



Highly efficient graphene oxide/porphyrin photocatalysts for hydrogen evolution and the interfacial electron transfer



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ABSTRACT

By implanting metal ions as interfacial linkers of the graphene oxide (GO) and 5,15-diphenyl-10,20-di(4-pyridyl)porphyrin (DPyP), a series of novel GO-DPyP nanocomposites were achieved. In these composites, GO and DPyP were bridged by the metal ions by means of electrostatic interaction and coordination interaction. It was shown that the metal ions can modify the morphology and structure of the GO-DPyP nanocomposite, and facilitate electron transfer between GO and DPyP. Furthermore, the photocatalytic hydrogen evolution activity and electron transfer mechanism were investigated. The results demonstrated that the strong interaction and efficient electron transfer between the metal ions and DPyP/GO were the important reasons for the improvement of the photocatalytic hydrogen evolution performance. Implanting metal ions in the interface of graphene oxide and porphyrin is a simple and efficient approach to optimize the transfer pathway of photogenerated electrons and improve catalytic performance of nanocomposites.

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1. Introduction

Due to the shortage of fossil fuels and environmental pollution, it is important to develop a new kind of energy. Hydrogen, as an exciting renewable and clean source, has been studied for many years. It is found that using solar energy to produce clean hydrogen through photocatalysis is a good choice [1]. However, the conversion efficiency of the current materials is still low due to weak light absorption ability, rapid recombination of electron-hole and low stability. It is the key to design and synthesize ideal catalysts for photocatalytic hydrogen evolution.

Graphene oxide (GO) possesses the excellent characteristics of graphene, such as large specific surface area, highly electronic and thermal conductivity [2]. In addition, the abundant functional groups, such as epoxide, hydroxyl and carboxyl groups, make GO easily be further modified. It is reported that GO can be functionalized with some photosensitive materials through the covalent or noncovalent interaction [3–7]. Subsequently, the electron transfer from excited photosensitive molecules to GO sheets can take place, which has been considered to be important means to improve photocatalytic properties of the graphene-based photocatalysts.

Porphyrin has been used in catalytic field because of its special structure and high thermal stability [8,9]. Porphyrin/carbon-based functional materials, such as porphyrin/carbon nanotubes and porphyrin/graphene sheets linked by covalently or non-covalently approaches have been one of the hottest candidates [10–14]. While improving electron transfer efficiency between graphene and porphyrin is an efficient way to enhance the photocatalytic activity of the graphene/porphyrin composites. The porphyrin/graphene composites linked by covalent bond show high electron transfer efficiency due to low interface resistance [11]. However, the complicated process and low yield are obstructions in practical application. How to improve the electron transfer between porphyrin and graphene by a facial method is an important topic in this field.

It is reported that multistep electron transfer via ZnO nanoparticles mediator linking graphene and porphyrin exhibits remarkably high photocurrent generation [12]. In addition, the graphene-based photocatalysts prepared by inorganic or organic modification on graphene sheets show enhanced catalytic activity [15,16]. It was found that, employing polyaniline as the coupling linker, the controlled growth of MO/MH (such as Co₃O₄, Fe₂O₃, and (Ni(OH)₂)NPs) on graphene was achieved, and the conductivity of MO/MH and the coupling effects between graphene and MO/MH were improved [17]. Using glucose as the linker and face-controlling agent, Zhang et al. prepared the

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TiO₂ with the (001) facets and a mesoporous structure [18]. Employing 2D GO/SnO₂ nanosheets as the basic building block and various amphiphilic polymers including poly(vinyl alcohol), Pluronic®F127, polyethylenimine and GO as the cross-linkers, macroporous graphene/SnO₂ frameworks with tunable macroporosity (2 to 50 μm) have been achieved [19]. Xu et al. prepared a GO/CdS nanoparticles with metal ions as the linker, which shows high photocatalytic activity in selective oxidation of benzyl alcohol and selective reduction of 4-nitroaniline [20]. Yu et al. prepared graphene oxide (GO)/polyacrylamide (PAM) hydrogels by the synergistic effects of GO and calcium ions. The role of the Ca²⁺ is mainly to induce dissipation of the on-loading crack energy of GO network, and contribute to the higher stretch ability [21]. It is known that the coordination of metal ions with nitrogen-based ligands is an important interaction [22]. Kira et al. found that pyridylfullerene (Py-C₆₀) acceptors can infiltrate into the metalloporphyrin zinc brush by the coordination of the pyridyl moiety to the zinc atom together with π-π interaction between the Py-C₆₀ moieties, which efficiently improves the performance of organic photovoltaic [23]. Due to its smaller radius, the metal ions as the interfacial linkers could be more profitable to decrease the interfacial resistance between GO and DPyP and to improve the transfer efficiency of photoproduced electrons.

In this paper, with various metal ions as the interfacial linker, (5,15-diphenyl)-10,20-di(4-pyridyl) porphyrin as light absorbing antenna, and graphene oxide as the electron transfer support, by coordination interaction and electrostatic interaction, a series of graphene oxide/porphyrin donor-acceptor nanocomposites (GO-DPyP) are constructed at room temperature by a simple and environmentally friendly approach. The influence of metal ions on the morphology and structure of the nanocomposites, photocatalytic activity and electron transfer mechanism for the composites are studied.

2. Experimental

2.1. Materials

5,15-diphenyl-10,20-di(4-pyridyl) porphyrin (DPyP) was purchased from J&K Scientific Ltd. Graphite powder with an average size of 30 μm and purity of >99.85% was purchased from Shanghai Chemical Reagent Company. All the other chemical reagents (A.R.) were purchased from Sinopharm Chemical Reagent Co. and were used without further purification. Double distilled water was used throughout the experiments.

2.2. Preparation of GO

GO was prepared by a modified Hummers method [24,25]. In brief, commercially available graphite powder (1 g) was mixed with NaNO₃ (1 g) and H₂SO₄ (80 mL) and sonicated in an ice bath for 30 min. Subsequently, KMnO₄ (8.5 g) was added in small portions to the mixture, and continually sonicated for 15 min. Then the

mixture was stirred for 1 h at 40 °C. Double distilled water (50 mL) was slowly added and stirred for another 1.5 h. The suspension was kept at 90 °C for 1 h. After adding H₂O₂ (45 mL, 30 vol.%) and HCl (500 mL, 10 vol.%), respectively, the mixture was aged for 24 h. The brown precipitate (GO) obtained by centrifuging was washed until the pH of the filtrate was about 7. Finally, the solid was dried overnight at 60 °C.

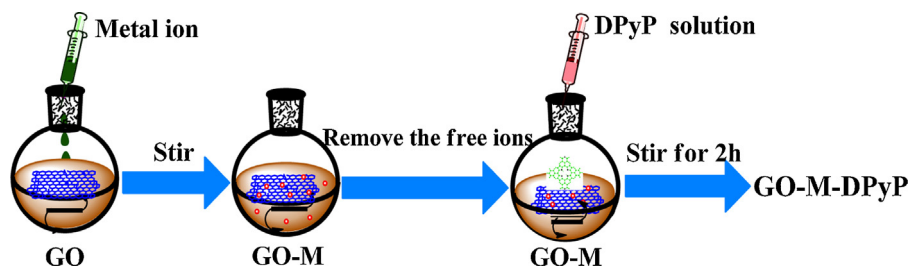
2.3. Preparation of GO-M-DPyP composite

The simple strategy used to prepare the GO-M-DPyP composites is depicted in Scheme 1. In a typical procedure, a certain amount of the salt solution (M = K⁺, Ca²⁺, Zn²⁺, Cu²⁺, Co²⁺ or Cr³⁺) was added to 200 mL of 0.5 mg mL⁻¹ GO aqueous dispersion solution. Next, the above mixture was stirred for 2 h at room temperature. Then, the mixture was centrifuged and washed for several times with double distilled water. Finally, the solid obtained (GO-M) was dried overnight at 60 °C. The implanted content of metal ions was about 10%.

DPyP tetrahydrofuran (THF) solution (5 mL, 1 mmol L⁻¹) was injected into GO-M aqueous dispersion (155 mL, 0.5 mg mL⁻¹) under vigorous stirring, and stirred for 2 h at room temperature. Afterwards, the GO-M-DPyP composite was achieved by centrifuged and dried at 45 °C. By replacing the GO-M with the GO, the GO-DPyP composite was prepared in the same procedure as that of the GO-M-DPyP composite. The content of DPyP in the composites was about 4 wt.%.

2.4. Characterizations

UV-vis absorption spectra were recorded with a UV-3900 spectrophotometer (Japan). Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 6700 FTIR spectrometer (USA). Transmission electron microscope (TEM) images were taken with a JEOL JEM-2100F microscope device (Japan), and the accelerating voltage was 200 kV. The morphology of the composite was observed by S-3400N Hitachi High Technologies scanning electronic microscopy (SEM, Japan). The element maps were taken with FEI Tecnai G² 20 high resolution transmission electron microscope (USA). Nitrogen adsorption-desorption isotherm was obtained at 77 K by using Micrometrics Model ASAP 2020 volumetric adsorption analyzer (USA). The sample was pre-outgassed at 333 K under vacuum. X-ray photoelectron spectra (XPS) were measured on a Thermo ESCALAB 250 X-RAY photo electron spectrometer with a monochromatic X-ray source (Al Kα hν = 1486.6 eV) (USA). X-ray powder diffraction (XRD) was carried out using a Bruker D8 Advance X-ray diffractometer (Germany). The thermo-gravimetric/differential thermal analyzer (TG-DTA) was recorded on a Mettler-Toledo TG/DTA instrument under N₂ atmosphere (Switzerland). The heating rate was 10 °C min⁻¹.



Scheme 1. The synthesis procedure for the GO-M-DPyP composite.

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