International Journal of Biological Macromolecules 120 (2018) 1789–1793

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: http://www.elsevier.com/locate/ijbiomac

Preparation and characterization of WS_2 decorated and immobilized on chitosan and polycaprolactone as biodegradable polymers nanofibers: Photocatalysis study and antibiotic-conjugated for antibacterial evaluation

Ali Fakhri [a,*], Vinod Kumar Gupta [b,*], Hanieh Rabizadeh [c], Shilpi Agarwal [b], Nima Sadeghi [d], Shiva Tahami [e]

[a] Young Researchers and Elites Club, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] King Abdullah University Jedhah, Saudi Arabia
[c] Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[d] Department of Environmental Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran
[e] Department of Biology, Karaj Branch, Islamic Azad University, Karaj, Iran

ARTICLE INFO

Article history:
Received 28 July 2018
Received in revised form 25 September 2018
Accepted 27 September 2018
Available online 02 October 2018

Keywords:
Tungsten disulfide
Nanofibers
Photocatalytic activity
Antibiotic conjugated

ABSTRACT

In the present work, WS_2 nanoparticles and immobilized on chitosan and polycaprolactone as biodegradable polymers as photocatalyst were developed and studied for photocatalytic degradation of representative Neomycin as an aminoglycoside antibiotic. The WS_2 nanoparticles were synthesized using the hydrothermal method. Further, the photocatalyst were characterized by different analytical instruments energy dispersive X-ray spectrometer (EDS), scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and UV–Vis absorption spectroscopy, in order to understand their physical and optical properties. The mean crystallite sizes of WS_2 nanoparticles, WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers were 80.00, 70.14 and 68.71 nm, respectively. The optical absorption study revealed the presence of direct band-to-band transition with band-gap ranging from 2.0 to 1.8 eV for WS_2, WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers, respectively. The photocatalytic activity of the three photocatalyst was tested by UV-light-induced degradation of Neomycin antibiotic. The WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers photocatalyst showed high amount of photodegradation in comparison to WS_2 nanoparticles. The optimum degradation using WS_2, WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers occurred under UV light at pH:7 in 40 min. The bactericidal test was determined under light illumination (visible source light) and that the neomycin conjugated WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers demonstrated good efficiency in antibacterial efficiency compared to pure WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers.

1. Introduction

Photocatalysis has received considerable attention all over the world because water pollution from different industries is among trending issues recently. Almost all pharmaceutical industries have released their pollutants as a wastewater in the environment. This issue is a major source of water pollution because pharmaceutical effluents contain a large group of non-biodegradable, toxic and carcinogenic organic compounds, which are harmful to the living organisms as well as environment. Accordingly, it is more vital to improving effective and economical routs for water treatment. So far, various techniques have been employed for water treatment like as membrane filtration, adsorption, flocculation, coagulation and particularly the photocatalytic degradation [1,2]. Out of them, the photocatalytic degradation is found to be a favorable and most effective technique to eliminate contaminants from wastewater. In concern to this semiconducting nanomaterial, in particular, metal oxides are proved to be an effective photocatalyst for wastewater treatment [3,4].

Among several semiconducting metal sulfides, Tungsten disulfide (WS_2) is a significant p-type semiconductor with great band-gap of about 2.0 eV and high electrical conductivity with moderate refractive index. This makes it constructive material for numerous applications such as photovoltaic [5], gas sensors [6], solar cells [7], optoelectronics [8], photosensors [9], and photocatalysis applications [10].

Therefore, considering the aforementioned facts, in the present research work, WS_2, WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers were used for the photocatalytic and antibacterial activity. The influence of the prepared samples with respect to the surface,

* Corresponding authors.
E-mail addresses: ali.fakhri88@yahoo.com (A. Fakhri), vinodfcy@gmail.com (V.K. Gupta).

https://doi.org/10.1016/j.ijbiomac.2018.09.207
0141-8130/

opt-electronic properties were also investigated and elucidated. Moreover, the photocatalytic activity of prepared samples is carried out to study the photodegradation of neomycin.

2. Materials and methods

2.1. Synthesis of catalyst

All the chemical compounds were purchased from Sigma-Aldrich Co., USA.

2.1.1. WS_2 nanoparticles

The aqueous solution of 0.005 M $(NH_4)_6W_7O_{24}.4H_2O$, 0.02 g PVP and C_2H_5NS (0.04 M) were mixed. Then the aqueous solution of acetic acid (40 mL, 5 vol%) was added to above mixture under vigorous stirring and put in a Teflon autoclave. The autoclaves were sealed at 140–190 °C for 8 h. The precipitates were washed and dried in vacuum at 100 °C for 3 h.

2.1.2. Polycaprolactone (PCL) and chitosan (CS) nanofibers

The suspension of PCL (M_w = 80,000) solution is taken into a syringe pump with flow rate of 1 mL/h, and voltage of 13–15 kV, with metallic needle of approximately 0.1 mm at 25 °C, and relative humidity 50–60% and a silicon substrate (6 cm) was applied on the needle tip to reap the PCL nanofibers and the chitosan nanofibres were prepared using the same method as reported elsewhere [11].

2.1.3. WS_2/CS nanofibers and WS_2/PCL nanofibers

The WS_2 nanoparticles coated CS nanofibers and PCL nanofibers were synthesized by dipping the CS nanofibers and PCL nanofibers in above suspensions i.e. aqueous solution of 0.005 M $(NH_4)_6W_7O_{24}.4H_2O$, 0.02 g PVP and C_2H_5NS (0.04 M) (Mentioned 2.1.1. section) and continued as pervious method.

2.2. Characterization tools

XRD analysis is carried out using Philips X'Pert for the determination of crystal structure and phase. The SEM and EDS investigation was made by using SU-800 (Hitachi High Technology Corporation Tokyo, Japan) for the analysis of surface and chemical composition of the prepared samples. The prepared samples were characterized by JASCO V-630 UV–Vis spectrophotometer for the study of their optical properties as well as photocatalytic degradation properties.

2.3. Photocatalytic activity experiment

The photo-degradation of Neomycin (NEO) as an aminoglycoside antibiotic (as models of water pollutants) using prepared samples under UV-light irradiation, were carried. Philips mercury lamp (11W, 254 nm) was used as a source of UV-light irradiation for photocatalytic study. Initially, NEO solutions of 10 ppm concentration were prepared in distilled water. In the actual photocatalytic experiment, 60 mL NEO solutions were taken in three separate 100 mL beakers containing of photocatalyst. With the help of UV–Vis spectrophotometer (JASCO V-630), the change in characteristic absorbance of NEO solutions were measured to evaluate the photocatalytic activity of WS_2/CS nanofibers or WS_2/PCL nanofibers. The degradation efficiencies (D) were calculated using the equation from the previously reported studies [12–16]:

2.4. Preparation of Neomycin on WS_2/CS nanofibers or WS_2/PCL nanofibers

The solution of NEO was prepared by dissolving 0.86 g of NEO into acetone. The NEO-WS_2-CS or NEO-WS_2-PCL nanocomposites were prepared by mixing a solution of NEO (5 mg/mL) with a known weight of each WS_2/CS nanofibers or WS_2/PCL nanofibers (40 mg/mL). The solution was magnetically stirred at 25 °C for 10 h to comfort NEO uptake.

2.5. Bactericidal efficiency

Bactericidal activity was performed by using *Escherichia coli* and *Staphylococcus aureus* as the standard negative/positive bacterium according to the shaking flask method. The prepared nano samples (0.2 g) were mixed with 20 mL of saline water (0.75 mM) and bacteria 10^8 CFU/mL under visible light irradiation. The suspension was separated after a 120 min process and diluted. The diluted solution was incubated at 60 °C for one day [17].

3. Results and discussion

3.1. Structural studies

XRD patterns are shown in the Fig. 1A–C for WS_2, WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers, respectively. From the Fig. 1(A), the characteristic peaks observed at 2θ values of 28.51, 32.04, 38.46, 48.43, 58.07, and 62.40° correspond to (004), (100), (103), (105), (110), and (112) planes, respectively. It is observed that the diffraction peaks of all samples are well defined and all the samples exhibit hexagonal phase of WS_2 (JCPDS no. 08-0237) crystalline phase [18]. The peak at 2θ = 25° is observed due to the amorphous crystal structure of chitosan nanofibers and polycaprolactone nanofibers. The crystallite size of WS_2, WS_2/chitosan nanofibers and WS_2/polycaprolactone nanofibers was calculated using Scherrer formula [19] and it was 80.00 nm, 70.14 nm and 68.71 nm, respectively.

3.2. Morphological studies

Fig. 2(A and B) showed the SEM image and EDS spectra of WS_2 nanoparticles. It indicates that the particles are almost spherical shape with a narrow size distribution. EDS study showed that the sample contains Tungsten (W), and sulfur (S). Fig. 2C, E demonstrated the surface morphology of nanofibers from chitosan nanofibers and polycaprolactone nanofibers. All nanofibers show a continuous and smooth fibrous

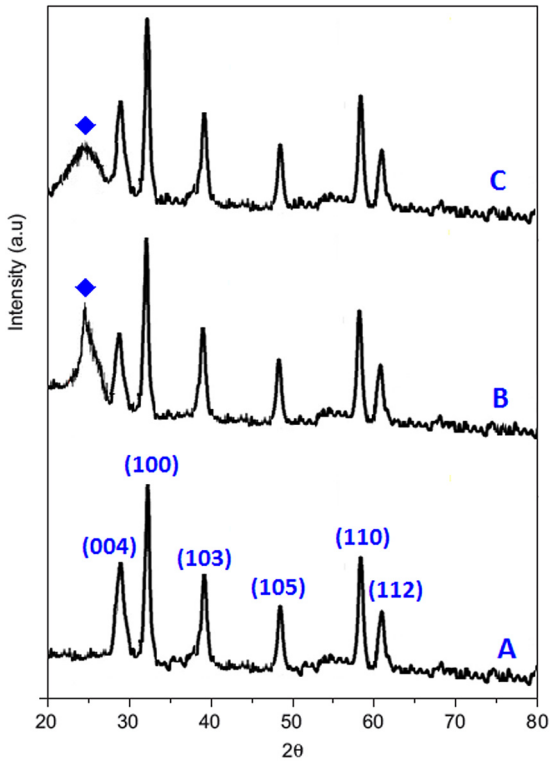

Fig. 1. XRD patterns of the WS_2 nanoparticles (A), WS_2/chitosan nanocomposites (B) and WS_2/polycaprolactone nanocomposites.