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# One-step synthesis of three-dimensional nitrogen and sulfur co-doped graphene networks as low cost metal-free counter electrodes for dye-sensitized solar cells

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## HIGHLIGHTS

- NS-GN was prepared through a facile one-step doping process.
- Doping graphene with S and/or N atoms created more active sites for  $I_3^-$  reduction.
- The N and/or S doping enhanced the electrocatalytic activity of graphene.
- The DSSC based on NS-GN showed a high power conversion efficiency of 9.40%.

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## ABSTRACT

Three-dimensional nitrogen and sulfur co-doped graphene networks are synthesized via a simple one-step hydrothermal route. The nitrogen and sulfur co-doping strategy significantly enhances the electrocatalytic activity for triiodide reduction. The dye-sensitized solar cell based on the nitrogen and sulfur co-doped graphene exhibits an efficiency of 9.40%, which is higher than the efficiency of the Pt-based device. The superior electrochemical performance can be attributed to the synergistic effect of sulfur and nitrogen atoms in graphene, the conductive three-dimensional graphene networks with a large surface area and an interconnected porous structure.

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## 1. Introduction

Dye-sensitized solar cell (DSSC) has attracted considerable attention as a promising alternative for traditional silicon solar cells in the last two decades owing to its low cost, environmental friendliness and easy production [1]. Typically, a DSSC uses a mesoporous network of  $TiO_2$  nanocrystals anchored with sensitizer as the photoanode, a platinumized FTO as the counter electrode (CE) and the iodide/triiodide ( $I^-/I_3^-$ ) based electrolyte [2–4]. In DSSC, the CE is one of the crucial components for regulating the device performance since it collects electrons from the external circuit

and catalyzes the reduction of oxidized species in the electrolyte [5–8]. Platinum (Pt) has been widely used as the CE material due to its excellent electrocatalytic activity towards  $I_3^-$  reduction and high conductivity. However, the relatively high cost and limited availability of Pt have hindered the large-scale commercial application of DSSCs. Therefore, it is highly desirable to develop alternative CE materials with low production cost, high electrical conductivity, excellent electrocatalytic activity and good stability [9–16]. Recently, a series of substitutes for Pt have been explored such as carbon-based materials (carbon black, activated carbon, carbon nanotubes, graphite, mesoporous carbon and graphene, etc.) [17,18], conductive polymers [19–21], and transition metals in the form of oxides [22], sulfides [23], selenides [24] and nitrides [25]. Among them, carbon-based materials are very promising candidates due to their relatively low-cost, easy preparation, good catalytic ability and high conductivity.

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Graphene, a two-dimensional aromatic monolayer of carbon atoms, has attracted great attention owing to its excellent electrical conductivity and large surface area [26–33]. However, pristine graphene is hardly suitable for CEs of DSSCs since the electrocatalytically active sites in highly conductive perfect graphene are very limited [34]. Recent progress reveals that functionalizing graphene with oxygen containing groups could create more catalytic centers and give rise to the enhancement of the material's apparent catalytic activity [35]. However, the oxygen doping also leads to the destruction of the conjugated carbon structure, thus reducing the conductivity of the graphene dramatically. Doping graphene with heteroatoms has been proved to be an effective strategy to overcome this dilemma. Among the heteroatoms doped in graphene, nitrogen is the most promising since it creates more catalytically active sites with a minimized change of the conjugation length [36,37]. Meanwhile, the lone electron pairs of nitrogen atoms can form a delocalized  $\pi$ -system with the  $sp^2$ -hybridized carbon framework, facilitating the electron-transfer ability of the material [38,39]. In addition, recent studies show that co-doping graphene by N and other elements could further improve the electrochemical properties due to the synergistic effect arising from the heteroatoms [40–42]. S atom is selected as a promising dopant to adjust the electrocatalytic activity for carbon materials since the S atoms could increase the charge density asymmetry of carbon atoms, create more catalytically active sites, and decrease the charge transfer resistance [43–46]. Thus, intercalating S and N heteroatoms into graphene networks is a promising pathway to modulate the electrical, chemical and electrocatalytic properties [47].

In this paper, we report the design and synthesis of nitrogen and sulfur co-doped graphene networks (NS-GN), by a one-step hydrothermal method. The nitrogen and sulfur heteroatoms endow the materials with high catalytic activity towards  $I_3^-$  reduction while the porous structure increases the specific surface area and facilitates the mass transport in the electrolyte. The DSSC fabricated with the NS-GN CE achieved a power conversion efficiency of 9.40%, which is superior to that of the device with Pt-based CE.

## 2. Experimental section

### 2.1. Preparation of the NS-GN, S-doped graphene networks (S-GN), N-doped graphene networks (N-GN) and reduced graphene oxide (RGO)

All commercially available chemicals were analytic grade and used as received without further purification. Graphene oxide (GO) was prepared using a modified Hummers method from natural graphite [48]. NS-GN was prepared by a combined hydrothermal assembly and freeze-drying process. In a typical procedure, 30 mg of GO was added to 20 mL of DI water and ultrasonically dispersed for 30 min, then 3.6 mmol thiourea ( $CN_2H_4S$ ) was added into the aqueous suspension and sonicated for 30 min. The resulting stable suspension was placed into a Teflon lined and hydrothermally treated at 180 °C for 12 h after which it was allowed to naturally cool down to room temperature. The resulting hydrothermal product was washed with excess water. Finally, the as-prepared sample was freeze-dried overnight, followed by vacuum drying at 60 °C for several hours. RGO was prepared under a similar experimental conditions using only GO without  $CN_2H_4S$ . S-GN and N-GN samples were prepared using similar preparation conditions with 3-mercaptopropionic acid and urea as the source of sulfur and nitrogen, respectively.

### 2.2. Preparation of the CEs

The CEs were prepared according to the following procedure. 3 mg of NS-GN, S-GN N-GN or RGO was dispersed in 600  $\mu$ L of

isopropanol and sonicated for 1 h to get good dispersion. A Surlyn ring was used to get a specific area (0.286  $cm^2$ ) on the pre-cleaned FTO glass. 40  $\mu$ L of NS-GN, S-GN, N-GN or RGO dispersion was dropped into the Surlyn ring of the FTO glass with a pipet. When the isopropanol completely evaporated, the Surlyn ring was removed from the FTO. Then the film was dried in the oven at 300 °C for 1 h. To prepare the Pt CE, 100  $\mu$ L of  $H_2PtCl_6$  in isopropyl alcohol (2 mg  $mL^{-1}$ ) was drop-casted on  $1.0 \times 1.5 cm^2$  FTO substrate, followed by heat treatment at 400 °C for 15 min.

### 2.3. Cell fabrication

A  $TiO_2$  electrode was prepared by screen-printing a layer of  $TiO_2$  paste on a clean FTO substrate, followed by thermal annealing at 400 °C for 30 min. The thickness of the resultant mesoporous  $TiO_2$  film was  $\sim 10 \mu m$ . The  $TiO_2$  electrode was stained by immersing it into C106 solution for 16 h. The photoanode was separated with a CE by a Surlyn hot-melt gasket and sealed by heating. The liquid electrolyte, which consists of 0.02 M  $I_2$ , 0.05 M LiI, 1 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M guanidine thiocyanate and 0.5 M 4-*tert*-butyl-pyridine in acetonitrile were used to backfill through the hole in the CEs of all the cells via vacuum back filling method.

### 2.4. Characterizations

Morphologies of as-obtained products were observed on a field emission scanning electron microscopy (FESEM, Hitachi S-8010). Transmission electron microscopy (TEM, FEI Tecnai G<sup>2</sup> F30) images were obtained under an acceleration voltage of 200 kV. The thickness of graphene was measured by atomic force microscope (Agilent 5500 AFM) under tapping mode. X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer (ThermoFisher Scientific Company) using Al K $\alpha$  (1486.6 eV) radiation. The surface area was measured by the Brunauer-Emmett-Teller (BET) method using ASAP2020. Additionally, Raman spectra were recorded at room temperature by employing an inVia Raman spectrometer using a 633 nm red laser with 10% intensity to determine the extent of graphitic disorder.

Cyclic voltammetry (CV) were carried out in a three electrodes system (10 mM LiI, 1 mM  $I_2$ , and 0.1 M  $LiClO_4$  in acetonitrile) with different CEs as the working electrode, a platinum mesh as the counter electrode, Ag/AgCl electrode as the reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were obtained with an impedance analyzer (Zahner IM6, Germany), and carried out by applying sinusoidal perturbations of 10 mV under the bias of 0 V in the dark, and the frequency ranges from 10 mHz to 1 MHz. The obtained spectra were fitted with Z-View software in terms of appropriate equivalent circuits.

For the photovoltaic measurements, devices were equipped with an UV cut-off filter and masked with a thin metal mask to give an active area of 0.1598  $cm^2$ . A model LS1000-4S-AM1.5G-1000W solar simulator (Solar Light Company, USA) in combination with a metal mesh was employed to give an irradiance of 100  $mW cm^{-2}$ . The light intensity was tested with a PMA2144 pyranometer and a calibrated PMA 2100 dose control system. The short-circuit photocurrent densities measured under this solar simulator are well consistent with the integral of IPCEs with the AM1.5G spectrum (ASTMG173-03).

### 2.5. Computational details

The density functional theory (DFT) with the B3LYP functional [49,50] with 6-31g\* basis set was employed for the geometry optimizations, harmonic vibrational frequencies calculations, and the NBO charge analysis. The polarizable continuum model (PCM)

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