Materials Letters 101 (2013) 99–102

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Synthesis of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites: An effective approach for photoinactivation of green tide under simulated solar light

Tae-Ho Kim [a], Yong-Hyun Jo [a], Gobinda Gyawali [a], Rajesh Adhikari [a], Tohru Sekino [b], Soo-Wohn Lee [a,*]

[a] Research Center for Eco Multi-Functional Nano Materials, Sun Moon University, Galsan-ri, Tangjung-Myon, Asan Chungnam, Republic of Korea
[b] Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Aoba-ku, Sendai, Japan

ARTICLE INFO

Article history:
Received 4 February 2013
Accepted 16 March 2013
Available online 25 March 2013

Keywords:
$TiO_{2-x}N_y$
Ag–$PbMoO_4$
Green tide
Simulated solar light
Photocatalyst

ABSTRACT

The $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites were prepared by sonochemical method. The as-prepared powders were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and diffuse reflectance UV–vis spectroscopy (UV–vis-DRS). The results revealed that the band gap energy absorption edge of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites red shifted as compared to $TiO_{2-x}N_y$ and Ag–$PbMoO_4$. According to FE-SEM studies, Ag–$PbMoO_4$ gets to be decorated with evenly distributed $TiO_{2-x}N_y$ nanoparticles. The photocatalytic activity of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites for photoinactivation of green tide (*Tetraselmis suecica*) under simulated solar light was enhanced as compared with $TiO_{2-x}N_y$ and Ag–$PbMoO_4$. The $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites showed the highest percentage (100%) of removing of *Tetraselmis suecica* after 25 min. The $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposite may facilitate the charge transfer process more efficiently by inhibiting electron–hole recombination, which enhanced the photocatalytic activity.

1. Introduction

Recently, semiconductor photocatalysts have been attracted much attention because of their high photocatalytic activity and chemical stability. Various heterogeneous photocatalysts have been utilized for many practical applications such as the purification of water and soil polluted with organic compounds [1,2] and, the photocatalytic decomposition of toxic agents in water [3].

Every year, massive red and green tides have been occurring in coastal waters around the world. Red and green tides are well known names of harmful algal bloom (HAB). The most evident effects of these kinds of red and green tides are associated with wildlife mortalities of marine and coastal species of fish, birds, marine mammals, and cause great economic loss and ecological damages. These events are continuously observed in oceans, rivers and lakes all over the world [4,5]. Recently, TiO_2 and nitrogen doped TiO_2 have been synthesized for different photocatalytic proposes [6–8]. It has been reported that microorganisms such as *Escherichia coli* [9–11], marine algae [12–14], fungi [15], and virus [16] are inactivated by using TiO_2 photocatalyst.

The aim of this research is to find an alternative way to deactivate green tide by employing heterogeneous photocatalysts. Ag–$PbMoO_4$ was selected as a starting material due to the fact that $PbMoO_4$ also has been used for photocatalytic purpose because this compound has comparable band gap energy to that of TiO_2. Moreover Ag nanoparticles have antibacterial and antifungal effects. Therefore, we fabricated the $TiO_{2-x}N_y$/Ag–$PbMoO_4$ composite photocatalyst. The $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites were prepared by sonochemical synthesis and characterized by means of XRD, UV–vis diffuse reflectance, and FE-SEM. The photoinactivation of *Tetraselmis suecica* (green tide) was performed to evaluate the nanocomposites under simulated solar light.

2. Experimental

Preparation of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites: In the preparation of $TiO_{2-x}N_y$, anatase TiO_2 (1.0 g) was finely milled with urea (2.0 g, oriental chemical industries), and then this combination was heated in a covered crucible at 400 °C for 2 h. The yellow-colored product was crushed and washed well with nitric acid (0.1 mol/L) and distilled water to remove any residual alkaline species adsorbed on the sample surface, and dried at 70 °C [17].

Ag–$PbMoO_4$ nanoparticles were prepared by a co-precipitation method using aqueous solutions of $Pb(NO_3)_2$ (Sigma-Aldrich, 99%) and H_2MoO_4 (Sigma-Aldrich, 85%). The aqueous solution of $Pb(NO_3)_2$ was added drop-wise into the H_2MoO_4 solution with vigorous stirring. The pH of mixture solution was adjusted to 10 with NH_4OH (J. T. Baker, 30%) and the solution was stirred for 30 min. After that, 0.3 mol% of $AgNO_3$ (Sigma-Aldrich, 99%) was photo-reduced into the reaction solution and the sonochemical synthesis was performed at 20 kHz, 1000 W for 2 h to get the

* Corresponding author.
E-mail address: swlee@sunmoon.ac.kr (S.-W. Lee).

0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.03.087

products. Finally, the solvent was washed and dried at 70 °C. After drying, the product was calcined at 400 °C for 2 h.

$TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites were prepared by sonochemical synthesis of $TiO_{2-x}N_y$ with Ag–$PbMoO_4$ and citric acid in a mixture of degassed ethanol, and exposed to ultrasonic irradiation (20 kHz, 800 W) for 2 h. First, 1 g of Ag–$PbMoO_4$ and 0.02 g citric acid were added to 200 mL of degassed ethanol and placed in ultrasonic irradiation for 10 min to assure its complete disaggregation. Then, 1 g of $TiO_{2-x}N_y$ were added to the mixture and placed in ultrasonic irradiation. The obtained precipitate was washed and dried at 70 °C.

Characterization of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites: The structure phase and surface morphology of the nanocomposites were characterized by X-ray diffraction (XRD, RIGAKU D/MAX2200HR diffractometer) analysis using a Cu-Kα radiation ($\lambda = 1.5406$ Å) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-7000F). The diffuse reflectance spectroscopy (DRS, JASCO V-570) spectra were obtained on a UV–vis spectrophotometer equipped with a reflectance sphere.

Photoinactivation of green tide: In a Petri dish 75 mL capacity, 25 mg of photocatalyst were suspended in a dispersion of 50 mL of *Tetraselmis suecica* (green tide) whose initial concentration was $250 \pm 20 \times 10^3$ cell mL^{-1}(Natural Live Plankton Co. Ltd.). Then, the suspension was magnetically stirred and exposed to simulated solar light irradiation (Portable solar simulator PEC-L01, Pecell) (Am 1.5 G). The experiments were performed at room temperature for 40 min, and 100 μL of the suspension were collected at every given irradiation time intervals and analyzed with an optical microscope (Optinity KB-200i) equipped with a CCD camera in order to obtain the counting living cells concentration. For comparative purposes, photoinactivation experiments were performed using $TiO_{2-x}N_y$-coupled Ag–$PbMoO_4$ nanocomposites, $TiO_{2-x}N_y$ and Ag–$PbMoO_4$. All the photoinactivation experiments were repeated at least twice.

3. Results and discussion

Characterization of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites: The XRD patterns for the $TiO_{2-x}N_y$, Ag–$PbMoO_4$ and $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites are shown in Fig. 1. The $TiO_{2-x}N_y$ nanoparticles correspond to the anatase TiO_2 crystalline structure (JCPDS 84-1286); no peaks for the rutile and brookite phases were detected. There is no diffraction peak for Ti–N, which can be attributed to the small amount of the doped nitrogen. The Ag–$PbMoO_4$ nanoparticles were correctly assigned to the tetragonal scheelite crystalline structure (JCPDS 74-1075). However, the diffraction patterns of Ag phase were not detected by XRD. One probable reason might be due the concentration of Ag particle was lower than the detection limit by XRD. Moreover, it can be confirmed that the $TiO_{2-x}N_y$ exhibits small broad peaks in the $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites. The average crystallite size, which was calculated according to the broadening of XRD peak using Scherrer's equation were 56, 170 and 122 nm for $TiO_{2-x}N_y$, Ag–$PbMoO_4$ and $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites, respectively. This result indicates different crystallite size of $TiO_{2-x}N_y$-coupled Ag–$PbMoO_4$ nanocomposites, which can be ascribed to the inhibition of aggregation of Ag–$PbMoO_4$ by the $TiO_{2-x}N_y$ nanoparticles during sonication.

The diffuse reflectance UV–vis spectra of the $TiO_{2-x}N_y$, Ag–$PbMoO_4$ and $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites are shown in Fig. 2. Compared to the absorption of Ag–$PbMoO_4$ (~378 nm), the absorption edge of $TiO_{2-x}N_y$ has an intense absorption in the visible region at 426 nm. For the $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites, the absorption edge was founded at around 414 nm. The absorption edge for the $TiO_{2-x}N_y$-coupled Ag–$PbMoO_4$ nanocomposites indicates that the Ag–$PbMoO_4$ be responded to visible region by combined with $TiO_{2-x}N_y$ [18]. The absorption edge of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites shifted towards longer wavelengths as compared to Ag–$PbMoO_4$. The absorption coefficient α could be calculated according to the Kubelka–Munk method based on the diffuse reflectance spectra [19–21], the estimated band gap energies for the photocatalysts are 2.91 eV, 3.28 eV and 3.00 eV for the $TiO_{2-x}N_y$, Ag–$PbMoO_4$ and $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites, respectively.

The particles morphology of $TiO_{2-x}N_y$/Ag–$PbMoO_4$ nanocomposites synthesized by the sonochemical method is shown in Fig. 3. It can be seen that the Ag–$PbMoO_4$ particles get decorated with evenly distributed $TiO_{2-x}N_y$ nanoparticles. It was found that the morphology of the Ag–$PbMoO_4$ was an incipient tendency of them to form polyhedron. The sonochemically synthesized

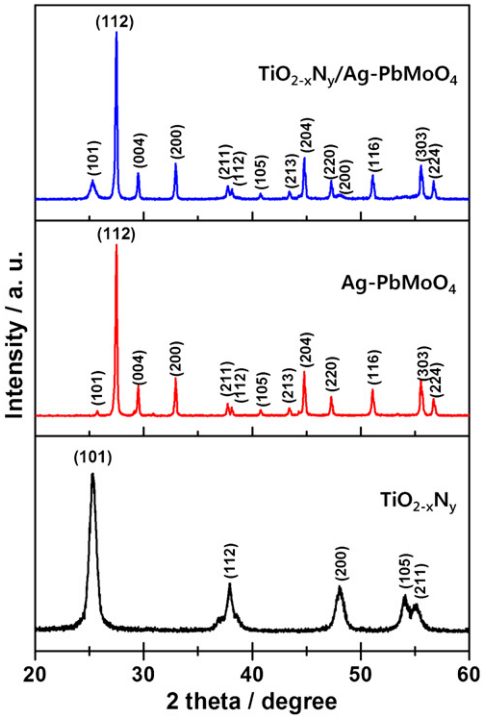

Fig. 1. XRD patterns of as synthesized powders.

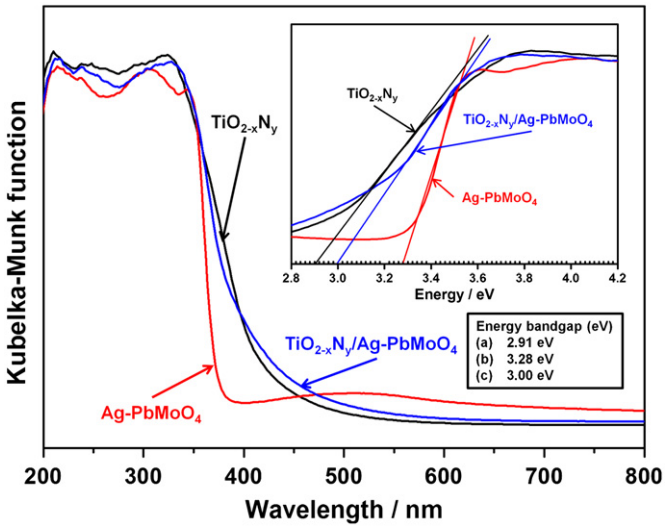

Fig. 2. Diffuse reflectance UV–vis spectra of as synthesized powders.