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Original Research

Synthesis of $ZnWO_{4-x}$ nanorods with oxygen vacancy for efficient photocatalytic degradation of tetracycline☆

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ABSTRACT

Persistent organic pollutants (POPs) especially tetracycline pose a great threat to human health, and the photocatalytic degradation of tetracycline by $ZnWO_4$ nanomaterials has drawn much attention. To improve the photo-response range and photoactivity, we prepared $ZnWO_{4-x}$ sample with oxygen vacancies by solvothermally treating $Zn(NO_3)_3$ and Na_2WO_4 in water/ethanol/PEG-400 mixture where ethanol could act as a reducing agent to selectively remove some oxygen atoms from $ZnWO_4$. $ZnWO_{4-x}$ sample is composed of nanorods with length of ~50 nm and diameter of ~20 nm. Furthermore, $ZnWO_{4-x}$ nanorods are brown and exhibit the obviously broadened photoabsorption from ultraviolet (UV) to near infrared (NIR) region, compared with the tradition white $ZnWO_4$ nanorod without oxygen vacancies and with UV absorption edge of 365 nm. Under the irradiation of UV or ultraviolet-visible-near infrared (UV–Vis–NIR) light, $ZnWO_{4-x}$ nanorods can photocatalytically degrade 91% or 78% tetracycline, higher than those (67% or 71%) by $ZnWO_4$ nanorods. The enhanced photocatalytic efficiency can be attributed to the introduction of oxygen vacancies which have been found to reduce photogenerated electron-hole pair recombination and narrow band gap.

1. Introduction

Persistent organic pollutants (POPs) are toxic chemicals that accumulate in the food chain and adversely affect human health as well as the environment worldwide. There are different types of POPs described by their uses, including pesticides (e.g. insect repellent), solvents (e.g. toluene), industrial chemicals (e.g. textile dyes) and pharmaceuticals (e.g. tetracycline) [1]. Among these POPs, tetracycline has been extensively used in the manufacture of antibiotics for aquaculture [2] and veterinary medicine [3,4]. However, a large amount of tetracyclines have been excreted as un-metabolized parent compound into water [5]. For removing tetracycline in water, different technologies have been developed, such as advanced oxidation/reduction processes [6], adsorption by micelle-clay [7], and ozonation in aqueous phase [8]. Unfortunately, these methods cannot remove or degrade tetracycline completely, hence the residual tetracycline in water/sludge has a significant threat to human health and the environment. Therefore, it is still necessary to develop more efficient technology to significantly degrade tetracycline.

It is well known that photocatalysis stands out as a green technology and an environmental remediation alternative to eradicate the pollutants [9]. Photocatalysis has many advantages over other treatment methods, including ecological friendliness, capability to be performed at ambient temperature and efficiency to mineralize POPs even at low concentrations [10]. The principal goal of photocatalysis is the development of effective photocatalysts [11–13]. Currently, many types of photocatalysts have been developed for degrading POPs, including simple oxides (e.g. TiO_2 [6,13]), nitrides (e.g. C_3N_4 [14]), sulfides (e.g. CdS [15]) and complex oxides (e.g. $CaBi_2O_4$ [16], Bi_2WO_6 [17], $Bi_{24}O_{31}Cl_{10}$ [18], MWO_4 [19] where M = Ni, Co, Fe, Cu and Zn). Among these photocatalysts, MWO_4 nanomaterials have attracted much attention due to good chemical stability, long afterglow to luminescence and moderate photocatalytic activity [20]. Specifically, $ZnWO_4$ nanomaterials have been used as efficient photocatalysts. For instance, Zhou et. al. reported the solvothermal preparation of $ZnWO_4$ samples ranging in shape from tiny nanocrystals (size: ~20 nm) to nanorods

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(length: ~35 nm) by adjusting the solvent ratio of ethylene glycol to water, and $ZnWO_4$ samples exhibited the morphology-dependent photoabsorption edge (from 350 to 500 nm) and photocatalytic activity in the degradation of rhodamine B dye [21]. To further improve the photocatalytic activity, Li et. al. decorated $ZnWO_4$ nanorods with Ag/AgBr, and the resultant Ag/AgBr/$ZnWO_4$ nanorods (diameter: ~100 nm, length: ~0.7 μm) could photocatalytically degrade 91% AR18 dye in 60 min, higher than that (2%, 1% or 30%) by $ZnWO_4$, TiO_2 or AgBr alone, respectively [22]. However, the practical application of $ZnWO_4$ is still limited due to unsatisfactory photo-response range and photocatalytic activity. To satisfy the requirements of future environmental technology, it is still necessary to improve the photo-response range and photocatalytic activity of $ZnWO_4$.

Recently, the introduction of oxygen vacancy into semiconductors has been demonstrated as an effective method for improving photo-response range and photoactivity [23–25]. For example, Tian et. al. [23] prepared Bi_2WO_6 nanosheets with oxygen vacancies (length: ~200 nm, thickness: ~20 nm) by a hydrothermal co-precipitation method, and the Bi_2WO_{6-x} nanosheets could absorb solar light efficiently from ultraviolet (UV) to near-infrared (NIR) wavelength and thus exhibited a higher photocatalytic activity than pure Bi_2WO_6 for degrading Methylene Orange dye. Furthermore, $BiPO_4$ nanocubes with surface oxygen vacancies [24] and hybrid CeO_2-graphene nanostructures with oxygen vacancies [25] were also prepared, and these oxygen-deficient nanomaterials exhibited the broadened photoabsorption range and improved photocatalytic activity compared to the ones without oxygen vacancies. However, to the best of our knowledge, there is no report related to the preparation of $ZnWO_4$ nanomaterials with oxygen vacancies as efficient photocatalysts.

As mentioned above, tetracycline as a POP poses a great threat to human health, and the introduction of oxygen vacancies can improve the photocatalytic activity of semiconductor nanomaterials. These features trigger our interests in developing $ZnWO_4$ with oxygen vacancies (denoted as $ZnWO_{4-x}$) as efficient photocatalysts for removing tetracycline. Herein, we have synthesized $ZnWO_{4-x}$ nanorods with oxygen vacancies through a modified one-pot solvothermal method with water/ethanol/PEG-400 as the solvent at 180 °C for 6 h. $ZnWO_{4-x}$ nanorods exhibit the obviously broadened UV–Vis–NIR photoabsorption compared with UV (edge: ~365 nm) absorption of pristine $ZnWO_4$. Under UV light (Hg lamp) or UV–Vis–NIR light (Xe lamp) irradiation, $ZnWO_{4-x}$ nanorods can photocatalytically degrade 91% or 79% tetracycline, exceeding that (67% or 71%) by $ZnWO_4$ nanorods.

2. Experimental section

2.1. Synthesis of $ZnWO_{4-x}$ and $ZnWO_4$ nanorods

Materials and chemicals are shown in Supporting information. $ZnWO_4$ nanorods with oxygen vacancies ($ZnWO_{4-x}$) were prepared by a modified one-pot solvothermal route as follows [26,27]. $Zn(NO_3)_3{\cdot}6H_2O$ (0.84 g, 1 mmol) was dissolved in the mixture (26 mL) containing deionized water (1 mL), ethanol (7.5 mL) and poly (ethylene glycol) (molecular weight = 400, abbreviated as PEG-400, 17.5 mL) under vigorous stirring. Aqueous solution (1 mL) containing $Na_2WO_4{\cdot}2H_2O$ (0.76 g, 1 mmol) was dropped into the above solution under continuous stirring for 10 min. The resultant suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed and heated at 180 °C for 6 h. $ZnWO_{4-x}$ sample was collected by centrifugation, washed with distilled water and absolute ethanol several times and finally dried in a vacuum oven at 80 °C for 4 h. For comparison, pristine $ZnWO_4$ was also synthesized by replacing the water/ethanol/PEG-400 mixture with pure water (26 mL) as the solvent under other identical conditions. The characterization process was shown in the Supporting information.

2.2. Photocatalytic activity

The photocatalytic degradation of tetracycline was performed by using $ZnWO_4$ or $ZnWO_{4-x}$ nanorods as photocatalyst at room temperature and atmospheric pressure, under the irradiation of UV lamp (Hg, 300 W, QVF135 Philips Lighting Luminaires Co. Ltd.) or Xenon lamp (300 W, PLS-SXE300 Beijing Perfect Light Co. Ltd.). Typically, 20 mg photocatalyst ($ZnWO_4$ or $ZnWO_{4-x}$ sample) was added into aqueous solution of tetracycline (100 mL, 20 mg L^{-1}, pH = 5.19). Then the dispersion was magnetically stirred in the dark for a period of 60 min to reach an adsorption-desorption equilibrium, and subsequently it was irradiated by UV or UV–Vis–NIR light. Monitoring of tetracycline concentration during the entire testing duration was achieved by collecting 3 mL aliquots of the suspension at 20 min intervals, filtering by 0.22 μm millipore filter to get a clear liquid, and analyzing it using UV1901PC Spectrophotometer (Shanghai Yoke Instrument Co. Ltd.) by measuring the intensity of characteristic adsorption peak of tetracycline at 357 nm. Additionally, the tests of quantum efficiency, total organic carbon (TOC) and photocatalytic stability as well as radical trapping experiments were conducted, as shown in the supporting information.

3. Results and discussion

3.1. Synthesis and characterization

$ZnWO_4$ sample was prepared by hydrothermally treating $Zn(NO_3)_3{\cdot}6H_2O$ and $Na_2WO_4{\cdot}2H_2O$ in water as the solvent. $ZnWO_{4-x}$ sample with oxygen vacancies were prepared by solvothermally treating $Zn(NO_3)_3{\cdot}6H_2O$ and $Na_2WO_4{\cdot}2H_2O$ in water/ethanol/PEG-400 mixture as the solvent, where ethanol could act as a reducing agent to selectively remove some oxygen atoms from the sample surface via redox reaction between $ZnWO_4$ and ethanol. The phases of $ZnWO_4$ and $ZnWO_{4-x}$ samples were analyzed by X-ray powder diffraction (XRD). XRD patterns (Fig. 1) reveal that both samples have some strong diffraction peaks at 15.5°, 18.9°, 23.8°, 24.6°, 30.5° and 36.4°, which can be respectively indexed to (010), (100), (011), (110), (111) and (021) crystal planes of monoclinic sanmartinite phase of $ZnWO_4$ with wolframite structure (JCPDS Card no. 15–0774) [28–30]. Furthermore, compared with the diffraction peaks from $ZnWO_4$, $ZnWO_{4-x}$ sample have the weakened but broadened diffraction peaks, due to oxygen atoms displacement that resulted in compressive stress state and lattice distortion. These broadening of diffraction peaks has been observed in other tungstate nanomaterials such as Bi_2WO_6 with oxygen deficiencies [23,31].

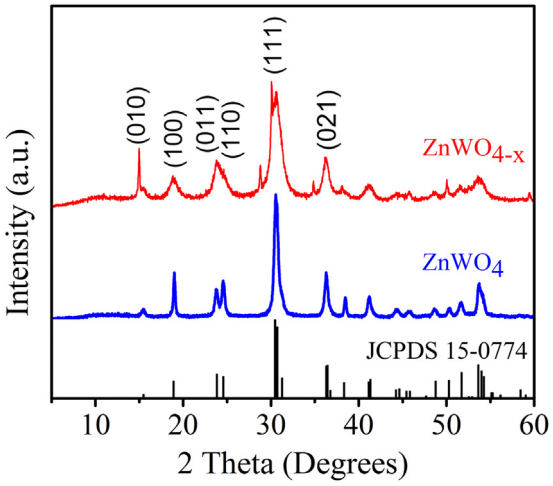

Fig. 1. XRD patterns for $ZnWO_4$ and $ZnWO_{4-x}$.