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Undamaged depositing large-area ZnO quantum dots/RGO films on photoelectrodes for the construction of pure Z-scheme

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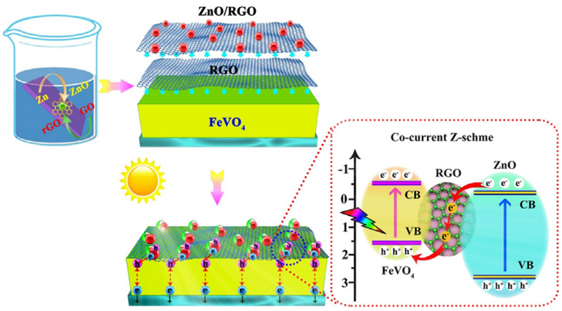
HIGHLIGHTS

- A facile deposition method of large-area RGO and ZnO QDs/RGO films have been proposed.
- Different from the traditional method, the direct self-assembly of RGO has been achieved.
- A pure Z-scheme is constructed, in which semiconductors are totally separated by RGO film.
- It is found only co-current Z-scheme is favorable for improving the PEC performances.

GRAPHIC ABSTRACT

A facile method to deposit large-area RGO and ZnO QDs/RGO films with tunable layers on diverse substrates has been firstly proposed through a self-assembly method. Consequently, a co-current Z-scheme system could be constructed by depositing RGO and ZnO QDs/RGO films on $FeVO_4$ photoelectrodes and the photocurrent density could be significantly enhanced due to the improved charge separation efficiency.



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ABSTRACT

In this work, we have firstly proposed a mild and facile method to deposit large-area RGO and ZnO QDs/RGO films on diverse substrates through a self-assembly strategy. RGO powders would aggregate to agglomerate in aqueous solution due to its hydrophobicity. Interestingly, it is found that RGO sheets would assemble to film when RGO ethanol solution is dropped into water, and the film layers could be rationally tuned by repeating the deposition procedure. Based on the convenient fabrication method, a co-current Z-scheme system could be constructed by subsequently depositing RGO and ZnO QDs/RGO films on $FeVO_4$ photoelectrodes, in which RGO serves as an electron mediator. Different from the traditional disordered Z-scheme system, the photo-excited electrons in co-current Z-scheme would move toward the same direction due to the absolute separation between $FeVO_4$ and ZnO. As a result, the PEC performances of $FeVO_4$ could be significantly enhanced because the running direction of photo-excited electrons in co-current Z-scheme is consistent with that in external circuit. For comparison, a counter-current Z-scheme has also been built up by replacing $FeVO_4$ with WO_3, in which the ruing direction of photo-generated electrons is opposite to the external circuit, and the photo conversion efficiency decreased consequently. Therefore, it can be concluded that the design of pure Z-scheme is not only beneficial

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for improving the charge separation efficiency and retaining their redox capability, but also favorable for uncovering the charge transfer mechanism.

1. Introduction

Photoelectrochemical (PEC) hydrogen evolution from water splitting over semiconductor photocatalysts has attracted increasing attention because of their great potential in alleviating current energy and environmental crisis [1,2]. It has been estimated that one percent of the earth's desert area (nearly 250 000 km^2) with a solar-to-hydrogen (STH) conversion efficiency of 10%, which could approximately generate 570 tons H_2 per day, would satisfy one third of the energy consumption of human beings in 2050 [3]. The powdered-type photocatalytic decomposition of water offers a promising route to produce hydrogen owing to its simplicity and low cost, however, the STH conversion efficiency (typically around 1%) is an order of magnitude lower than that of PEC-based water splitting systems [4]. Since the first demonstration of PEC water splitting on a TiO_2 photoelectrode [5], numerous strategies have been adopted to suppress the recombination of photo-generated electron-hole pairs [6–8] and many derivative functions based on photo(electro)catalysts have also been developed, such as or carbon dioxide and nitrogen reduction [9,10]. In comparison with single-phase photocatalyst, the construction of heterojunction system (usually type II heterostructures) is considered as an effective method to improve the separation of photo-induced charge carriers [11,12]. Nevertheless, the redox ability of photo-excited electrons and holes would be weakened by the fact that they would transfer into the conduction band (CB) and the valence band (VB) of opposite semiconductor, respectively [13,14]. By contrast, the artificial Z-scheme photocatalytic system, which mimic the natural photosynthesis of green plants, is preferable because it can not only facilitate the separation of photo-excited charge carriers, but also preserve their strong redox capability by quenching the electrons/holes with weaker reduction/oxidation potentials through electron mediators [15–17]. Recent progress has suggested that the electron transfer in mediators may play a rate-determining role in Z-scheme photocatalytic reactions [18].

Reversible redox couples, such as Fe^{3+}/Fe^{2+}, IO^{3-}/I^- and NO_3^-/NO_2^-, are often employed as electron mediators for shuttling electrons between the two semiconductors in Z-scheme system [19–21]. Despite being active in relaying electrons, these redox mediators have inescapable drawbacks including backward reactions, light shielding and low stability, which may severely suppress the STH conversion efficiency [14,18,22]. Hence, the all-solid-state Z-scheme system has been proposed in 2006 [23] and greatly developed in the past decade, in which noble metal particles (such as Au, Ag or Pt) [24–26] or non-metal materials (graphene oxide (GO) or reduced graphene oxide (RGO)) [27,28] are usually used as solid-state electron mediators between two semiconductors. However, up to now nearly all of the particulate Z-scheme PEC systems are disordered and the inevitable aggregation of nanoparticles would not only lead to the adverse non-Z-scheme transfer of electrons due to the direct contact of semiconductors, but also result in the difficulties in uncovering the charge transfer mechanism owing to the compresence of Z-scheme and non-Z-scheme types [29]. Moreover, it is believed that the challenge in developing all-solid-state Z-scheme lies in achieving a dynamic equilibrium of charge carriers between the two semiconductors because it is unreasonable to simply adjust the semiconductor ratios if they could not be separated totally by the electron mediators [17]. To avoid the undesirable back-reaction, a spatially separated Z-scheme PEC cell with a tandem configuration has recently been constructed for the unassisted solar water splitting [30–32]. Although being effective in facilitating the charge separation and remaining the redox potential of photo-excited electrons and holes, the two delicately separated photoelectrodes, which both needs light sources and co-catalysts, would definitely complicate the fabrication process and the PEC devices. Therefore, it is highly desired to construct a well-designed Z-scheme system, in which the two semiconductors are partitioned thoroughly by the electron mediator for the pure Z-scheme system and the dynamic electrons equilibrium could be facilely satisfied by varying the semiconductor ratios.

Among these solid electron mediators, graphene, which is firstly discovered by mechanical exfoliation in 2004 [33], is relatively cost-effective compared with precious metals. More importantly, as an emerging two-dimensional material with unique sp^2-bonded carbon atoms, graphene has stimulated wide interests due to its large specific surface area, excellent charge mobility, strong mechanical strength and superior flexibility [34,35]. Thus, graphene might be the most promising candidate for the construction of pure Z-scheme PEC system, in which the large-area graphene film is sandwiched between two semiconductors. The major challenge, however, is the nondestructive growth of large-area graphene film on different photoelectrodes, which may possess irregular and rough surfaces. The intrinsic insolubility and aggregation properties of graphene entail the utilization of either RGO or chemical vapor deposition (CVD) sources for large-area film [36]. Although the recent progress of CVD is capable of producing high-quality grapheme film, the use of high temperature and the subsequent transfer procedure complicates the integration of graphene into practical devices [37,38], involving photoelectrodes. An alternative fabrication strategy for large-area grapheme film is the reduction of exfoliated GO, in which the GO film is firstly obtained using water-soluble GO dispersions and then reduced to RGO film by thermal annealing or chemical reduction [39,40]. The GO-based chemical approach is appealing because it offers an opportunity to produce graphene film in bulk quantity and low cost [38]. Nevertheless, this method is not universal for the fabrication of pure Z-scheme photoelectrodes with sandwich structure since the bottom semiconductor under GO film might also be reduced or polluted during the deoxygenating process. Additionally, the as-prepared GO films might be stiffened and disintegrated by reductants in the reduction treatment [41], which is unfavorable for the electrons transport. Thereby, it is urgent to develop a mild and convenient method to uniformly deposit large-area graphene film on the bottom semiconductor for the construction of pure Z-scheme system.

In this work, we have firstly proposed a facile and reproducible method to deposit large-area RGO or ZnO quantum dots (QDs) decorated RGO films with tunable layers on diverse substrates through a self-assembly strategy. Different from traditional procedures, which usually obtain the GO film first and then carry out the reduction treatment, we initially reduced GO aqueous solution to RGO suspensions with Zn foil and then performed the self-assembly of RGO on the surface of water. Although RGO powders would aggregate in water due to its hydrophobicity, it is interesting that the RGO sheets would assemble on the surface of water to ultrathin large-area film when RGO ethanol solution was dropped into water. More importantly, the film layers could be rationally tuned by repeating the deposition operation and no post-treatment is required. Based on the simple preparation method of RGO films, a pure Z-scheme system has been constructed through depositing RGO and ZnO QDs/RGO films on nanoporous $FeVO_4$ photoelectrodes, in which RGO served as an electron mediator. All the photo-excited electrons in this system would transport toward the same direction due to the complete separation between $FeVO_4$ and ZnO, which is in accordance with the running direction of electrons in the external circuit. As a result, the photocurrent density of $FeVO_4$ could be significantly enhanced due to the efficient charge separation,