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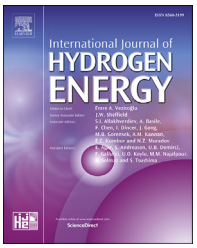

Two dimensional N-doped ZnO-graphitic carbon nitride nanosheets heterojunctions with enhanced photocatalytic hydrogen evolution

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ABSTRACT

The effective separation of photogenerated charge carriers, their transport and interfacial contact is of great significance for excellent performance of semiconductor based photocatalysts. Herein, we report the fabrication of two dimensional (2D) nanosheets heterojunction comprising of N-doped ZnO nanosheets loaded over graphitic carbon nitride (g-C_3N_4) nanosheets for enhanced photocatalytic hydrogen evolution. The prepared 2D-2D heterojunctions with varying amount of g-C_3N_4 nanosheets have been characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) techniques. The optimized heterojunction photocatalyst with 30 wt% of g-C_3N_4 nanosheets (NZCN30) exhibit hydrogen evolution rate of 18836 μmol h^{-1} g_{cat}^{-1} in presence of Na_2S and Na_2SO_3 as sacrificial agents under simulated solar light irradiation. The enhanced photocatalytic performance of NZCN30 heterojunction has been supported well by photoluminescence and photoelectrochemical investigations, which shows the minimum recombination rate and high photoinduced current density, respectively. In addition, the existence of 2D-2D interfacial contact plays a major role in enhanced H_2 evolution by high face-to-face contact surface area for separation of photogenerated charge carriers in space which facilitate their transfer for H_2 generation. This work paves way for the development of 2D-2D heterojunctions for diverse applications.

Introduction

The demand for clean, affordable, reliable and environmentally benign energy supply has increased nowadays due to the continuous depletion of fossil fuels [1,2]. This growing concern about energy and environmental issues have stimulated extensive research on semiconductor based heterogeneous catalytic materials to generate clean and renewable energy

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[3,4]. In this regard, hydrogen (H_2) has been accepted as an ideal future energy carrier to reduce dependence on non-renewable energy sources and ultimately cut-down the harmful emissions into environment [5,6]. In its pure diatomic form, H_2 can be used in the fuel cells and hydrogen combustion engines to release stored energy cleanly. Moreover, hydrogen is one of the abundant element present in water and most of organic compounds [7]. Since, water contains only H_2 and O_2, so extra by-products are not released in its decomposition, which makes entire process cyclic, eco-friendly and advantageous over other processes such as steam methane reforming, partial oxidation of methane and coal gasification for H_2 generation [8]. Recently, many research groups have reported their studies on semiconductors based photocatalysts for hydrogen evolution reactions [9–11], pollutants removal [12–14] and conversion of CO_2 into useful organic/inorganic compounds, such as CH_4, CH_3OH, CO, etc [15,16]. Hence semiconductors based photocatalysis has emerged as one of the most promising technologies to generate clean and renewable energy in the form of H_2 [17]. Among various semiconductors, ZnO is a versatile and technologically important material to explore for photocatalytic applications [18]. Its wide, direct band gap (3.37 eV), large exciton binding energy (60 meV), non-toxic nature and abundance makes it a perfect photocatalytic material. Although TiO_2 is widely explored material for photocatalytic H_2 evolution [19–21], but there are reports, which proves high charge carrier mobility and retarded electron-hole recombination in ZnO [22]. The ZnO can absorb only the UV region (4%) of solar spectrum because of wide band gap energy and has no characteristic absorption in the visible region, which constitutes about 43% of solar spectrum [18]. Hence the development of visible light active ZnO based photocatalysts for H_2 evolution is highly anticipated.

In recent years, metal free, polymeric graphitic carbon nitride (g-C_3N_4) has attracted attention towards visible light driven photocatalytic and photoelectrocatalytic H_2 generation [23,24]. g-C_3N_4 absorbs visible light due to its band gap energy (~2.7 eV), and its suitable conduction band (CB), valence band (VB) positions shows promising H_2 and O_2 evolution in water splitting reactions [25]. In addition to this, g-C_3N_4 possess excellent chemical and thermal stability, unique surface properties with unsaturated N-atoms for anchoring active sites [26]. But pure g-C_3N_4 suffers from poor light absorption and fast recombination of photogenerated charge carriers, which leads to low photocatalytic efficiency and limits its applications [26]. To overcome these shortcomings, various strategies have been adopted such as metal doping [27], non-metal doping [28], coupling with other carbon based materials [29] and coupling with other semiconductors [30–32]. In addition, Sun et al. [33] have demonstrated that, exfoliation of g-C_3N_4 in isopropanol (IPA) has been found to increase its aspect ratio, specific surface area and enhanced absorption in visible light region, which increases the photocatalytic activity significantly for H_2 evolution. Furthermore, one of the recent studies has shown the enhanced photocatalytic H_2 evolution over g-C_3N_4 with high specific surface area, prepared from mixture of urea and thiourea by calcination and recrystallization as compare to g-C_3N_4 prepared from urea and thiourea, respectively [34]. All these method have proven to be very effective to improve charge separation and light absorption in g-C_3N_4 to make it more efficient photocatalytic material. Particularly, coupling of g-C_3N_4 with wide band gap semiconductors to form heterojunction is of great interest and significance due to their suitable CB and VB positions, wherein charge transfer can be drastically enhanced. Recently, Zhang et al. [25] reported a highly efficient CeO_2-g-C_3N_4 n-n type heterojunction for pollutant removal and H_2 production under visible light irradiation. The high photocatalytic efficiency in this n-n type heterojunction has been attributed to the intimate interactions across the interfaces, which facilitates the separation of photogenerated charge carriers. In addition, Wang et al. [35] investigated the visible light driven photocatalytic performance of N-doped TiO_2 coupled with g-C_3N_4, wherein the heterojunction formation between N-TiO_2 and g-C_3N_4 suppresses the recombination of photogenerated charge carriers.

It is noteworthy to mention here that, in addition to wide solar light absorption and fast carrier transport across heterojunction, the high specific surface area of the catalyst is also a crucial parameter that influences the catalytic activity significantly. Thus in our understanding, inspired by the research on two dimensional (2D) materials like graphene, we have focused our study on 2D materials rather than bulk material. These 2D nanosheets (NS) possess extraordinary properties in comparison to 0D and 1D material as [36,37],

(i) High specific surface area with more number of catalytic active sites on surface.
(ii) Good conductivity and high electron mobility due to p-n conjugations and hence exhibit prolonged electron life time and improved charge transfer kinetics as a result of short diffusion path coupled to quantum confinement effects, which eventually makes 2D semiconductors a promising photocatalysts.
(iii) Excellent catalyst support to other materials to form effective heterojunctions, which is beneficial for rapid charge transfer and catalyst dispersion. Also the fast charge transfer in 2D materials heterojunctions could be attributed to the face-to-face contact (2D-2D) as compared to point-to-face contact (0D-2D) and line-to-face contact (1D-2D) in materials forming heterojunctions.

Very recently, our group has investigated the 2D materials (reduced graphene oxide, MoS_2) supported ZnO nanocomposite heterojunctions for excellent photocatalytic hydrogen evolution under natural sunlight irradiation [38]. The high photocatalytic activity towards hydrogen generation has been attributed to the fast charge transfer across heterojunction, high surface area and abundant reaction sites on 2D support materials. In this work, we have designed and developed a very interesting, novel N-doped ZnO nanosheets coupled with g-C_3N_4 nanosheets as 2D-2D heterojunction photocatalysts through facile hydrothermal synthesis method. ZnO NS has been doped with nitrogen to alter the band gap energy of ZnO as there could be significant overlapping between the p orbital of N-dopant with valence band O-2p orbital, which can result in the visible light absorption and enhancement in photocatalytic performance as reported in one of the previous works by our group [18]. Furthermore, various compositions with varying amount of g-C_3N_4 as 10 wt%, 20 wt%,

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