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Graphene quantum dots mediated charge transfer of CdSe nanocrystals for enhancing photoelectrochemical hydrogen production

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ABSTRACT

We demonstrated the use of CdSe/graphene quantum dot (QD) nanoheterostructures as the photoanode for remarkable photoelectrochemical hydrogen production. By employing a delicate hydrothermal cutting approach, reduced graphene oxide (RGO) sheets with the lateral size in a desirable range can be obtained, from micrometer size (micro-RGO), to 30–100 nm (nano-RGO), and to 2–4 nm (QD-RGO). Because of the significant zigzag edge effect, nano-RGO and QD-RGO possessed well-defined band structure which enabled efficient light absorption and distinctive photoluminescence emission. Time-resolved photoluminescence spectra showed that nano-RGO and QD-RGO surpassed micro-RGO in enhancing the charge separation efficiency of CdSe. According to the cyclic voltammetry data, a type-II vectorial charge transfer model was considered for CdSe/nano-RGO and CdSe/QD-RGO nanoheterostructures, fundamentally different from the unidirectional electron transfer mechanism of CdSe/micro-RGO. Among the three CdSe/RGO samples tested, CdSe/QD-RGO achieved the highest photocurrent generation in the photoelectrochemical cell, which exceeded 5 times the value of CdSe. The incident photon-to-electron conversion efficiency (IPCE) spectra suggested that the significantly enhanced photoactivity of CdSe/QD-RGO originated from the type-II vectorial charge transfer feature, which not only promoted charge carrier separation but also improved the overall light harvesting. Furthermore, no appreciable decay of photocurrent was found for CdSe/QD-RGO after continuously used in the photoelectrochemical cell for over 2 h, revealing its substantially high stability during the water reduction process. The demonstrations from this work may facilitate the use of graphene QDs in semiconductor-based photocatalysis, in which the efficient light harvesting and high chemical inertness of graphene QDs can be well employed.

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1. Introduction

Graphene, a two-dimensional (2D) single sheet of sp^2-bonded carbon atoms, has spurred immense scientific interest since it became experimentally accessible in 2004 [1–3]. Because of the 2D atomic layer feature and unique electronic band structure, graphene exhibits many intriguing properties that make it a good candidate for potential applications in a wide array of fields, which include electronics, photonics, mechanics and materials chemistry [4–8]. Of particular importance is the use of graphene sheets in semiconductor-based photocatalytic applications. Recent developments have demonstrated the remarkable photocatalytic properties for semiconductor/graphene nanoheterostructures [9,10]. Due to the high electrical conductivity, graphene sheets may serve as an effective electron acceptor for semiconductor nanostructures, which promotes charge carrier separation to enhance the photocatalytic efficiency. Besides, the high surface area of graphene sheets can increase the contact between the photocatalyst and reaction species, which is also conducive to improving the overall photocatalytic performance. Until now, various types of semiconductor/graphene nanoheterostructures have been proposed and investigated to facilitate further research and advancement [11–15]. In addition to photocatalysis, nanoheterostructures comprising graphene also find potential use for efficient energy conversion and storage, such as electrochemical cells, supercapacitors, photovoltaics and light emitting diodes [16].

Pristine graphene is a zero-gap material which behaves as a semi-metal with the massless Dirac fermions [17,18]. To diversify the electronic and optical applications, considerable efforts

to open up the bandgap of graphene are being pursued. Chemical modifications such as covalent functionalization and molecular doping have proven effective in modifying the electronic properties of graphene from near metallic to semiconducting [19–21]. For example, n-type electronic doping for graphene can be achieved via an appropriate covalent functionalization with nitrogen species [20]. This achievement affords the successful fabrication of n-type graphene field-effect transistors that can operate at room temperature. On the other hand, structural engineering that leads to quantum confinement, lattice perturbations, or edge effects also endows graphene with an energy gap [22–25]. In this regard, graphene structures with the lateral dimensions down to a few nanometers are particularly appealing because bandgap tailoring is made possible by controlling the characteristic size of the ultra-small graphene. As a representative example, graphene quantum dots (QDs) with a typical lateral size of 3–20 nm have emerged as a promising modified version of graphene. They possess many favorable attributes, such as tunable bandgap, large optical absorptivity, high photostability, good biocompatibility and fine dispersity in common solvents, which may push forward their practical applications in technologically important fields [26–33]. Especially, the calculated energy levels of graphene QDs suggest the capability of efficient light harvesting as well as the possibility of electron injection from graphene QDs to semiconductor [32,34], which shall stimulate further interest to combine graphene QDs and semiconductor nanostructures for photocatalysis applications, although it has not been well addressed thus far [35,36].

In this work, we investigated the photocatalytic properties of semiconductor/graphene QD nanoheterostructures for photoelectrochemical hydrogen production. The heterostructure samples were prepared by linking CdSe nanocrystals to graphene QDs using chitosan as the linker molecule [37]. Here, graphene QDs were obtained with the hydrothermal cutting approach [38], which involved the breaking of micrometer-sized reduced graphene oxide (RGO) sheets into nanometer-sized RGO pieces in the hydrothermal process. By suitably modulating the experimental condition, the lateral size of the resultant nanometer-sized RGO can be controlled in a desirable range, from 30–100 nm (sample was denoted as nano-RGO) to 2–4 nm (denoted as QD-RGO). For comparison purpose, micrometer-sized RGO sheets (denoted as micro-RGO) were also coupled with CdSe nanocrystals for photoelectrochemical tests. Due to the significant zigzag edge effect, nano-RGO and QD-RGO possessed well-defined band structure that enabled efficient light absorption and distinctive photoluminescence emission. For nano-RGO and QD-RGO, they can act as an effective hole acceptor for CdSe due to their higher highest occupied molecular orbital (HOMO) level (+1.15 V vs. NHE) than the valence band level of CdSe (+1.70 V vs. NHE). With the staggered band alignment, CdSe/nano-RGO and CdSe/QD-RGO nanoheterostructures exhibited remarkably enhanced charge separation for increasing the performance in photoelectrochemical hydrogen production. As to the micro-RGO, the metallic conductive nature made it susceptible to accepting photoexcited electrons from CdSe, which also caused effective charge separation to benefit the photoelectrochemical performance. Among the three CdSe/RGO samples tested, CdSe/QD-RGO achieved the highest photocurrent generation in the photoelectrochemical cell, exceeding 5 times the value of pure CdSe. The incident photon-to-electron conversion efficiency (IPCE) spectra suggested that the significantly enhanced photoactivity of CdSe/QD-RGO was due to the pronounced charge separation as well as the improved light harvesting, as a result of the type-II vectorial charge transfer scenario. Furthermore, no appreciable decay of photocurrent was found for CdSe/QD-RGO after continuously used in the photoelectrochemical cell for over 2 h, revealing its substantially high stability during the water reduction process.

2. Experimental

2.1. Chemicals

All chemicals were analytical grade and used without further purification. Special attention should be paid when dealing with the hazardous Cd source.

2.2. Synthesis of CdSe nanocrystals

CdSe nanocrystals were synthesized with a cysteine-assisted aqueous synthetic method [39]. In the typical procedure, an aqueous solution containing $CdSO_4$ (2.0 mL, 0.15 M) and L-cysteine (2.6 mL, 1.0 M) was first prepared in a vial, and the pH was adjusted to 10.0 using 1.0 M NaOH. The mixed solution was then diluted to 200 mL with deionized water, followed by the dropwise addition of Na_2SeSO_3 solution (0.75 mL, 0.1 M). The reaction solution was stirred at room temperature for 1 h, producing a stable, yellow dispersion of CdSe nanocrystals. These cysteine-capped CdSe colloids were then allowed to stand for later use.

2.3. Synthesis of micrometer-sized RGO

In this work, GO sheets were hydrothermally treated to produce RGO, an ideal substitute for graphene. GO sheets were obtained from graphite powder by using the Hummers' method [40]. A desirable amount of GO (25 mg) was then dispersed in deionized water (50 mL), and the pH was adjusted to 7.0 using 0.1 M NaOH. Afterwards, the GO suspension was transferred to a Teflon-lined autoclave (100 mL in capacity) and heated at 200 °C for 24 h. After cooling to room temperature, the resultant black precipitate (micrometer-sized RGO, denoted as micro-RGO) was collected by suction filtration and dried in vacuum for later use.

2.4. Synthesis of nanometer-sized RGO

Hydrothermal cutting approach was employed to break the micro-RGO sheets into nanometer-sized RGO pieces [38]. The approach involved the acid oxidation treatment and the hydrothermal deoxidation process. By adjusting the acid treatment time, the lateral size of the resultant ultra-small RGO can be controlled in two different ranges, 30–100 nm and 2–4 nm; the sample was respectively denoted as nano-RGO and QD-RGO. In the typical procedure, GO sheets from Hummers' method (50 mg) were sonicated in a mixed solution of concentrated H_2SO_4 (75 mL) and HNO_3 (25 mL). After refluxed at 100 °C for 8 h, the mixed solution was filtered through a 0.22-μm microporous membrane to remove the acids. The brown filtrate was then transferred to a Teflon-lined autoclave (100 mL in capacity) and heated at 200 °C for 24 h. After cooling to room temperature, the resultant brown suspension (nano-RGO) was collected by centrifugation and re-dispersed in deionized water for later use. To obtain QD-RGO, the same procedure mentioned above was used except that the refluxing time during acid treatment was prolonged to 24 h. The resultant hydrothermally treated brown suspension was further purified in a dialysis bag for 3 days, producing highly stable QD-RGO suspension.

2.5. Preparation of CdSe/RGO nanoheterostructures

The coupling of RGO with CdSe nanocrystals was achieved by using chitosan as the linker molecule [37]. First, RGO (micro-RGO, nano-RGO or QD-RGO, 2.0 mg) was dispersed in the chitosan solution (0.50 wt%, 4.0 mL) and the pH was adjusted to 4.5 using 0.1 M HCl. This process would result in the formation of RGO–chitosan composite. Subsequently, a given concentration of CdSe nanocrystal suspension (9.0 mmol, 8.0 mL) was added to the RGO–chitosan