GREEN BIOSYNTHESIS OF SnO$_2$ NANOPARTICLES BY PLECTRANTHUS AMBOINICUS LEAF EXTRACT THEIR PHOTOCATALYTIC ACTIVITY TOWARD RHODAMINE B DEGRADATION

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In this paper, we report the first time preparation of SnO$_2$ nanoparticles (NPs) using a green chemistry method. The leaf extract of Plectranthus amboinicus was used as reducing and stabilization agent for synthesizing SnO$_2$ NPs. The synthesized SnO$_2$ NPs were characterized by SEM, EDX, XRD and UV-vis spectroscopy. Results showed that the biosynthesized SnO$_2$ NPs owing a high purity. The photocatalytic property of the biosynthesized SnO$_2$ NPs was investigated by photodegradation of rhodamine B (Rh B) under visible light illumination. Results indicated that the photocatalytic performance of the biosynthesized SnO$_2$ NPs is much higher than that of commercial SnO$_2$. Moreover, the biosynthesized SnO$_2$ also exhibited an excellent reusability.

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1. Introduction

Numerous efforts have been made to development of semiconductor nanoparticles (NPs) in the last two decades due to their novel optical, chemical, photo-electrochemical and electronic properties which are different from that of bulk. Stannic oxide (SnO$_2$) is a well know n-type wide-bandgap (E$_g$ = 3.6 eV) semiconductor. Nano-sized SnO$_2$ is regarded as a highly preferred multitasking metal oxide, such as gas sensors and lithium rechargeable batteries [1-13]. SnO$_2$ NPs are commonly synthesized by wet chemical route [14, 15], vapor phase process [16, 17], hydrothermal method [18-20], precipitation [21, 22], electrodeposition and sonochemical method [23-25]. However, chemical methods lead to the presence of some toxic chemicals adsorbed on the surface that may have adverse effects in applications and environment. Thus, to design a simple and green route to synthesize SnO$_2$ NPs is of considerable necessary.

Recently, development of an eco-friendly method for the synthesis of nanoparticles via biological methods has been attracted lots of attentions. Using bacterial, fungi and plant extract are three main routes for biosynthesis of nanomaterials. For example, Singh et al. [26] reported the synthesis of ZnO NPs using the cell extract of the cyanobacterium, Anabaena strain L31. Jain and co-workers reported the preparation of ZnO NPs using the extracellular fungal proteins [27]. Jayaseelan et al. [28] demonstrated the synthesis of Au NPs using seed aqueous extract of Abelmoschus esculentus. Among them, synthesis of nanomaterials using plant extract attracted lots attention by researchers due to its lower cost and simplicity. To the authors’ best knowledge and review of the literature, the biosynthesis of SnO$_2$ only conducted by using bacterium Erwinia herbicola as reducing agent [29].

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Plectranthus amboinicus is a tender fleshy perennial plant in the family Lamiaceae with an oregano-like flavor and odor. The biogenic synthesis performance of Plectranthus amboinicus has been tested by Ajitha et al. [30]. They reported the utilization of Plectranthus amboinicus leaf extract as reducing agent for synthesizing Ag NPs. The synthesized Ag NPs exhibited an excellent antimicrobial property. Herein, we report for the first time synthesis of SnO\(_2\) NPs using Plectranthus amboinicus leaf extract as reducing agent. A series of techniques have been used for characterizing biosynthesized SnO\(_2\) NPs. The photocatalytic activity of biosynthesized SnO\(_2\) NPs was then evaluated by photodegradation of RhB under visible light.

2. Experimental

2.1 Materials

Plectranthus amboinicus plants were purchased from a local nursery of Zhejiang province, China. The plant was taxonomically identified and authenticated by the botanical survey of Hangzhou botanical garden. The plant leaves were cleaned with double distilled water. Then, 5 g of Plectranthus amboinicus leaves were washed with water and cut into small pieces. The leaf extract was obtained sonication of leaves for 1 h. Then, the extract was collected, filtered through Whatman No. 1 filter paper and stored in refrigerator for further experiments. Tin(II) chloride dehydrate (SnCl\(_2\)•2H\(_2\)O) and rhodamine B (Rh B) were purchased from Sigma-Aldrich. All other chemicals used were analytical grade reagents without further purification.

2.2 Biosynthesis of SnO\(_2\) NPs

For synthesis of SnO\(_2\) NPs, 0.5 M zinc nitrate solution was prepared with 30 mL water. Then 20 mL Plectranthus amboinicus leaf extract was added to above solution and stirring for 10 min. Afterward, 0.5 mL H\(_2\)SO\(_4\) (5 M) was added into the above dispersion. The suspension was transferred to 50 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 200°C and maintained for 3 h in an oven and naturally cooled down to the room temperature. The sediments were centrifuged, washed with water, and calcined at 300°C for 2 h to result SnO\(_2\).

2.3 Characterization of the synthesized SnO\(_2\) NPs

The morphology of as-synthesized SnO\(_2\) NPs was observed using a ZEISS, SUPRA 55 field emission scanning electron microscopy (FESEM) measurements. The particle size of the biosynthesized SnO\(_2\) NPs was measured using a particle size analyzer (SALD-7500nano, SHIMADZU). The crystal phase information of sample was characterized from 20° to 80° in 2θ by a XRD with Cu Kα (λ = 0.1546 nm).radiation (D8-Advanced, Bruker). The optical analysis was obtained by UV-vis spectrophotometer (Perkin Elmer Lambda 950).

2.4 Photocatalytic activity evaluation

The photocatalytic activity of the biologically synthesized SnO\(_2\) NPs and commercial SnO\(_2\) was compared by degradation of RhB in aqueous solution as a model system. The visible light used in the present study was obtained using the filter with cut-off wavelength of 420 nm. In a typical photodegradation process, 20 mg sample was added to 10 ml of RhB (20 mg/L) solution. The absorbance spectrum of the solution was monitored using UV-Vis spectrophotometer at wavelength 553 nm at different time intervals.

3. Results and discussion

The morphology of biosynthesized SnO\(_2\) NPs was observed by SEM. Figure 1 shows the SEM images of SnO\(_2\) NPs at different magnifications. It can be seen that the formed SnO\(_2\) NPs
show a cluster structure. Due to the aggregation, the individual size of the biosynthesized SnO$_2$ cannot be measured visually. The particle size analyzer indicated the average size of the biosynthesized SnO$_2$ NPs is 63 nm.

![Fig. 1: SEM images of biosynthesized SnO$_2$ at (A) low and (B) high magnification.](image)

Fig. 2A displays the EDX spectrum of biosynthesized SnO$_2$ NPs, which confirmed the presence of elemental stannum and oxygen signals. No other impurity element was observed in the sample, indicating the high purity of the biosynthesized SnO$_2$ after calcination process. Therefore, using *Plectranthus amboinicus* leaf extract for SnO$_2$ synthesis is a reliable method.

The crystal structure of the biosynthesized SnO$_2$ NPs was characterized by XRD. Figure 2B represents the XRD pattern of biosynthesized SnO$_2$ NPs, which displays various well-defined diffraction peaks. It can be observed that the diffraction peaks at 26.75°, 37.88°, 39.35°, 51.95°, 54.50°, 57.93°, 62.09°, 64.95°, 66.08°, 69.32°, 71.70° and 79.13° can be indexed to (110), (200), (111), (211), (220), (002), (310), (112), (301), (202) and (321) crystal planes of tetragonal SnO$_2$ (JCPDS card No. 41-1445). It is worth noting that the diffraction peaks related to any impurities were not observed, further indicating the proposed biosynthesis route could be applied for high purity SnO$_2$ NPs production.

![Fig. 2. (A) EDX spectrum and (B) XRD pattern of biosynthesized SnO$_2$ NPs.](image)

The light absorbance properties of biosynthesized SnO$_2$ NPs were investigated using UV-vis spectroscopy and its disuse reflectance. Figure 3A shows the diffuse absorption spectra of commercial SnO$_2$ and biosynthesized SnO$_2$ NPs. It can be clearly observed that the biosynthesized SnO$_2$ NPs exhibit a higher absorbance than commercial SnO$_2$. From the reflectance spectrum of SnO$_2$ NPs (Figure 3B), we also can observe a high light reflectance, which light could result in a
high rate of light harvesting [31]. The high absorbance and scattering of the SnO$_2$ NPs can increase the number of photo-generated electrons and holes to involve in the photocatalytic reaction and enhance the photocatalytic performance [32].

\[\frac{-dC}{dt} = \frac{k_{L-H} K_{ad} C}{1 + K_{ad} C'}\]

Where $K_{ad}$ is the adsorption coefficient of the reaction on SnO$_2$ NPs, $k_{L-H}$ is the reaction rate constant and $C$ is the concentration at any time $t$.

\[\ln\left(\frac{C_0}{C}\right) = K (C - C_0) + k_{L-H} K_{ad} t\]

Where $C_0$ is the initial concentration. Because the $K_{ad} C$ is very small, Thus it can be simplified and integrated as:

\[\ln\left(\frac{C_0}{C}\right) = k_{L-H} K_{ad} t = kt\]

Where $k = k_{L-H} K_{ad}$ is the first order reaction rate constant.

The photocatalytic activity of the biosynthesized SnO$_2$ NPs was investigated by photodegradation of RhB, and compared with commercial SnO$_2$. The Langmuir and Hinshelwood models [33] were adopted for explaining the relationship between the photodegradation rate in the presence of SnO$_2$ NPs with respect to time. The rate equation can be express as:

The photodegradation profiles of different photocatalysts are shown in Figure 4A. A control experiment was firstly performed without adding any catalyst in RhB solution to check if any degradation appears under visible irradiation. The small decreasing of the concentration with time was attributed to the occurrence of cleavage in the aromatic ring of the RhB molecules. It was observed that the Rh B concentration had decreased by about 5.3 % after 120 min irradiation. While the photodegradation rate of commercial SnO$_2$ was 42.7% after 120 min visible light irradiation. In contrast, the biosynthesized SnO$_2$ NPs displayed a much higher performance, which could degrade more than 95% of RhB in after 120 min light illumination. The photocatalytic degradation of RhB using SnO$_2$ can be explained as follow: the conduction band electrons and the valence band holes are firstly generated when the SnO$_2$ NPs are illuminated by light. OH$^-\text{radicals}$ are produced on the hydroxyl group at the SnO$_2$ when the holes are trapped on the surface. While, the superoxide radical anions O$_2^-\text{are produced when the reaction of dissolved oxygen molecule with electrons. Then, the superoxide radical anions O}_2^-\text{can produce hydroxyl radicals, HO}_2$ by
protonation. Finally, the RhB molecules are degraded by these radicals [34-38]. The superior photocatalytic activity of the biosynthesized SnO$_2$ NPs could ascribe to their high specific surface area, which provides maximum exposure for reactant to the active site [29].

Fig. 4B shows the first-order kinetic linear curves of different photocatalysts. The apparent rate constant of commercial SnO$_2$ and biosynthesized SnO$_2$ NPs can be calculated to be 0.0015 and 0.0121/min, respectively. The reusability of the biosynthesized SnO$_2$ was also investigated. After 5 cycles test, the biosynthesized SnO$_2$ NPs remain more than 91% of photodegradation performance, suggesting that the proposed photocatalyst owning an excellent stability.

![Fig. 4: (A) Comparison of RhB photodegradation in the absence and presence of different photocatalysts under visible light irradiation. (B) The first-order kinetic model fit for different photocatalysts.](image)

4. Conclusion

In summary, *Plectranthus amboinicus* assisted synthesis of SnO$_2$ NPs was achieved using a simple one-pot hydrothermal approach. The average size of synthesized SnO$_2$ NPs was determined as 63 nm. EDX and XRD characterizations suggest the proposed biosynthesis method could results high purity of SnO$_2$ NPs. Moreover, the proposed biosynthesis method has advantages over the other methods, such as ease with the process which can be scaled up and economic viability. Moreover, the biosynthesized SnO$_2$ NPs showed a superior photocatalytic performance towards dye molecules degradation.

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Reference