Graphene doped with silver nanoparticle as p-type dopants in efficient perovskite solar cells

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ARTICLE INFO

Article history:
Received 4 March 2020
Received in revised form 28 March 2020
Accepted 3 April 2020
Available online 12 April 2020

Keywords
p-type, Perovskite, Graphene, silver nanoparticles,

ABSTRACT

Perovskite materials have been shown to be involved in energy conversion and environmental applications. Graphene doped with silver nanoparticle (Ag@G) is designed and synthesized for the first time as p-type dopants in solid-state perovskite solar cells (PSCs) applications. The fabricated nanocomposite was emphasized by X-ray diffraction (XRD), Raman spectroscopy and field emission scanning electron microscopy (FESEM). By characterizing the optical and electrochemical properties, graphene doped with silver nanoparticles is eligible for oxidation of N₂N′N″N‴-octakis(4-methoxyphenyl)-9,9′-spirobi[9H-fluorene]2′,7,7′-tetramine (Spiro-OMeTAD), the commonly used hole-transport material (HTM). The results revealed that the Ag@G nanocomposite was successfully synthesized. Furthermore, the efficiency of PSCs as high as 10 percent was achieved when the prepared material was applied as a p-type. This could be attributed to the boosting of the charge carrier transfer between the absorbing layer and the fabricated material. Therefore, the fabricated Ag@G nanocomposite is a promising candidate for a solar cell technology as a p-type dopant.

1. Introduction

Perovskite solar cells (PSCs) are rapidly growing as the most innovative photovoltaic technologies, grabbing attention in the world energy situation and drawing the attention of the scientific community to establish effective and stable perovskite-based devices [1-10]. Methylammonium lead triiodide (CH₃NH₃PbI₃), the most popular perovskite, is featured by high mobility, outstanding absorption coefficient, durability of band gaps, low diffusion length and low cost of material [11-16], making perovskite material potentially promising in the PV field. Two types of architectures have now been adopted for perovskite solar cells. One is a mesostructured solar cell composed of semiconducting metal oxides (TiO₂, ZnO₂, etc.) with a mesoporous (mp) electron transport layer (ETL). The other is a solar cell structured p-i-n or p-n junction planar without the mp-ETL [17]. Graphene and associated two-dimensional components have recently been implemented into the device framework to enhance load injection and/or electrode collection: an increase in power conversion efficiency and long-term stability [18] has been achieved.

Indeed, interfaces between perovskite and transportation layers have lately been shown to have a drastic effect on the recombination of load and material instability processes within the operating machine. Nonetheless, if available charges are easily introduced into the transport layer of the electron from perovskite, degradation of perovskite is delayed and non-radiative recombination is decreased.

In general, the introduction of (Ag@G) into the perovskite solar cell as the HTL finely increase cell conversion efficiency (11 percent) by illustrating the primary function of graphene interface design in perovskite-based devices [19]. Therefore, to finely increase the photovoltaic efficiency of devices, the impact of graphene-modified matrix (Ag@G) on the perovskite solar cell needs to be assessment in more detail.

Herein, we report the facile approach for the fabrication (Ag@G) composite. The performance of the fabricated Ag@G composite in solid-state perovskite solar cells (PSCs) as p-type dopants is reported.

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2. Materials and methods

2.1 Materials

All the chemicals were analytical pure. Graphite powder, NaNO₃, potassium permanganate, H₂O₂, sulphuric acid, HCl, AgNO₃ was obtained from Sigma-Aldrich. All reagents were applied without further purification.

2.2 Materials Fabrication

The literature indicates that methylammonium iodide (MAI) has been synthesized as described in the previous work [20]. Graphene oxide was prepared using modified hummer method in this work. The following procedure was used to prepare Ag with reduced graphene oxide composite (Ag@G). GO dispersion was permitted for 1h to sonicate. Then, under continuous stirring for 1h, a required amount of AgNO₃ solution was slowly added to the GO suspension. The product was stirred for 3 hours; the slurry obtained was transferred to an autoclave of 50 mL Teflon-lined stainless steel and heated for 6 hours to 150°C. The superannuated liquid was discarded after the reaction and the precipitate has been cooled to room temperature washed with water, centrifuged and dried in a 55°C oven and labeled as composite (Ag@G).

2.3 Characterization

With a Renishaw confocal Raman microscope, Raman was obtained using a 514 nm excitation line with a 100X objective lens and 1mW as an incident intensity. PANALYTICAL X-Ray Diffractometer (XRD) with copper Cu Ka radiation (30 mA, 40 kV) to assess and determine the crystalline phases. Field emission scanning electron microscope (JOEL JSM-7500 FA) emphasized the morphology of the prepared materials. PL assessments were carried out in a quasi-back-scattering system, holding the samples in a closed cycle cryostat and increasing the temperature from 10 to 300 K. (J–V) curves, were assessed from a Newport 91160A 300 W Solar Simulator (Class A) in a nitrogen filled glove box using a Keithley 2400 source meter with standard 1 sun AM 1.5 simulated solar irradiation (100 mW cm⁻²).

2.4 Cell fabrication

The glass substrate coated with indium tin oxide (ITO) and exhibit with a sheet resistance of ~ 10 Ω sq-1 was cleaned with soap, sonicated in acetone and ethanol and then dried by nitrogen. To prepare mesoporous TiO₂ dilute Titanium diisopropoxide acetylene aceton (TiAA) with ethanol (for 0.1 M, 1:19 vol/vol, for 0.3 M, 1:6 vol/vol), spin-cast 0.1 M TiAA at 5000 rpm for 30 sec, after that dry on hot plate at 100°C for 5 min, finally Sinter in furnace at 500°C for 30 min. (The temperature is raised gradually.) Dissolve PbI₂(Sigma Aldrich, 99.999 %) and CH₃NH₃I in anhydrous DMF at 45 wt%(molar ratio 1:1), (DMF 1 ml), stir the precursor solution for 30 min spin-cast the precursor solution at 6500 rpm for 4 sec, ramp time is 0.5 sec, then dry and anneal on hot plate at 100°C for 10 min. To prepare hole transport layer suspension solution of (Ag@G) three times and dried well. Finally coat with carbon paste as cathode.

3. Result and Discussion

3.1 X-Ray diffraction investigation

Fig.1 shows the XRD pattern of the synthesized Ag@G. The fabricated Ag@G nanocomposite exhibited four diffraction peaks displayed at 38.1°, 44.42°, 64.5°, 77.5°, which were ascribed to the characteristics metallic silver (111), (200), (220), and (311), crystal planes respectively suggesting the existence of Ag metal in the composite [21].

![XRD patterns (Ag@G) nanocomposite.](image)
3.2 Raman Assessment

The Fig. 2 displays the Raman spectra of \((\text{Ag@G})\) nanocomposite. It is noted that the composite exhibits a G band at \(1587\text{ cm}^{-1}\) and D band at \(1349\text{ cm}^{-1}\), respectively. The intensity disorder ratio is higher after hydrothermal treatment \((\text{ID/IG=0.99})\) which further confirmed the reduction \([22]\). Raman spectra confirmed the formation of crystalline Ag with graphene during hydrothermal treatment.

![Raman spectra of Ag@G nanocomposite](image1.png)

**Fig.2.** Raman spectra of Ag@G nanocomposite

3.3 SEM Investigation

Scanning electron microscope (SEM) investigated the morphology of the synthesized composite. Fig. 3 shows the nanocomposite SEM image. It displays a uniform AgNP decoration on the sheets of graphene. The average particle size is approximately 21 nm.

![SEM images of Ag@G nanocomposite](image2.png)

**Fig.3.** SEM images of Ag@G nanocomposite

3.4 Cell assessment

Fig. 4 displays the current density–voltage curves \((\text{J–V})\) of the hybrid organic solar cells (composed of glass / ITO / TiO2 as an electron transport layer (ETL), \(\text{CH}_3\text{NH}_3\text{PbI}_3\) perovskite as active layers, thin Ag@G film as the HTL and carbon paste cathode as normal 1 sun AM 1.5 simulated solar irradiation. The cell shows significant efficiency with \(\text{VOC} = 0.99 \text{ V}, \text{J SC} = 16.1 \text{ mAcm}^{-2}\), and \(\text{FF} = 0.71\), equivalent to a PCE of \(11.3\%\) under standard 1 sun AM 1.5 simulated solar irradiation. Table 1 summarizes the parameters of photovoltaic devices obtained at 100 mW \(\text{cm}^{-2}\) under AM 1.5 G solar illumination. As shown from the information, to obtain a high-performance machine \([23, 24]\), the existence of an effective hole conductor is critical.

3.5 Photoluminescence measurement

Photoluminescence (PL) is one of the significant optical properties in the study of photovoltaic products, providing several parts of data including bandgap, chemical purity, and separation of charges \([25]\). Furthermore, measurements of PL quenching are a quick and easy way to explore separation of charges. If perovskite is in the vicinity with an electron acceptor (n-type quencher) or hole acceptor (p-type quencher), electron or hole separation charges will reduce the PL intensity compared to the isolated state. The degree and effectiveness of load separation can be evaluated from the change in PL intensity.

Figure 5 demonstrates the shift in PL intensity in the lack and presence of Ag@G as p-type quenchers for the \(\text{CH}_3\text{NH}_3\text{PbI}_3\) perovskites. There is a substantial reduction in PL intensity when both perovskite materials come into contact with Ag@G accepting hole. Load separation occurs well in the existence of inorganic hole conductors such as Ag@G, as demonstrated by important PL quenching shown in Figure 5. PL quenching investigations are thus a helpful instrument for studying load segregation and obtaining data on interfacial contacts. Load separation occurs well in the presence of inorganic hole conductors such as Ag@G, as demonstrated by important PL quenching shown in Figure 5. PL quenching investigations are thus a helpful instrument for studying load segregation and obtaining data on interfacial contacts.

4. Conclusions

In summary, as a hole conductor for the perovskite solar cell, we have successfully developed (Ag@G) and a champion 30 efficiency of up to 11.3 percent has been shown. The under laid layer (Ag@G) can effectively remove the hole from the perovskite, promote the creation of homogeneous great environments and enhance surface performance.
Fig. 4. Current–voltage characteristics of PSCs containing HTLs based on Ag@G.

Table 1. Photovoltaic characteristics of perovskite solar cells with various hole conductors

| Hole conductor layers | Voc a (V) | Jsc a (mA/cm²) | FF a | PCE a (%) |
|-----------------------|----------|----------------|------|-----------|
| PEDOT:PSS             | 0.93     | 15.09          | 0.66 | 9.26      |
| GO (0.5)              | 0.99     | 15.02          | 0.67 | 9.96      |
| GO (0.25)             | 0.99     | 15.59          | 0.72 | 11.11     |
| Ag@G                  | 0.99     | 16.1           | 0.71 | 11.3      |

*aAll the parameters of photovoltaics are the average of six devices.

Fig. 5. PL quenching behaviors for: (a) CH₃NH₃PbI₃/Ag@G system
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