fully dispersed at first, and then adding reducing agents in the liquid phase. Finally, the ionic reactants are reduced to metals to successfully prepare the target nanocomposites. Reducing agents include commonly used ethylene glycol, sodium borohydride, and hydrazine hydrate.

Liu et al.[22] prepared Pt/graphene nanocomposites as the anode electrocatalyst for direct borohydride fuel cell by an ethylene glycol reduction method. At 298 K, the maximum power density of Pt/graphene nanocomposites was 42 mW cm^{-2}, apparently higher than that of Pt/Vulcan XC-72R nanocomposites (34 mW cm^{-2}). *Wang et al.*[23] prepared $w = 40$ % Pt/graphene composite as the electrocatalyst for oxygen reduction reaction by sodium borohydride chemical co-reduction. The results showed that the initial activity of the obtained Pt/graphene was lower than that of Pt/C because of the inhibition of oxygen diffusion. However, the subsequent degradation tests indicated that Pt/graphene (50 %) was less stable than Pt/C (79 %).

The chemical reduction method is simple, easy to operate, and can be employed in mass-production. However, since the formation of metals occurs in the liquid phase and on the surface of the carriers, the metal cores growing in catalyst particles usually distribute randomly on the surface of the carriers. In addition, the reducing agent and organic solvents can deteriorate the binding strength between graphene and nanoparticles. Thus, the performance of the nanocomposites synthesized using this method may not be very high.

2.2.2 Sol-gel method

The sol-gel method usually uses metal alkoxides or metal chlorides as the precursors and treats them by a series of hydrolysis and condensation reactions. Finally, the cured composite catalysts are prepared after drying and calcining.[24] *Sun et al.*[25] prepared five different nanoparticles of Pt/sulfonated graphene (Pt/sG) as anode electrocatalysts on alkaline direct ethanol fuel cell by the sol-gel method. The different particle diameters of the electrocatalysts were 1.7 nm, 2.5 nm, 3.5 nm, 4.4 nm, 13.9 nm, respectively (Table 1). Theoretical calculations showed that the sulfonic acid groups in sG can enhance the adsorption energy of Pt, and in consequence decrease the adsorption capacity of CO on Pt. The experimental results showed that Pt/sG (2.5 nm) has the highest peak current of CV (3480 mA g^{-1}, a ratio to Pt mass). The ethanol oxidation activity of Pt/sG (2.5 nm) was also higher than that of carbon black supported Pt of the same size (2.5 nm).

The sol-gel method is an effective method for preparing thin-film coating materials. The method works at low reaction temperatures and is easy to conduct, but there still exist many confounding factors in the process of forming a sol. Meanwhile, a rubber reunion phenomenon is apt to occur.

2.2.3 Electrochemical deposition method

The electrochemical deposition method has rapidly developed into a technology of great industrial importance. Certain substrates were selected as the electrodes and a mixed solution of catalyst precursors was used as the electrolyte of electrolytic cells. The electrochemical deposition method can easily obtain uniform distribution of the nanoparticle layer by controlling the current, potential and deposition time.[26] *Shi Guoyu et al.*[27] used ITO conductive glass substrates as the electrode to prepare PtCo/graphene nanosheets composite electrocatalysts by the constant potential deposition method. The results showed that when the ratio of Pt and Co was 1 : 2.93, the electro-catalytic

Table 1 – Particle size effects of Pt/sG nanoparticles on ethanol electrooxidation[25]
Tablica 1 – Učinci veličine nanočestica Pt/sG na elektrooksidaciju etanola[25]

Sample Uzorak	Synthesis pH pH sinteze	Average particle size / nm Prosječna veličina čestica / nm	Standard deviation / nm Standardna devijacija / nm	ECSA / cm² $c(NaOH) = 0.1$ mol l^{-1}		ESCA (surface area to Pt mass) / m² g^{-1} ESCA (prema masi Pt) / m² g^{-1}
				Pt(110)	Pt(100)	
Pt-sG (1.7 nm)	11.8	1.7	0.4	1.41	0.34	79.77
Pt-sG (2.5 nm)	11.3	2.5	0.6	1.42	0.43	80.04
Pt-sG (3.5 nm)	6.4	3.5	0.7	0.54	0.14	30.68
Pt-sG (4.4 nm)	1.0	4.4	0.9	0.65	0.15	51.84
Pt-sG (13.9 nm)	<1	13.9	5.8	0.41	0.11	36.14

performance of methanol oxidation was the most superior with a current density to Pt mass ratio reaching 662 Ag^{-1}. The PtCo/graphene catalysts prepared by the electrodeposition method are of higher catalytic stability, better oxidation kinetics, and has practical significance on efficient methanol fuel cell.

Preparing electrocatalysts by the electrochemical deposition method has advantages of good controllability, easy operation, and environmental compatibility. However, the obtained metal composite nanoparticles cannot penetrate into the graphene sheets completely but deposit mainly on graphene coating surface and then lead to unreliable binding. Therefore, this method remains to be further studied on the binding strength.

2.2.4 Hydrothermal/Solvothermal method

The temperature range of the hydrothermal method is usually between 130 and 250 °C and the corresponding water vapour pressure is 0.3–4 MPa. These conditions are the main differences distinguishing hydrothermal from sol-gel and co-precipitation methods. The hydrothermal method simply generates high vapour pressure in a fixed volume at a high temperature to prepare inorganic nanocomposites. Water plays as both the pressurization agent and chemical reaction media. In such state, water can completely (or partially) dissolve most of the reactants, making the reaction in close homogeneous phase, thus speeding up the reaction. Lee et al.[28] prepared PtRu/graphene and PtRu/multi-walled carbon nanotubes (PtRu/MWCNT) by the hydrothermal method. The main process includes mixing ethylene glycol, $H_2PtCl_6 \cdot H_2O$, $RuCl_3$ and graphene together, adjusting pH of the mixture to 9 by adding KOH, and then transferring the above mixture to the autoclave, which was followed by annealing at 150 °C for 5 h. The ratio of electrochemically active surface area to Pt mass of the produced PtRu/graphene was measured to be 68 $m^2 g^{-1}$, which was higher than that of PtRu/MWCNT (20 $m^2 g^{-1}$). The above results showed that compared to PtRu/MWCNT, the PtRu/graphene electrocatalyst had higher electrochemical activity, longer and higher resistance to CO poisoning in the process of oxidation of methanol. In addition, the high performance PtRu/graphene prepared by the hydrothermal method can be applied to direct methanol fuel cells as the anode catalyst.

Graphene nanocomposites from the hydrothermal method have characteristics of good crystallinity, less agglomeration, high purity, narrow particle size distribution, and morphology controllability. Currently, electrocatalysts prepared by this method have good electrochemical activity, therefore this method has wide potential applications and is worthy of being further developed.

The solvothermal method is developed on the basis of the hydrothermal method, but the solvent is organic or other rather than water. In the solution under certain temperatures and authogenic pressure, the original mixture reacts chemically.[29] Typical solvents include: ethylenediamine, methanol, ethanol, benzene, toluene, phenol, and ammonia. The solvothermal process is relatively simple and easy to control. The reaction in a closed system can also

effectively prevent the leaking of toxic vapour, as well as avoid the exposure of sensitive precursors to air, thus it is an effective method to prepare nanomaterials.[30]

2.2.5 Other chemical preparation methods

Recently, sonochemical processing has been proved a useful technique for preparing nanomaterials. Neppolian et al.[31] synthesized graphene oxide-supported (GO) monometallic Ag and Au, as well as Au-Ag bimetallic catalysts by a dual frequency sonochemical method. The activities of these catalysts were tested using a 4-nitrophenol (4-NP) reduction process. The results revealed that the bimetallic catalysts showed higher activity than other monometallics. Marinkasa et al.[32] successfully prepared Pt/graphene, Pt/graphene/carbon black and Pt/graphene/multi-walled carbon nanotube composites by a thermally induced chemical reduction method, and analysed these three composite materials. The results showed that the addition of carbon black particles or multi-walled carbon nanotubes destroyed the structure of graphene and formed a porous layer, which was effective for mass transport, and then the performance PEMFC had improved. Sun Hongmei et al.[33] successfully constructed three-dimensional porous graphene/PtPd bimetallic hybrids (3DPPG) by combining the solvothermal strategy with the ice template technique. At 180 °C, this group mixed ethylene glycol solution containing GO, precursor of PtPd and polyacrylic acid (PPA) in the reaction vessel. The obtained 3DPPG greatly enhanced the physical activity and stability of methanol oxidation, and provided a new platform for new and efficient electrocatalysts of direct methanol fuel cells.

2.3 High-energy ball milling

High-energy ball milling is a combination of physical and chemical methods, and it is an important method for the preparation of nanomaterials. The basic principle is that chemical reactivity of crystalline materials in the process of fine grinding can be activated by the mechanical force, which makes the reaction occur at a lower temperature.

Mondal et al.[34] transformed graphene oxide to reduced graphene oxide (rGO) by high-energy ball milling, which is a new green and scalable approach to synthesizing rGO starting from GO. The graphene oxide powder was ball-milled by different zirconium oxide balls of 5 mm diameter and mass ratio between the ball and GO was kept constant at 20 : 1. The milling was operated with a rotatory speed at 800 rpm in inert Ar atmosphere. Yu et al.[35] employed high-energy ball milling to synthesize ZnO/graphene nanocomposites, and evaluated the product as an anode material in lithium-ion batteries. Their ZnO nanoparticles were created by a top-down wet-chemistry synthesis process. The ball-milling treatments were performed with a rotatory speed of 500 rpm at room temperature in air atmosphere for 20 h. They found that the synthesized nanocomposite exhibited an initially reversible capacity of 783 $mAh g^{-1}$ and maintained a capacity of 610 $mAh g^{-1}$ after 500 cycles at 100 $mA g^{-1}$. Rashad et al.[36] used graphene nanoplatelets and carbon nanotubes as reinforcement fillers to enhance

Table 2 – Characteristics of different preparation methods used to synthesize graphene nanocomposites
Tablica 2 – Karakteristike različitih metoda priprave korištenih za sintezu nanokompozita grafena

Preparation methods Preparativne metode	Advantages Prednosti	Disadvantages Nedostatci
physical methods fizikalne metode	easy to prepare jednostavno pripravljanje	difficult to control teško se kontrolira
chemical methods kemijske metode	common preparation methods and basically can meet the requirements of synthesis of uniform graphene nanocomposites uobičajene metode, mogu se sintetizirati uniformni grafenski nanokompoziti	preparation may be complex and cannot be massively produced priprava može biti složena i ne može se proizvoditi na veliko
other methods (high-energy ball milling) druge metode (intenzivno kuglično mljevenje)	reaction can be carried out at a lower temperature reakcija se može provesti pri nižoj temperaturi	the product size distribution is not uniform and impurities are easily introduced raspodjela veličine nije ujednačena i lako se unose nečistoće

the mechanical properties of AZ31 magnesium alloy by high-energy ball milling, sintering and hot extrusion techniques. They found both graphene and carbon nanotubes increased the mechanical strength of AZ31 magnesium alloy.

With further development, this method will not only be widely used in the preparation of nanomaterials and new metal materials, but also in the preparation of other amorphous and ceramic materials. However, there are still some shortcomings for the ball milling method, such as: (1) the product size distribution is not uniform and it is easy to introduce impurities; (2) some powder materials suffer from dispersion and agglomeration problems; (3) the structures of mills are complex and with many consumable parts. The maintenance cost of the mill renders large-scale production costly and uncompetitive. Therefore, high-energy ball milling is attractive but need further optimization.

2.4. Summary of the preparation methods of graphene nanocomposites

Table 2 summarizes the advantages and disadvantages of various methods including physical, chemical, and other preparation methods of graphene nanocomposites.

3. Conclusion

Hopefully, the studies on the performance of various graphene nanocomposites preparation methods and their improvements will be more abundant. In the future, research into graphene nanocomposites will focus on the following objectives:

(1) To seek new recipes to reduce the loading amount of noble metal on graphene and increase the catalytic performance, so that graphene-based catalysts can be more attractive by lowering the cost of fuel cells;

(2) To develop new methods of preparation or combining with existing preparation methods to improve the uniformity and stability of graphene nanocomposites electrocatalysts;

(3) To achieve large-scale production of graphene nanocomposites. Currently, methods of graphene-based electrocatalysts are suitable for preparation in the laboratory. For the wider use of graphene-based electrocatalysts, it is necessary to realize a large-scale production and preparation process, which should also be easy to operate and control, as well as pollution-free.

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List of abbreviations and symbols
Popis kratica i simbola

3DPPG	– three-dimensional porous graphene/PtPd – trodimenzionalni porozni grafen/PtPd
4-NP	– 4-nitrophenol – 4-nitrofenol
CV	– cyclic voltammetry – ciklička voltammetrija
ECSA	– electrochemical surface area, cm^2 – elektrokemijska ploština površine, cm^2
ESCA	– electron spectroscopy for chemical analysis – elektronska spektroskopija za kemijsku analizu
GO	– graphene oxide – oksid grafena
ITO	– indium tin oxide – indijev kositrov oksid

MBE	– molecular beam epitaxy
	– epitaksija molekulskim snopom
PEMFC	– proton exchange membrane fuel cell
	– gorivni članak s protonskom izmjenjivačkom membranom
PPA	– polyacrylic acid
	– poliakrilna kiselina
Pt/sG	– Pt/sulfonated graphene
	– Pt/sulfonirani grafen
PtRu/MWCNT	– PtRu/multi-walled carbon nanotubes
	– PtRu/višestjenčane ugljikove nanocjevčice
rGO	– reduced graphene oxide
	– reducirani oksid grafena
c	– amount of substance concentration, $\mathrm{mol\,l^{-1}}$
	– množinska koncentracija, $\mathrm{mol\,l^{-1}}$
w	– mass fraction, %
	– maseni udjel, %

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SAŽETAK

Napredak u istraživanju metoda priprave nanokompozita grafena za niskotemperaturne gorivne ćelije i litij-ionske baterije

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Zbog jedinstvene dvodimenzionalne strukture, velike specifične površine, visoke električne vodljivosti te niza drugih izvrsnih svojstava, grafen ima veliki potencijal za primjenu u katalizi, elektronici, senzorima, skladištenju energije i drugim područjima. Nanokompoziti grafena obećavajući su nosači za katalizatore za niskotemperaturne gorivne ćelije te anodni nanomaterijali za brze litij-ionske baterije s visoko reverzibilnim kapacitetom, što je potaknulo niz novih istraživanja.

Prikazane su metode kojim se pripravljaju nanokompoziti grafena ponajprije za niskotemperaturne gorivne ćelije. Posebno je dan sažetak napretka u istraživanjima i principima fizikalnih (epitaksija molekulskim snopom) i kemijskih metoda priprave (kemijska redukcija, elektrokemijska depozicija, hidrotermalne/solvotermalne metode itd.) te intenzivnog kugličnog mljevenja (*high-energy ball milling*). Razmatrane su mogućnosti primjene nanokompozita grafena u niskotemperaturnim gorivnim ćelijama.

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