Enhanced Photoelectrochemical Performance in Reduced Graphene Oxide/$BiFeO_3$ Heterostructures

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- Current $BiFeO_3$(BFO)-based ferroelectric could be used as visible-light-driven photoelectrodes for oxygen production; however, its photoelectrochemical performance is inferior, and its fabrication process is expensive.

- In comparison to current BFO-based ferroelectric, newly developed reduced graphene oxide (RGO)/BFO composite film exhibits a 600% improvement of the short-circuit photocurrent density and threefold enhancement of incident photon-to-current efficiency; it also outperforms the noble-metal/BFO cells under the same reaction conditions. The optimized RGO/BFO composite film is also cheap to produce, so it could be used as a potential material for ferroelectric photoelectrodes.

Introduction

- How to convert light energy into chemical and electrical energies triggered intensive research. The efficiency of photoeletrochemical(PEC) cells are limited by the PEC performance of semiconductor photoelectrodes. Recent goal is to fabricate narrow-bandgap ferroelectrics for the photoelectrodes of PEC cells.

- There are a few advantages: switchable photovoltaic outputs, above-bandgap photovoltage, and above Shockley-Queisser-limit efficiency.

- However, the microscopic mechanism of the ferroelectric photovoltaic effect has not been clarified yet; some deficiencies(oxygen vacancies) and their effects remain enigmatic.

- There are two advantages in Multiferroic BiFeO3 (BFO): robust room-temperature ferroelectricity and a band gap within the visible light range.

- BFO will show different physical and chemical properties when in different crystal structures, resulting in different PEC performances. Joint effort has been paid to find a microscopic structure that best optimizes the PEC performance.

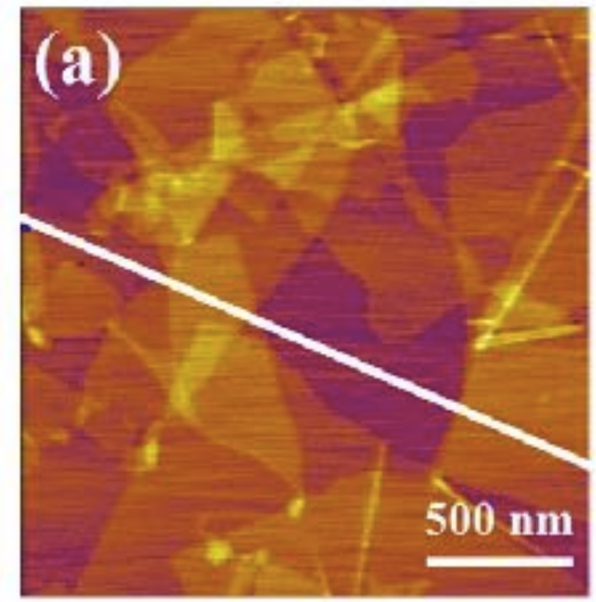
- It has been demonstrated that **by decorating the BFO surface with appropriate amount of Ag nanoparticles, the maximum short-circuit photocurrent density could be doubled**. It has also been proposed, by research into the crystal structure and physical and chemical properties, that **RGO(as an intermediate state) offers an opportunity to fabricate composite photoelectrodes**.

- According to these studies and analysis, composite films are produced for photoelectrodes; the mutual impact of RGO and BFO are systematically analyzed.

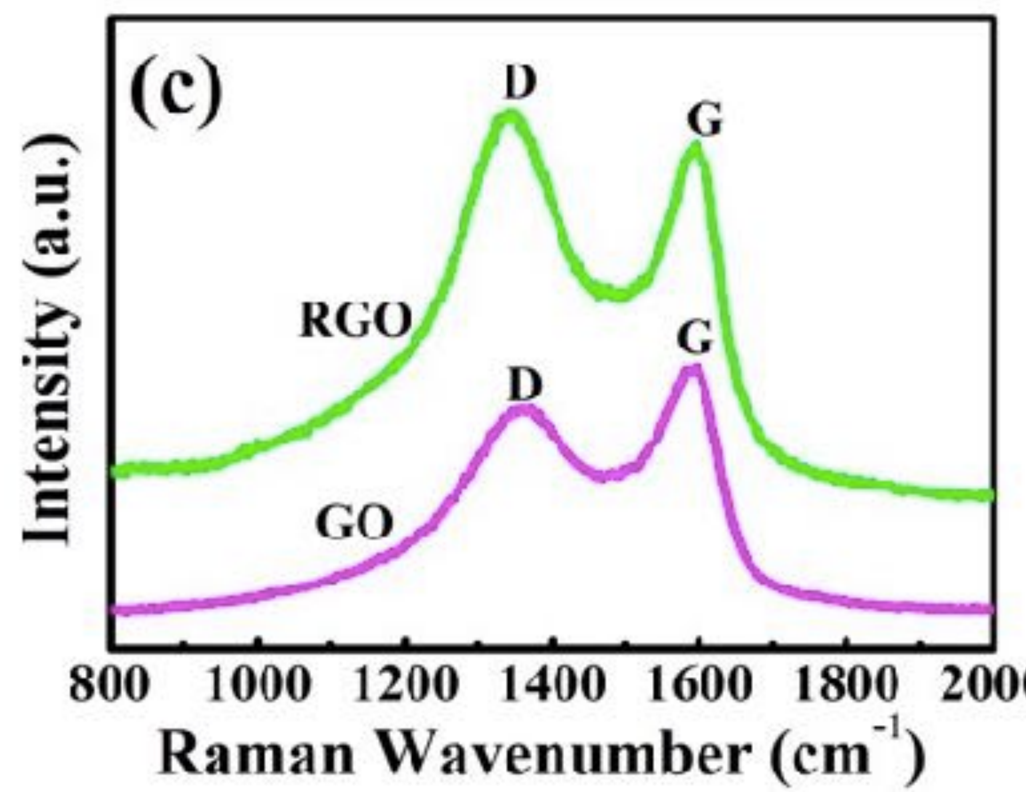
- Subsequently, a mechanism for PEC reaction in the RGO/BFO system has been proposed, opening up a brand new pathway for further study in improving the PEC effect of ferroelectric films.

Results and Discussion

- The morphologies and the thicknesses of the RGO nanosheets are measured by atomic force microscopy (AFM).



- The Raman spectra of RGO is later compared with that of GO; it is revealed that the D/G intensity ratio of RGO is higher than that of GO because of the restoration of sp^2-hybridized carbon during the reduction reaction.



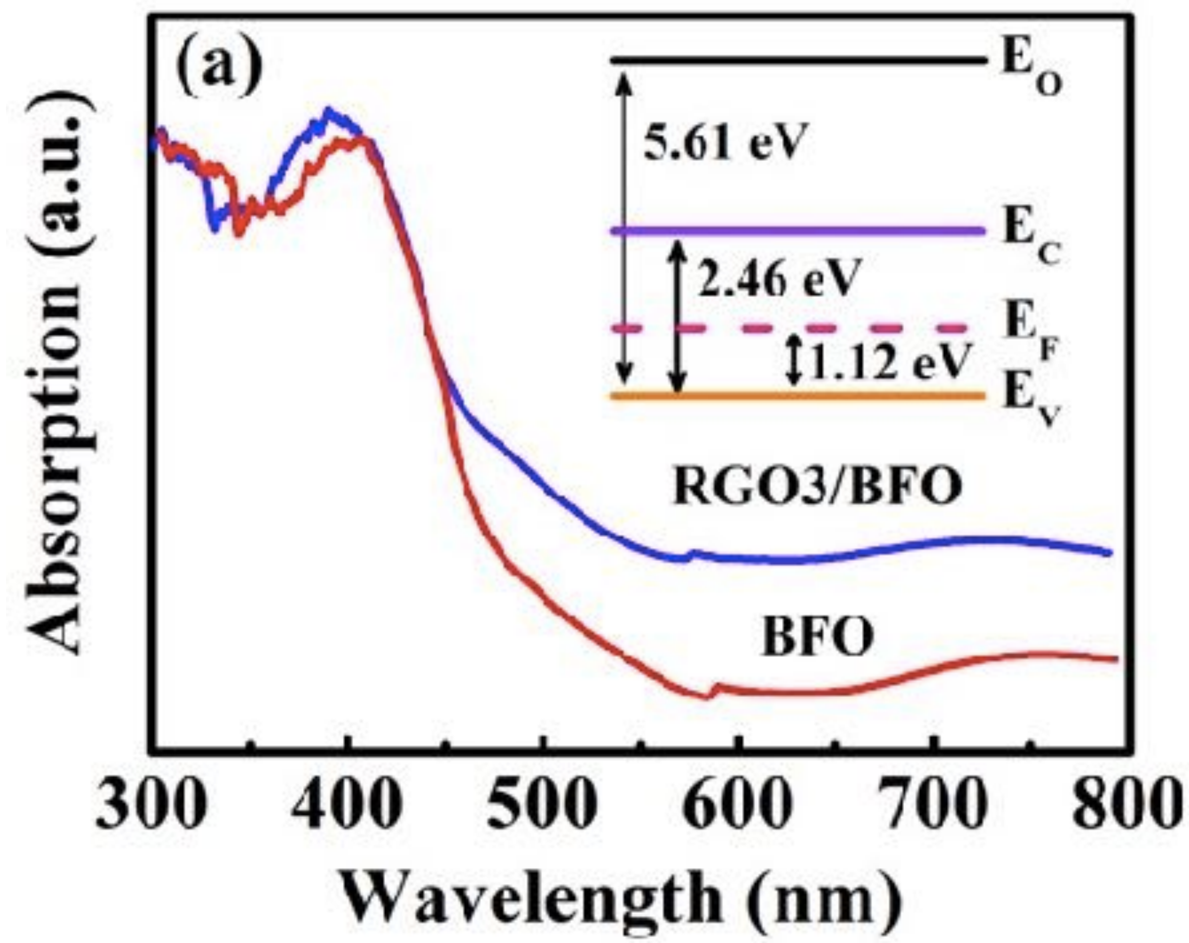
- The crystal structures of the BFO thin film before and after RGO decoration were measured by X-ray diffraction (XRD).

- The microscopic ferroelectric properties of the BFO film is verified by piezoresponse force microscopy (PFM). Later, Raman spectroscopy is used to confirm the existence of RGO.

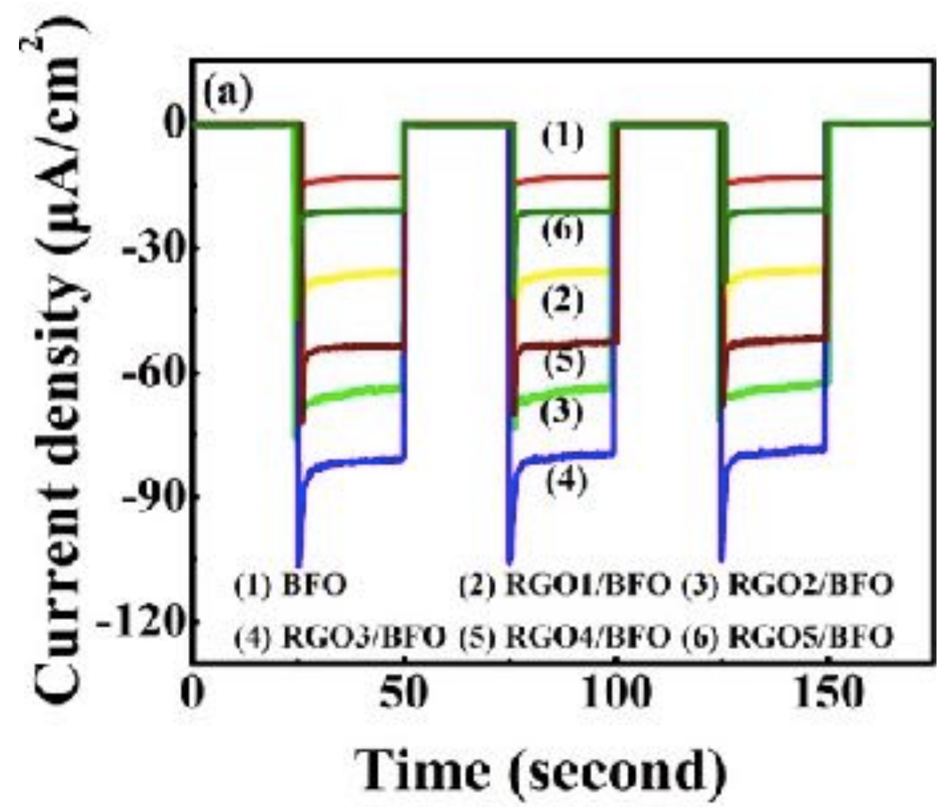
- The results observed match the ideas before perfectly. Desired RGO/BFO composite films have been achieved.

- The absorption spectra of the BFO before and after decorated with the RGO nanosheets is measured: the RGO3/BFO sample shows better light absorption capability in the whole visible-light range because of the existence of RGO.

- It is also demonstrated that the BFO film in this study could be considered as a P-type conductor by calculating the work function and the energy level of E_F–E_V.



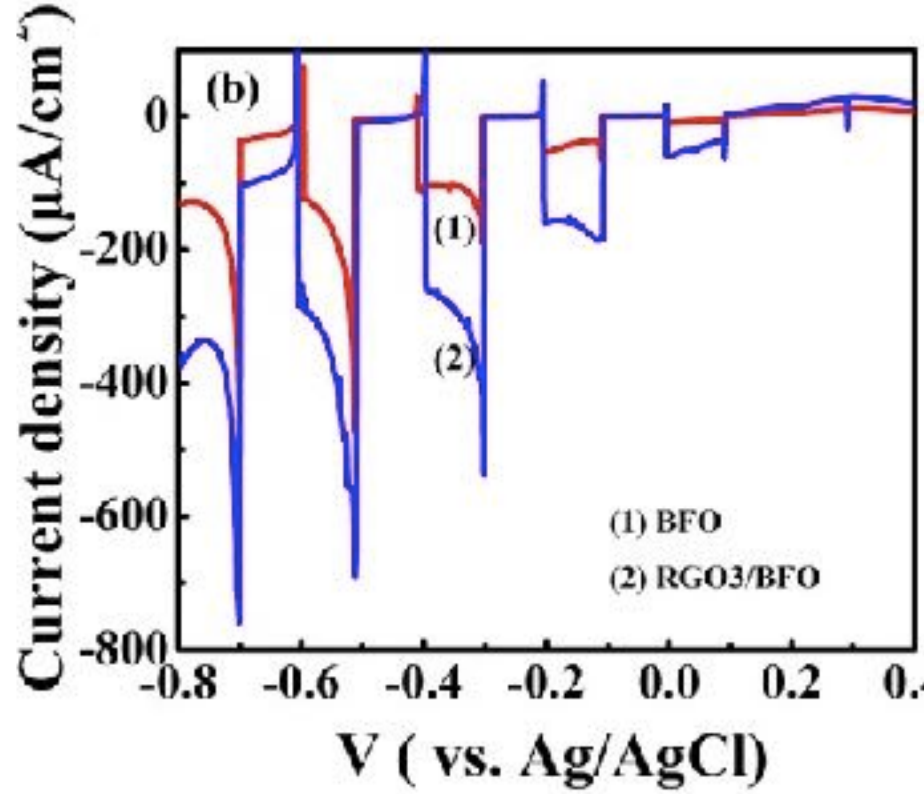
- The photocurrent density of the composite film when decorated with different quantities of RGO nanosheets is analyzed: the initial increase of photocurrent density can be ascribed to the increased content of RGO nanosheets, which enhances the separation of photogenerated carriers.
- However, the higher coverage of RGO nanosheets reduces the surface area of BFO in direct contact with the electrolyte, and decreases the intensity of light absorbed by the BFO film.



- The figure shows that there is a steady increase in photocurrent density with increasing applied potential, and that BFO and RGO3/BFO have a fast photocurrent response during every switch on and switch off event.

- It is also proved that the RGO3/BFO sample outperforms BFO in photoenergy conversion.

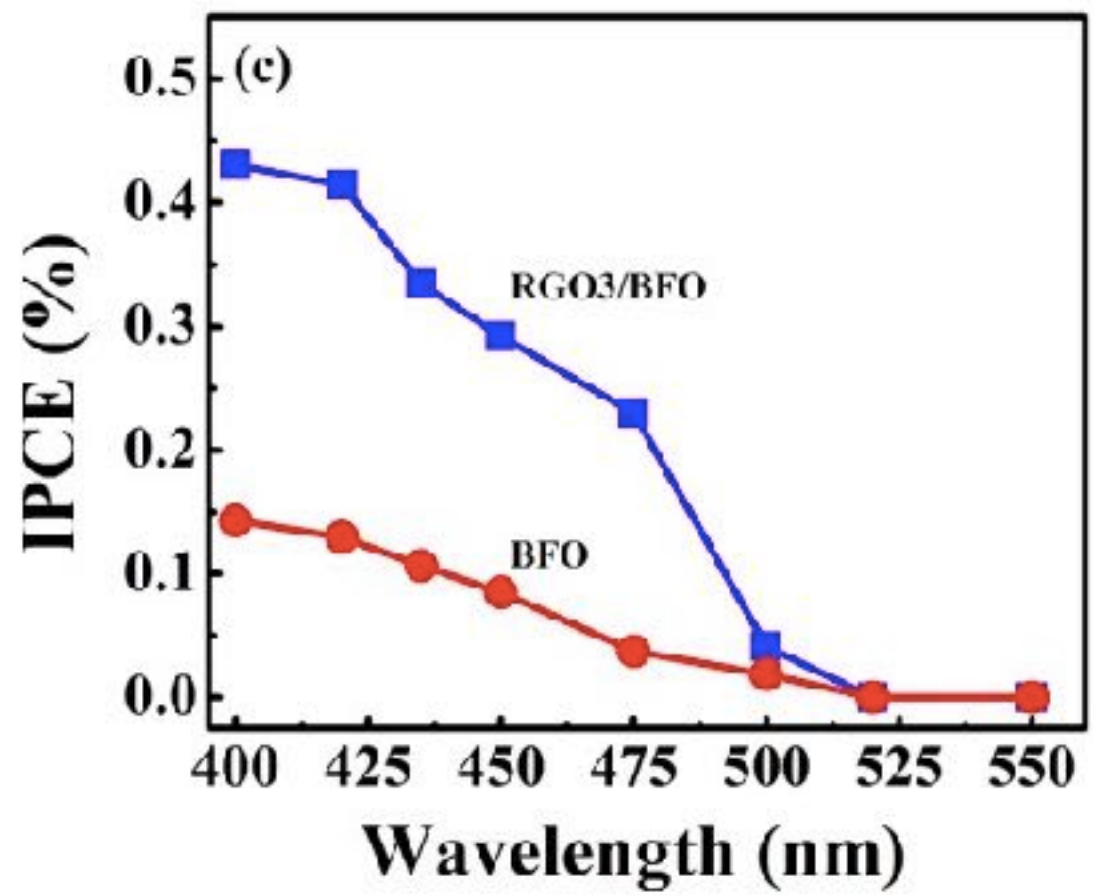
- In conclusion, RGO/BFO composite photoelectrodes not only show superior PEC performance, but also exhibit the advantage of the low-cost and simple fabrication process.



- The incident photo-to-current conversion efficiency (IPCE) is measured to verify the advantage of adding RGO nanosheets.

- The IPCE value of the pure BFO lm is 0.15% (at 400 nm), whereas the IPCE response shows a remarkable enhancement to 0.43% when RGO is incorporated.

- The relationship between the PEC performance and the ferroelectric polarization is also investigated; experimental date is analyzed and explanations are made.



- The electrochemical impedance spectroscopy(EIS) is used to study the charge-transfer process of the PEC cell: surface charge-transfer process dominates the PEC reaction.

- Because the arc radius of the RGO3/BFO sample is smaller than that of pure BFO sample, the interfacial charge transfer between RGO3/BFO photoelectrodes is faster; therefore the separation of photogenerated carries is more efficient.

- It could be concluded that **the photocarrier separation and the charge-transfer process play a more important role compared to the light absorption** in this system.

- A mechanism is proposed on the basis of these physical and electrochemical characterizations to explain RGO/BFO-enhanced photoelectrochemical properties.

- Besides **the light absorption, the charge transportation and separation** were also considered to be key factors on improving the photoelectronchemical activity. These factors are all derived from **the unique delocalized conjugated structure and superior electrical conductivity**.

- In conclusion, higher photocurrent density results from **the combination of photoactive ferroelectrics and electrically benign 2D materials**, which will become the new focus in PEC field.

Conclusion

- The RGO/BFO composite material greatly enhances the photocurrent density and IPCE in the hybrid PEC cells due to its **unique microscopic structure and superior electrical conductivity**.

- A simple and efficient method is found to improve the PEC performance of ferroelectric photoelectrodes: **add 2D materials**.

Experimental Section

- The fabrication process of the RGO/BFO composite material and its characteristics are introduced.

Thanks!