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In situ preparation of highly stable polyaniline/$W_{18}O_{49}$ hybrid nanocomposite as efficient visible light photocatalyst for aqueous Cr(VI) reduction

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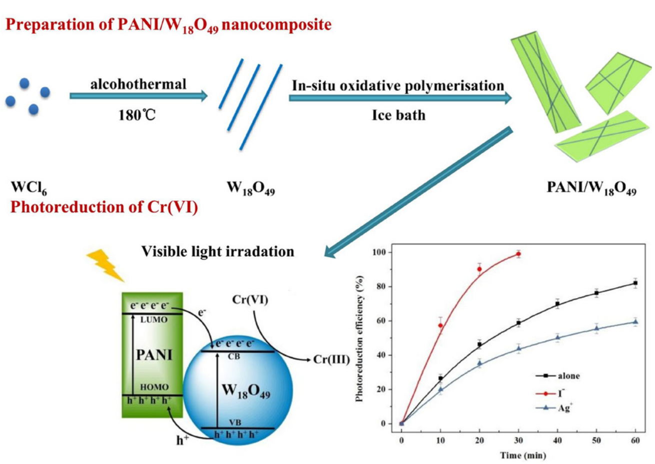
GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, we prepared novel polyaniline supported $W_{18}O_{49}$ (PANI/$W_{18}O_{49}$) nanocomposite by in situ oxidative polymerisation method. We herein focused on enhancing the stability and the photocatalytic performance of $W_{18}O_{49}$. The prepared PANI/$W_{18}O_{49}$ was thoroughly characterized by FTIR, TEM, XRD, BET, UV–vis DRS and PL. The PANI support presented a great effect on the light harvesting and photo-charge transfer of the $W_{18}O_{49}$, and the optimum percentage of was found to be 10 wt%. As for treating Cr(VI), the effect of important water quality parameters (such as pH, ions, NOM, DO, temperature and SOAs) on photocatalytic performance was investigated under the visible light irradiation ($\lambda > 420$ nm). SOAs were shown to exert a dramatic accelerating influence on Cr(VI) reduction in the system. The obtained 10%-PANI/$W_{18}O_{49}$ can completely catalytically reduce 1 mM Cr(VI) in the presence of tartaric acid (1:3) within 50 min. Meanwhile, it can be recycled at

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ten times without any loss of photocatalytic efficiency, indicating the high stability of the as-prepared photocatalyst. The results of the study demonstrate the potential of the new obtained photocatalyst in efficient utilization of solar energy for treating aqueous Cr(VI).

1. Introduction

Chromium, a serious heavy metal contaminant, widely presents in industrial waste discharges, such as those from textile manufacturing, steel fabrication, leather tanning, paint fabrication and petroleum refining [1,2]. The two most common naturally occurring oxidation states of chromium in aqueous solutions are Cr(III) and Cr(VI) [3]. Cr(VI) has been demonstrated to be highly toxic, mutagenic and carcinogenic to living organisms with significant public health implications; as such, the maximum permissible limit of Cr(VI) is very low, only 0.05 mg/L for drinking water [4]. In contrast, Cr(III) is comparatively nontoxic and even considered to be an essential micronutrient [5,6]. Hence, the conversion of Cr(VI) to Cr(III) is usually regarded as an efficient method for treatment of wastewater and environmental remediation of Cr(VI) [7–9].

Photocatalytic reduction of Cr(VI) has been proposed as an efficient and viable technique due to its tremendous potential in water treatment [10–12]. In the past, wide band gap materials (e.g., TiO_2, ZnO, and NiO) were mostly used for the photocatalytic reduction of Cr(VI) under ultraviolet (UV) light irradiation [13–15]. However, for developing the practical applications, there is a great demand for visible light response photocatalysts. In this regard, a considerable effort has been devoted to designing and exploring photocatalysts with lower suitable band gap [16–18]. In particular, hybrid composite architecture is very promising for improving photocatalytic activity, because the photo-induced electrons and holes will be quickly separated through the well-matched band structure [19–21].

In recent years, nanostructured materials have been widely investigated, they offer a large surface area for interfacial charge collection and a short diffusion distance for charge transfer [23,24]. Currently, $W_{18}O_{49}$ nanosturctured materials have attracted considerable attention owing to their remarkable oxygen defect structure and wide light absorption [25,26]; however, rapid recombination of electrons and holes limits their photocatalytic applications [27]. Moreover, the band levels of $W_{18}O_{49}$ often lie within the systems oxidation or reduction potential, allowing them to participate in reduction or oxidation reactions [28]. For instance, $W_{18}O_{49}$ nanowires displayed excellent performance in CO_2 reduction under visible light. Unfortunately, the oxidation took place on the surface of the nanowires during the photocatalysis process, blue $W_{18}O_{49}$ sample gradually changed to yellow due to the formation of WO_3 [29]. Therefore, the fabrication of efficient and stable $W_{18}O_{49}$ still remains a challenge.

For the sake of enhancing the stability as well as photocatalytic performance of $W_{18}O_{49}$, it is vital to modify the $W_{18}O_{49}$ through physical or chemical routes. Among the so far investigated functionalized materials, polyaniline (PANI) is considered as one of the most promising conducting polymers due to its low cost, easy synthesis, good electron conductivity and environmental stability [30–32]. These characteristics make it an ideal candidate for $W_{18}O_{49}$. Meanwhile, they have matched band potentials: both the LUMO and HOMO potentials of PANI are more negative than conduction band and valence band potentials of $W_{18}O_{49}$. This thermodynamically allows the photogenerated electron transfer from the LUMO of PANI to the conduction band of $W_{18}O_{49}$ under visible light irradiation. Combining p-type polyaniline polymer and n-type $W_{18}O_{49}$ in a heterogeneous structure should boost the separation and transfer of generated electron-hole pairs. Such a combination could also result in long term stability to endure the oxidative radical attack during exposure to light [33]. However, to our knowledge, there is still no report about preparing PANI/$W_{18}O_{49}$ composite as photocatalyst.

Herein, a rapid and facile chemical route is demonstrated for the preparation of novel PANI/$W_{18}O_{49}$ nanocomposite to overcome the shortcomings of $W_{18}O_{49}$. For the first time, as we known, a $W_{18}O_{49}$ based photocatalyst was systematically studied for photocatalytic reduction of Cr(VI). It is found that $W_{18}O_{49}$ has the ability to catalytic reduction of Cr(VI) under the visible light ($\lambda > 420$ nm) irradiation, and the introduction of PANI can significantly enhance the activity and stability of $W_{18}O_{49}$. Effect of important water quality parameters such as pH, ions, natural organic matter (NOM), dissolved oxygen (DO), temperature and small molecular weight organic acids (SOAs) on photocatalytic performance was investigated, and the reasons accounting for the photocatalytic results are also discussed.

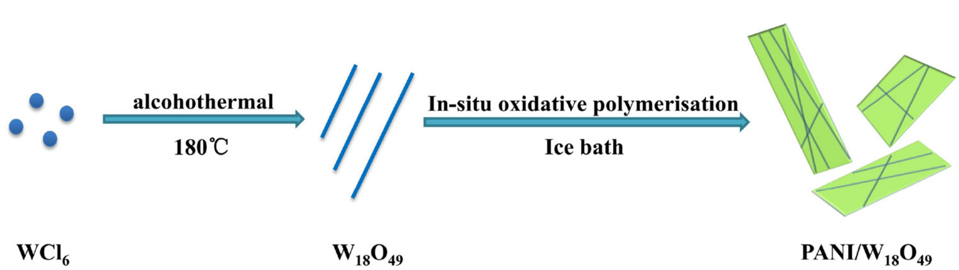
2. Experimental

2.1. Materials

All chemicals were used as received and of analytical grade unless otherwise stated. Anhydrous tungsten hexachloride (WCl_6), aniline, and ammonium persulfate (APS) were purchased from Shanghai Aladdin Chemical Reagents Company. Humic acid (Ha, CAS: 1415-93-6) was obtained from Sigma-Aldrich. Other chemical reagents were supplied by Tianjin Chemical Reagents Company.

2.2. Preparation of PANI/$W_{18}O_{49}$ nanocomposite

The procedures for preparation of PANI/$W_{18}O_{49}$ nanocomposite are illustrated in the Scheme 1. An alcohothermal method was used to obtain $W_{18}O_{49}$ nanorods from WCl_6 [29]. In a typical procedure, 0.04 g of WCl_6 was dispersed in 80 mL of absolute ethyl alcohol by ultrasonication and stirred to form a homogeneous dispersion. Next, this solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 180 °C for 18 h. After the autoclave cooled to room temperature, the resulting product was collected by centrifugation and purified with water. The obtained $W_{18}O_{49}$ sample was dehydrated via a freeze-drying process.



Scheme 1. The schematic procedure for the preparation of PANI/$W_{18}O_{49}$ nanocomposite.