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Review Article

Photocatalytic properties of two-dimensional graphene and layered transition-metal dichalcogenides based photocatalyst for photoelectrochemical hydrogen generation: An overview

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ABSTRACT

Hydrogen production through photoelectrochemical (PEC) water-splitting process has drawn significant research attention because it is a promising clean source of energy for improving earth climate in the future. Two-dimensional (2D) graphene and transition metal dichalcogenides (TMDCs), as the core of the system, have become versatile materials for the development of photocatalyst due to their distinct optical, electrical, thermal and mechanical properties. TMDCs have received significant consideration because of low-cost and earth-abundant catalysts that can replace noble metals, such as Pt. Therefore, comprehensive discussions on the structure and properties of 2D graphene and layered TMDCs materials are presented. We also gather and review various fabrication methods for TMDCs-based and graphene-TMDCs-based photocatalysts that can affect the PEC performance and hydrogen evolution. The inherent limitations and several future trends on 2D graphene and layered TMDCs-based photocatalyst for PEC water-splitting application are also discussed.

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Introduction

The current global warming is highly related to societal advancement. A prominent issue related to global warming is the continuous consumption of fossil fuel for human daily living. Fossil fuel combustion releases carbon to the atmosphere, thereby causing serious environmental issues and risks to the global climate. Hence, a clean and carbon-neutral alternative energy sources should be determined to preserve the environment [1,2]. Solar energy is generally accepted as a free, rich and continuously renewable resource of clean energy that can satisfy the current and future human energy needs [2]. Solar-driven photoelectrochemical (PEC) water splitting, as an alternative method, offers promising approaches to transform solar irradiation into a storable and environment-friendly H₂ fuel [3,4].

Numerous active catalysts, such as metal oxides [5], metal chalcogenides [6], and carbides [7] have been actively discussed for PEC water splitting because of their abundant resources without compromising their photoactivity performance [8,9]. Among them, 2D layered transition metal dichalcogenides (TMDCs), such as MoS₂ [4,10–12], WS₂ [11,13], TiS₂ [14], MoSe₂ [11,15], and WSe₂ [11,16] have received significant consideration due to their excellent catalytic activities [12], sizable bandgaps [17], distinct crystal structures, notable physical and chemical properties [18] and potentials for hydrogen evolution reaction (HER) catalysis [11]. The improved properties of these atomic TMDCs are also attainable through coupling with other 2D layered materials, such as graphene [19,20], C₃N₄ [21] or other TMDCs with common properties [18]. 2D–2D layered composite photocatalysts show much interfacial interaction between the sheet structures which can provide sufficient charge transfer to increase the photocatalytic performance. Generally, graphene exhibits an excellent charge carrier mobility and fast transfer pathway to suppress charge recombination and enhance the interfacial charge transfer processes to improve the PEC water splitting performance [5,22]. Various efforts have been constructed to combine graphene with semiconductor photocatalysts to improve their photocatalytic performances [23]. Due to the suitable optical absorption range and the capability to absorb light energy efficiently, TMDCs is among the best of photoactive materials in supercapacitor, solar cell and water splitting to generate H₂. Hence, the coupling of TMDCs with

graphene could promote a unique cocatalyst owing to the unusual synergetic effect.

PEC water splitting process using semiconductors (p-type or n-type) is effective in converting water into hydrogen and oxygen by using solar energy [24]. Cathodic photocurrent (p-type semiconductor) occurs when the transport of electrons to the electrolyte is faster than that of holes; anodic photocurrent (n-type semiconductor) occurs when fast hole transport to the electrolyte results in anodic PEC water splitting [24]. Therefore, hydrogen evolution can be fabricated using a p-type photocathode that is electrically attached to an oxygen-evolving metal electrode; oxygen evolution is constructed by using n-type photoanode [25]. As shown in Fig. 1 [26], the water splitting process take place in three steps: (1) generation of electron–hole pairs in photoelectrodes upon absorption of photons, (2) transport and charge separation into to the catalyst surface and (3) redox reactions of adsorbed species to generate oxygen and hydrogen from water [27]. Nevertheless, low-efficiency photocatalysis may occur because of the unstable and easily combined photogenerated electrons and holes in the excited conditions that scatter the input energy as heat [23]. By using light absorbing materials, such as semiconductors or molecular systems, PEC system serves to capture photons and convert the incident photons to excited electron-hole pairs. Recombination of photo-excited electron-hole pairs can be avoided if they are transferred quickly by suitable acceptor, making more charge carriers to create reactive species [28]. The internal energy in these excited states can be transferred to the interface between the light absorber and an electrolyte, at which reactive sites can facilitate oxidative or reductive electron-transfer half reactions by using cocatalysts that are efficient of supporting in electron–hole separation and improving the overall effectiveness. The oxidative half-reaction produces O₂ while the reductive half-reaction produces H₂. The creation of a suitable hetero-junction between the cocatalyst and the semiconductor is the main issue for stimulating the charge separation and transfer from the semiconductor to the cocatalyst [2,29].

This review provides a comprehensive discussion on the incorporation of graphene and TMDCs for photocatalyst fabrication. Their photocatalytic properties and morphological structures influencing the PEC performance are also discussed. Furthermore, the challenges in dealing with this

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