



## Full Length Article

# Extended light absorption and enhanced visible-light photocatalytic degradation capacity of phosphotungstate/polyimide photocatalyst based on intense interfacial interaction and alternate stacking structure



Pengcheng Meng, Junhao Huang, Xia Liu\*

College of Science, China Agricultural University, Beijing 100193, PR China

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## ABSTRACT

In previous research, phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , PW)/polyimide (PI) composites were constructed using insoluble heptazine melem. We found that the introduction of PW can cause a slight increase in the light absorption of the composites. To further study the effects of polyoxometallate on the light absorption and photocatalytic activity of photocatalysts, a novel phosphotungstate/polyimide photocatalyst (MPWPI) was constructed via in situ solid-state thermal polymerization using melamine phosphotungstate ( $(\text{C}_3\text{N}_6\text{H}_7)_x[\text{PW}_{12}\text{O}_{40}]$ , MPW) synthesized by water-soluble triazine melamine ( $\text{C}_3\text{H}_6\text{N}_6$ , MA) and PW. The structural and morphological results confirm the successful construction and the alternate stacking structure of MPWPI. The alternate stacking structure is more favorable for the contact between polyoxometallate and polyimide, and it also facilitates the electron delocalization through the intermolecular phosphotungstate anions- $\pi$  interactions. This will lead to the extended light absorption and enhanced visible-light photocatalytic degradation capacity. The UV–visible diffuse reflectance spectroscopy (UV–Vis DRS) results display that the light absorption of MPWPI can be obviously extended to 800 nm. Compared to the inactive polyimide and phosphotungstate, MPWPI exhibits extraordinary photocatalytic activity of imidacloprid under visible light irradiation ( $\lambda > 400$  nm) for the extended light absorption and suppressed carriers recombination. For this photocatalytic system, the  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  are the main active species. Furthermore, the encapsulated phosphotungstate anions in the specific structure of MPWPI give it excellent recyclability for the inhibited polar solvent dissolution.

## 1. Introduction

The ever-increasing investigations of visible light photocatalysts for the conversion and application of solar energy in the energy, environmental and catalysis fields illustrate their importance in modern materials and catalytic science [1]. Among the various photocatalysts, organic photocatalysts have attracted much attention recently [2]. Conjugated polymers have made great strides as a representative organic photocatalyst. Unfortunately, when using polymeric carbon nitride as an example, although the aromatic  $\pi$ -stacking gives carbon nitride the capacity for visible light absorption, the utilization of solar energy is also limited by the high charge recombination rate and inefficient charge transfer [3]. It is fortunate that the semiconductor properties of conjugate polymers can be controlled and tuned by modifying the electronic and band structures through doping [2], copolymerization [4,5], polymerization modulation [6,7], coordination interaction [8], covalent or noncovalent modification [9], and

hydrogen bonds modulation [10]. Especially, the donor-acceptor structure is remarkably used to tune the band structure [11]. Polyimides (PI), which are excellent engineering materials, are a typical representative of this class of substance [12]. Polyimides are affected by their own material properties and have a lower preparation temperature than the carbon nitride [13]. Nonetheless, when photocatalytically degrading other various contaminants other than dyes, these materials are still weak with respect to the inherent transfer property, the persistent recombination of photogenerated carriers and the negative valence band (VB) potential [12–15]. A series of studies, including those on cocatalysts [16–19], doping [20], and heterojunctions [21–23], have been conducted to modify the performance of the crystalline polyimide. Recently, our group reported on the enhanced photocatalytic degradation efficiency of polyimide-based materials by constructing heterojunctions with tungstic oxide and polyoxometallate [6,21]. From the previous research, phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , PW)/polyimide composites were constructed using insoluble heptazine melem (PI-

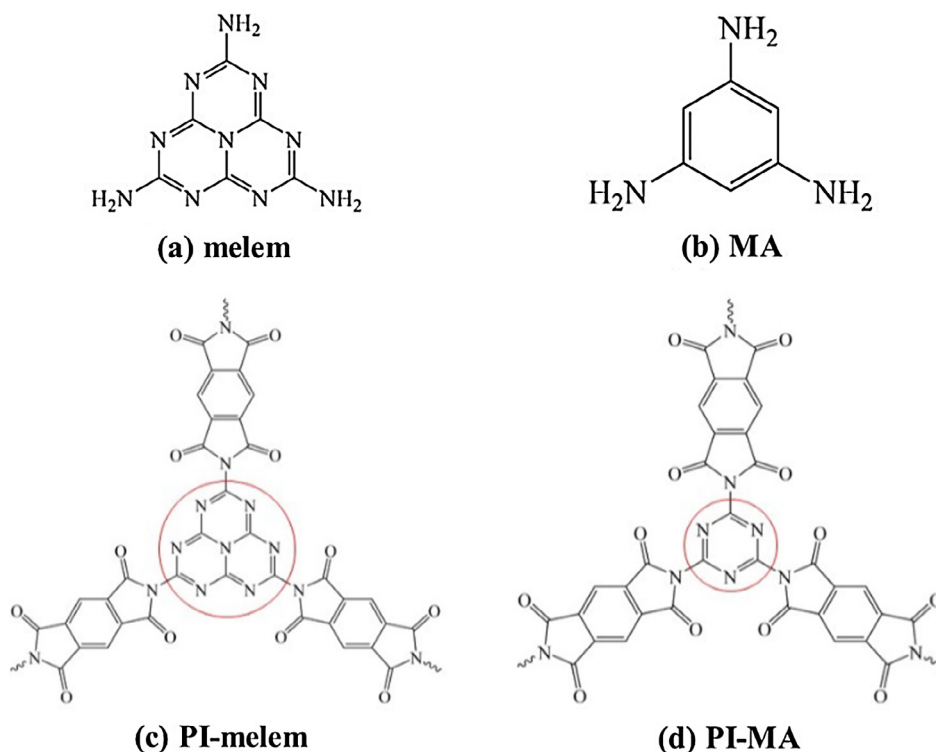
\* Corresponding author at: College of Science, China Agricultural University, Yuanmingyuan West Road No.2, Haidian District, Beijing 100193, PR China.  
E-mail address: [liuxiacau@163.com](mailto:liuxiacau@163.com) (X. Liu).

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**Fig. 1.** The chemical structure of melem (a) and melamine (b), and the duplicate chemical building block of PI-melem (c) and PI-MA (d).

melem, Fig. 1a and c) via a one-pot method [6]. The positive effects of PW on the synthesis of polyimide and electron transfer were investigated. We found that the introduction of PW can cause a slight increase in the light absorption of the composites. However, the light absorption of those above polyimide-based materials is still based on the bulk absorption of polyimide, and the utilization of solar energy is still restricted. Therefore, how to improve the utilization of solar energy for polyimide-based materials by extending the visible light absorption is an urgent problem that needs to be solved. Since the introduction of PW can improve the light absorption of composites, how can we further extend the light absorption of the photocatalyst? Is it possible to use polyoxometallates-based (POMs-based) organic-inorganic hybrid materials to construct POMs/polyimide photocatalysts and obtain extended light absorption?

Polyoxometallates (POMs), which are defined as transitional metal-oxygen anionic clusters, have unique applications in catalysis [24], electronics and magnetism [25,26], photochemistry [27,28], and medicine [29]. With the development of the application of POMs in the catalysis field, its advantages for the construction of photocatalysts have gradually emerged. It is noteworthy that, for POMs-based photocatalysts, the crystalline organic-inorganic hybrid materials have attracted considerable interest [27,28]. In those materials, the introduction of organic ligands can construct new band structures with the POMs anions [26]. The POMs, as the electron acceptors and transfer mediators, can be reduced by one or more electrons to mixed-valence clusters with minimal structural modifications [25,26]. Generally, electrons are delocalized within a single POMs cluster in a bulk solid [30]. For the crystalline mixed-valence POMs-based organic-inorganic hybrid materials, the conjugated organic ligands can extend their conjugation to the POMs framework [31], and the electrons will fully delocalize over the organic-inorganic framework through strong intermolecular interactions [32–34]. Accordingly, linking conjugated organic ligands to POMs through unusual POMs anion- $\pi$  interactions can improve the electronic transfer while keeping their respective structures in order to significantly modify the redox properties of the hybrids [31,35]. For these organic-inorganic hybrid materials, their structures

tend to consist of layered organic molecules that are alternately stacked with POMs layers [25,26]. The above structure can effectively solve the problem that most POMs are easily soluble in polar solvents. Additionally, this structure can also facilitate the electron transfer and delocalization between the POMs and the conjugated polymer. Nevertheless, for the POMs containing organic amine ligands, when these hybrids are used as photocatalysts under light irradiation, they are usually partially dissolved in water for the reduction [27]. The post-functionalization may provide ideas for solving this problem and obtain some windfalls.

The main purpose of this paper is to investigate the possibility of enhancing the light absorption and photocatalytic activity using the electron delocalization and the alternate stacking structure from the strong intermolecular interfacial phosphotungstate anions- $\pi$  interactions between POMs and conjugated polyimide. Moreover, the photocatalyst mentioned in this paper is different from the previous work with respect to its research purposes, chemical composition and structure, and construction theory. Unlike PI-melem, the polyimide involved in this paper is a triazine-based material (PI-MA, Fig. 1b and d), and it does not show visible-light photocatalytic activity with the selected contaminants due to its relatively negative valence band position. Because the electrons will fully delocalize over the organic-inorganic framework, we choose soluble melamine ( $C_3H_6N_6$ , MA) to construct the melamine phosphotungstate ( $(C_3N_6H_7)_x[PW_{12}O_{40}]_x$ , MPW) and build the alternate stacking structure of the phosphotungstate/polyimide photocatalyst (MPWPI) to facilitate the electronic delocalization. For PW, it is a typical commercial Keggin-type heteropolyacid. The PW and its salts not only possess the properties of the POMs mentioned above but are also typical and widely researched among many types of heteropolycyclic compounds, such as Silvertone-type, Dawson-type, Anderson-type, and so on. These works are based on the postfunctionalization of MPW due to its inherent alternate stacking structure and large number of exposed amino groups.

In view of the above background, herein, a two-step strategy was designed and adopted to construct the phosphotungstate/polyimide photocatalyst using MPW as a precursor to simultaneously compensate

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