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Synthesis of MoO_3 microrods via phytoconsituents of *Azadirachta indica* leaf to study the cationic dye degradation and antimicrobial properties

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ABSTRACT

This work is to report an environmental benign route for the fabrication of MoO_3 (MO) microrods using leaf extract of Azadirachta indica. The optical, structural, compositions and specific surface area properties of the MO microrods were characterized by UV-DRS, PL, FT-IR, XRD, SEM, EDX, and BET technique. Methylene blue (MB) dye was used to assess the photocatalytic activity of Azadirachta indica leaves modified MoO_3 (AzI-MO) microrods under visible irradiations. Controlling various parameters such as AzI-MO dosage, initial MB concentration, and pH value of (cationic dye) MB solution can lead to the enhancement of the photocatalytic degradation of the microrods. The pseudo-first order kinetics was followed by AzI-MO. The antimicrobial performance of MO and AzI-MO were tested, and it shows tremendous activity against gram positive, gram negative and fungal strain.

1. Introduction

Transition metaloxide photocatalysis is a favorable move towards environmental remediation purpose and garners as much consideration as their unique optical, magnetical, electronic properties etc. [1,2]. These properties grasps assures for remarkable performance in the field of application, including catalytic, magnetic, mechanical and biological application. MoO_3 is the well-studied semiconductor with superior properties and are extensively used as active material in photoelectrocatalysis, sensors, superconductor and in lithium ion batteries. Additionally, CdS/MoS_2 [3], TiO_2/MoS_2 [4] and g-C_3N_4/MoS_2 [5] photocatalyst are designed as a probable co-catalyst for visible-light-driven photocatalysis activity.

There have been a huge number of synthesis method were used to produce MoO_3 microrods such as evaporation of Mo foil by IR [6], direct oxidation [7], flash evaporation [8], hydrothermal method [9], precipitation method [10] and microwave plasma process [11]. Since most of these methods are radically expensive and also incorporate with the use of toxic, a hazardous chemical which may acquire potential environmental and biological risks. As a result, growth of biocompatible, non-hazardous, clean and ecological method for nanoparticles preparation has deserved the pros.

The use of natural organisms such as the microorganism, plant extract and plant biomasses are purposeful on operation of the environment-friendly, worthwhile and biocompatible reducing agent for the production of nanoparticles. Methodical agreement from several scientific investigations implies that various plant, herbs and spices contain the highest level of powerful antioxidants as the phytochemical constituent in their roots, stems, fruits and leaves [12–15]. These non-toxic antioxidants can decrease the metal ion and concurrently they shield from the aggregation of metal oxide nanoparticles. For example, green synthesis of Hematite using green tea leaves [16] and ZnO using Acalypha indica [17].

In our earlier account the $NiWO_4$ was synthesized using

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Azadirachta indica (neem) by effortless co-precipitation method shows an admirable photocatalytic activity [18]. Azadirachta indica leaves extract contains various types of phytochemicals like alkaloids, flavonoids, triterpenoids, saladucin, valassin, meliacin, nimbidin, geducin and Azadirachtin, that performs as a reducing as well as capping agent [19]. The tree has some therapeutic function such as in the cure of human ailments and domestic pesticide [20,21]. The plant extract shows a resistance against more than 500 pathogens [22].

In the current work, we report the novel class of synthesized MoO_3 microrods by means of leaf extract as a reducing and capping agent through green synthesis. Methylene blue a cationic dye was selected as a model toxin for the photodegradation study of AzI-MO. The various reaction parameters like catalyst concentration, dye concentration and pH influencing the photodegradation of MB were analyzed. AzI-MO microrods were explored regarding their prospective antimicrobial application.

2. Experimental methods

2.1. Preparation of Azadirachta indica leaf extract

The Azadirachta indica leaves on the uppermost branches were collected from Theni District and the leaves was washed with double distilled water to eliminate the contaminants and Azadirachta indica leaves were sliced to suitable size. In a wide neck borosil conical flask 100 mL of distilled water and 10 g of the fresh leaves exposed to boiling for 30 min. The resultant rough and ready extract was percolate by No.1 Whatman and used for the production of MoO_3 microrods [23].

2.2. Production of MoO_3 microrods

Appropriate amounts of $Na_2MoO_4 \cdot 2H_2O$ were mixed with 5 mL of the plant extract followed by stirring for 3 days. Dilute HCl were used to acidify $Na_2MoO_4 \cdot 2H_2O$ to obtain the molybdic acid precipitate and further matured for 2 days without disruption. The precipitate was detached by centrifugation, washed cautiously with double distilled water and to attain fine particles it is dried in an oven at 50 °C and to eliminate the volatile foreign matter [24] and to increase the crystallinity of the microrods it is calcinated for 4 h at 500 °C in the muffle furnace. The same method is followed devoid of leaf extract for the preparation of MoO_3.

2.3. MoO_3 microrods characterization

After production of microrods, the fine particles was monitored by UV–vis-DRS using Shimadzu UV-2450 spectrophotometer for optical properties of MoO_3 at a wavelength of 200–800 nm. Photoluminescence emission was measured using a Horiba Fluorolog – 3 modular spectrofluorometer at an excitation wavelength of 350 nm and recorded over the range 360 nm–500 nm. JASCO-FT-IR-460 plus was used to characterized the surface structure. The crystallinity and phases of AzI-MO were characterized by X-ray diffractometer (XRD; XPERT PRO X-RAY) with Cukα radiation ($\lambda = 1.5412$ Å) in the range of 10°–80° and the JCPDS powder diffraction files for the reference of the structural assignments. Additionally scanning electron microscopy (SEM) image were obtained (JSM 6701F–6701). EUTECH instrument pH meter was used to observe the pH.

2.4. Photocatalytic activity evaluation

Visible light is irradiation on MB (model dye) at pH 10, the photodegradation of AzI-MO microrods was deliberated. In a cylindrical glass container, 300 mL solutions of MB with a definite quantity of photocatalyst were engaged, which was bounded by a circulating water jacket to cool the visible light source. To provide a continous source of dissolved oxygen an air pump was introduced in the dye solution. Before irradiation, the MB solution was vigorously stirred in the absence of light for 15 min to make sure that the suspension is homogeneous [25,26]. A 300 W Xe arc light source with an cut-off filter of ultraviolet ($\lambda > 400$ nm) was used. All through the course of irradiation, at a regular time intermission of 15 min 5 mL supernatant solutions were withdrawn. The remaining concentration of dye present in the supernatant solution was determined using UV–visible absorption spectrophotometer at 660 nm using the following equation:

$$Photodegradation(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where initial concentration of MB is C_0 and concentration of MB after 15 min of time interval is C.

2.5. Antimicrobial assay

Antimicrobial analysis was followed using standard agar well diffusion method to study the antimicrobial activity of MO and AzI-MO. *Staphylococcuses aureus* (Gram positive), Escherichia *coli* (Gram negative) (bacterial strain) and *Aspergillus flavus*, *Candida albicans (fungal strain)* were used for the analysis. Sterile cotton swab was used on ager plate to develop the lawn of investigation organism. Five-millimeter diameter wells were cut from the agar using a sterile cork-borer and dissolved samples solution (200 mg in 1000 mL DMSO) were poured into the wells and ketoconazole as a reference drug. The samples were incubated for 24 h at 37 °C. The inhibition of microbes was measured in diameter (millimetres) [27].

3. Result and discussion

3.1. Characterization

In Fig. 1 (a) shows the light absorption characteristics of electronic state of MoO_3 microrods. It could be found that after modification with plant extract the resulting AzI-MO microrods exhibited a characteristic absorption at 533 nm (ie red shifted). The shift is well to agree with the color change of AzI-MO from bright yellow to dark gray during synthesis of microrods (clearly indicates the formation of metal oxide). By using Tauc approach the band gaps can be evaluated [28].

$$\alpha h\nu = A(h\nu - Eg)^n \quad (2)$$

A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ afforded band gap of the samples. Tauc plot of MO and AzI-MO were depicted in Fig. 1(b) and (c). The excellent visible light photocatalytic activity of AzI-MO (2.25 eV) is due to narrow band gap of microrods when compared to MO (3.05 eV).

Fig. 2 shows the emission peak at 445 nm, 459 nm and 485 nm of the photoluminescence spectra of MO and AzI-MO. The peak positioned at 445 nm and 459 nm might match to the band-to-band transition. It is detected that AzI-MO has a lower intensity than MO due to slow recombination rate of photogenerated electron-hole pair, which may own a higher photocatalytic activity. This can be attributed to π-π^* (HOMO-LUMO) transition of the phytochemical backbones. It may be recalled that UV–vis absorption spectra showed an increase visible light absorption for plant extract modified than chemical synthesized microrods.