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Graphene/semiconductor nanocomposites (GSNs) for heterogeneous photocatalytic decolorization of wastewaters contaminated with synthetic dyes: A review

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ABSTRACT

The advent of graphene revolution in recent years has opened up immense possibilities for creating and exploring new carbon-based materials for innovative technological applications. Recent advancements have shown that graphene/semiconductor nanocomposites (GSNs) can be envisaged as a promising new class of catalysts for the heterogeneous photocatalytic treatment of industrial wastewaters. While GSNs have been found effective in degrading and mineralizing a myriad of organic contaminants, photocatalytic degradation of synthetic colorants has been most extensively investigated. We present here the state-of-art review on GSNs in the context of photodecolorization of textile effluents. Various approaches to the synthesis of GSNs are first integrated and demonstrated by representative examples. The efficacy of these composite photocatalysts in decomposing selected dye pollutants is then discussed. We conclude the review by emphasizing the future research challenges and opportunities toward the large-scale commercialization of GSNs.

1. Introduction

The rapid pace of industrialization has largely contributed to the severe deterioration of our freshwater resources. A wide range of toxic and hazardous substances are continually being released into the surrounding water bodies due to lack of effective effluent treatment at the source, among which synthetic dyes have attracted considerable attention. Worldwide, 280,000 t of synthetic dyes have been estimated to be released into the environment every year through industrial wastewater discharges [1]. Dyes are tinctorially strong and hence easily visible in contaminated waters even at very low concentrations. Their synthetic origin and complex aromatic structure makes them stable and difficult to be biodegraded [2]. Dyes can affect the photosynthetic activity and dissolved oxygen concentration in aquatic systems by preventing the transmission of light (reflection and absorption of sunlight), thus causing disturbance to the ecology of the receiving waters [3]. Dyes are also often highly toxic, carcinogenic, and mutagenic in nature, and can even bio-accumulate in the food chain [4]. The direct release of colored wastewaters into the aquatic ecosystems is, therefore, both environmentally unsafe and aesthetically unacceptable.

In view of the rising awareness of the importance of water quality preservation and improvement, the development of a clean and efficient water purification technology has been the focus of considerable research in the last few decades. Among the numerous treatment techniques that have been proposed, heterogeneous photocatalysis has emerged as one of the most powerful methods of water decontamination because of its potential to transform recalcitrant organic contaminants into mineral salts and relatively innocuous end products such as CO_2 and H_2O [5–7].

Heterogeneous photocatalysis involves the utilization of a semiconductor catalyst (such as TiO_2, ZnO, Fe_2O_3, CdS, GaP or ZnS), irradiated with light of an appropriate wavelength, to generate highly reactive transitory species (i.e., $\bullet OH$, $\bullet O_2^-$, $\bullet HO_2$) for mineralization of organic impurities [5,8]. This green technology offers a number of advantages such as ambient operating conditions, low operating costs, complete mineralization of organic pollutant without any secondary pollution, all of which have promoted its wide application in wastewater treatment [9]. Unfortunately, the insufficient quantum efficiency, narrow excitation wavelength, high recombination rate of the photoproduced electron–hole pairs, poor adsorption capacity, and deactivation of the semiconductor photocatalyst limit the practical application of this technique [10,11]. Even though a variety of approaches have been attempted to improve the photocatalytic behavior of semiconductors, including metal particle loading, co-catalysts, dye sensitization, metallic

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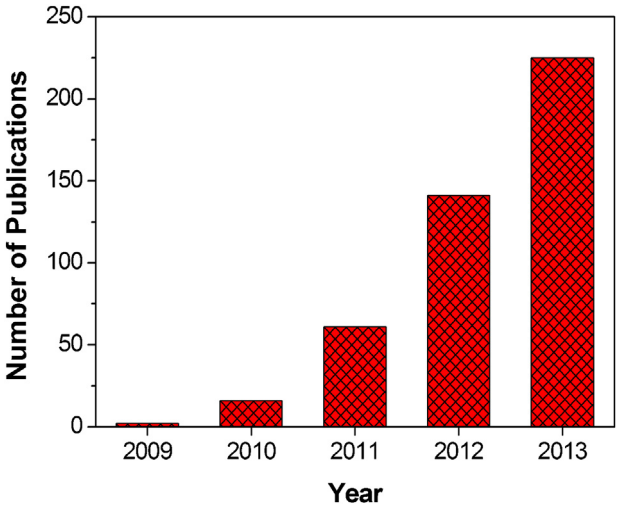

Fig. 1. Number of scientific articles published on GSN-mediated heterogeneous photocatalysis over the past five years (source: http://www.scopus.com; search terms: "graphene" and "photocatalysis").

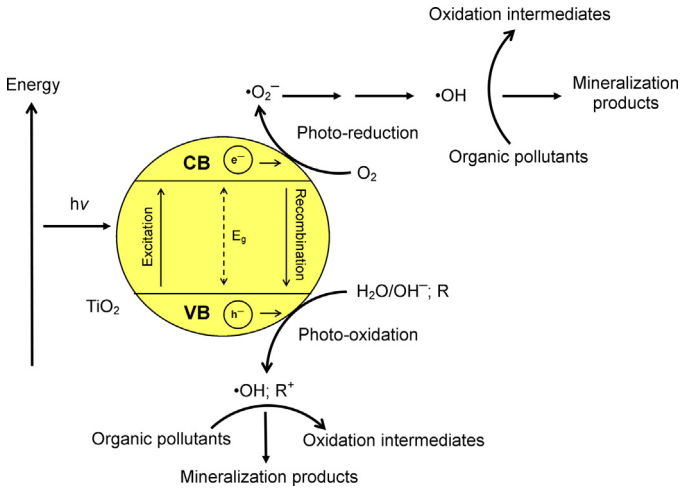

Fig. 2. Schematic of reactions occurring during heterogeneous photocatalysis over TiO_2. Adapted from [6].

doping and non-metallic doping, the development of an efficient and commercially viable photocatalyst still remains a significant challenge [12].

With rapid advancements in nanoscience and nanotechnology, much attention is currently directed toward harnessing the outstanding physicochemical properties of graphene – the newest member in the family of carbon allotropes – for designing next-generation photocatalyst systems with enhanced activity and performance. While other carbon nanomaterials such as fullerenes (C_{60}), carbon nanotubes (CNTs) and activated carbon are widely investigated for many years for photocatalytic applications with varying levels of success [12], graphene adds a new dimension to the ever progressing field of heterogeneous photocatalysis. Graphene is a single layer of sp^2 hybridized carbon atoms covalently packed into a continuous hexagonal lattice [13,14]. This one-atom-thick pseudo-infinite nano-crystal is characterized by a large theoretical specific surface area ($2630\,m^2\,g^{-1}$) [15], high electron mobility at room temperature ($200{,}000\,cm^2\,V^{-1}\,s^{-1}$) [16], exceptional thermal conductivity ($5000\,W\,m^{-1}\,K^{-1}$) [17], superior mechanical properties with Young's modulus of 1100 GPa [18], and excellent optical transmittance (97.7%) [19]. Such a combination of intriguing properties makes graphene an ideal electronic sink, or electron-transfer bridge and a 2D support matrix for photocatalyst carrier or promoter [10–12]. In view of these attractive attributes, there has been an increasing research interest in the recent times, seeking to couple graphene with photoactive semiconductors to develop graphene/semiconductor nanocomposites (GSNs) with high photocatalytic performance toward pollution control and abatement [10,11]. The conjugation of graphene with semiconductor solid particles results in photocatalysts with improved charge separation, reduced recombination of the photogenerated electron–hole pairs, increased specific surface area, and an adequate quantity and quality of adsorption sites [10]. In addition, recent developments have shown that the chemical relatives of graphene such as graphene oxide (GO) and reduced graphene oxide (rGO), because of their rich surface chemistry [20,21], also offer exciting opportunities for the development of novel photoactive nanocomposites for the transformation of environmental contaminants.

Since the first pioneering article in 2008 [22], scientific publications on the preparation and characterization of GSNs for photocatalytic applications appear to have risen almost exponentially (Fig. 1). GSN-mediated heterogeneous photocatalysis has been demonstrated to be an efficient tool for degrading a myriad of organic contaminants—the photodecomposition of synthetic dyes being rigorously investigated and reported. Despite some recent reviews on graphene-based nanocomposites for photocatalytic applications [10,11,23], the progress on photodecolorization of wastewaters contaminated with dyes has perhaps received less coverage than is warranted. The present review is thus an attempt to provide a comprehensive update of the key advancements in the development of GSNs for photodecolorization of textile effluents. The goal of the review is not just to integrate results from the studies reported in the literature, but identify current research directions and provide insights into the synthesis of GSNs and their photocatalytic performance for removal of selected dye pollutants. Moreover, the challenges posed on the commercial development of these novel composite photocatalysts and the scope for further enhancements of their photocatalytic activity have also been discussed for future research directions and opportunities.

2. Principle of heterogeneous photocatalysis

Heterogeneous photocatalysis is based on a complex sequence of reactions, the underlying principles of which are well established [24–26]. Briefly, when a semiconductor is illuminated with light energy, electrons (e^-) are excited from the valence band (VB) to the conduction band (CB). Electrons raised to the CB correspond to missing negative charges in the VB, called holes (h^+). Both the e^- and h^+ then migrate to the surface where they can initiate redox reactions with other chemical species adsorbed on the semiconductor. The photogenerated holes oxidize the hydroxyl groups or water molecules to produce •OH radicals while the photogenerated electrons reduce the dissolved oxygen to form superoxide radical anion ($•O_2^-$) [6,27], which then reacts with H^+ to form $•HO_2$, followed by rapid decomposition to •OH [28]. The •OH radical, being a very strong oxidizing agent (standard redox potential +2.8 V vs. normal hydrogen electrode) oxidizes the surface adsorbed organic pollutant into readily biodegradable compounds [29]. The basic photophysical and photochemical processes involved during heterogeneous photocatalysis are illustrated in Fig. 2 and are often represented by the following chain reactions [6,29,30]:

$$\text{Photoexcitation}: \quad SC + h\nu \rightarrow SC\ (e^- + h^+) \tag{1}$$

$$\text{Ionization of water}: \quad SC\ (h^+) + H_2O \rightarrow •OH + H^+ \tag{2}$$

$$\text{Oxygen ionosorption}: \quad SC\ (e^-) + O_2 \rightarrow •O_2^- \tag{3}$$