SnO$_2$:Au/Carbon Quantum Dots Nanocomposites: Synthesis, Characterization, and Antibacterial Activity


Carbon quantum dots-based nanostructures have been found more attention in recent years. In this study, Au-doped tin oxide/carbon quantum dots (Au:SnO$_2$/carbon quantum dots) nanocomposites was prepared via simple and friendly to the environment route. The obtained results from X-ray diffraction (XRD) analysis, Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) analysis, photoluminescence spectroscopy (PL), and Ultra violet-Visible (UV-Vis) spectroscopy showed the formation of the pure and regular shape of Au:SnO$_2$/carbon quantum dots. Then, prepared Au:SnO$_2$/carbon quantum dots was utilized for the testing of antibacterial activity using Aspergillus niger, Bacillus subtilis, Candida albicans, Escherichia coli, Klebsiella pneumonia, pseudomonas aeruginosa, Salmonella paratyphi-A serotype, Shigella dysenteriae, Staphylococcus aureus, Staphylococcus epidermidis, and Streptococcus pyogenes. The modified sample showed significant improvement against tested bacteria. The best antibacterial activity was observed in Au:SnO$_2$/carbon quantum dots against pseudomonas aeruginosa with MIC values of 62.5 μg/ml. The obtained results demonstrate Au:SnO$_2$/carbon quantum dots nanocomposites are highly suitable as an antibacterial agent against both Gram-negative and Gram-positive bacteria.
INTRODUCTION
Bacterial infection is the main cause of chronic infection and death [1-5]. Antibiotics are the preferred treatment for bacterial infections because they are cost-effective and powerful [6-10]. However, some studies have provided direct evidence that the widespread use of antibiotics has led to the emergence of multi-drug resistant strains [11-14]. Most of the current molecular antibiotics have an effect on microorganisms via one among the three microorganism targets: cell wall, change of location machinery, and deoxyribonucleic acid replication [15, 16]. Although nanoparticles (NPs) can react simultaneously through several processes, such as (1) generation of reactive oxygen species (ROS), (2) electrostatic interaction with cell membranes, (3) release of ions e (4) internalization [17-20]. Due to the unique properties of nanoparticles due to their size, nanostructures are widely used in antibacterial applications. It is necessary to acknowledge that whereas some metals, akin to copper, tin, and silver, exhibit antibacterial mechanisms in their bulk type, different materials, such as iron oxide, don’t seem to be antibacterial in their bulk form however might exhibit antibacterial properties in nanostructure form [21-26]. Tin compound (SnO₂) is one of the notable metal oxides that possess glorious electrochemical, optical and electronic properties. For their excellent properties, SnO₂ -based nanomaterials have found more attention in antibacterial application [27-31].

Eduardo B. Tibayan Jr et al. synthesized silver/tin oxide (Ag/SnO₂) nanocomposites as coating materials with high antibacterial activity. They applied scanning electron microscope (SEM) and density functional theory (DFT) methods to characterize the nanocomposite structures and confirm that Ag (1 1 1) and SnO₂ (1 1 0) form nanorods of Ag/SnO₂. They found that toxicity to E. coli and S. aureus increased with respect to the amount of silver within the composite, with the best antibacterial activity being observed at a 4:1 ratio of Ag/SnO₂. Also, the antimicrobial activity of the Ag/SnO₂ were increased when particle sizes were reduced to nanoscale [32].

A. Arfaoui et al. prepared SnO₂, SnO₂/MoO₃ and SnO₂/WO₃ thin films via the thermal evaporation technique. They characterized prepared thin films via XRD, AFM, SEM, and UV-Vis analysis. It is found that SnO₂/MoO₃ and SnO₂/WO₃ nanomaterials showed higher photocatalytic activity than of SnO₂. The antibacterial activity investigation towards Pseudomonas Aeroginosa revealed that only SnO₂/WO₃ thin film has shown antibacterial activity[33].

This study aimed to examine the effect of Au:SnO₂/carbon dots nanocomposites in preventing bacterial growth. First, Au:SnO₂/carbon dots nanocomposites is synthesized via novel and simple route. The structural properties of prepared samples are characterized via XRD, FTIR, EDS, SEM, TEM, UV-Vis, and PL analysis. The antibacterial activity of Au:SnO₂/carbon dots nanocomposites is examined against various Gram-negative and Gram-positive bacteria.

MATERIALS AND METHODS

Synthesis of carbon dots
Pears were used to greenly synthesize carbon quantum dots by the hydrothermal method. First, 10 mL of pear water was added to 10 mL ethanol. Then, the prepared solution was placed on the magnetic stirrer for 30 minutes. The obtained solution was transferred into stainless steel autoclave and heated for 5 hours at 190 °C. Finally, the solution was centrifuged several times and keep in the 4 °C for further tests.

Synthesis of SnO₂ nanoparticles
Rosemary plant extract was used for the green synthesis of tin oxide nanoparticles. First, 10 mL of the extract was distilled in 20 ml of deionized water. Then, the SnCl₂.2H₂O was distilled in 30 ml of water, then after 20 minutes the Rosemary plant extract solution was added to the tin-containing solution and brown-colored precipitate was obtained. Using a centrifuge, the solid was separated and washed with water. The obtained solid was dried for 12 hours at 60 °C. The prepared solid was calcined for 3 hours at 450 °C to formation pure SnO₂ nanoparticles.

Synthesis of Au:SnO₂
Au:SnO₂ nanomaterial was synthesized similar to the preparation of SnO₂ nanoparticles, except that before adding Rosemary plant extract, HAuCl₄.3H₂O was added to the solution.

Synthesis of Au:SnO₂/carbon dots nanocomposites
0.1 g of as-obtained Au:SnO₂ nanoparticle was dissolved in 20 cc of distilled water, then 5 cc of the prepared dot was added to the Au:SnO₂ nanoparticle mixture. The obtained mixture was
stirred for 24 h vigorously. Finally, the solid was dried for 12 hours at 60 °C.

**Antimicrobial activity assay**

For the antimicrobial activity test, a concentration of 10 mg/ml Au:SnO$_2$/carbon dots was prepared, then the bacterial suspensions were diluted to $10^6$ CFU / ml and finally exposed to treatment with 300 μl Au:SnO$_2$/carbon dots for 1, 2, 3 and 4 days at 37 °C. Aliquots (10 μl) were taken from each sample tube, diluted to $10^3$ CFU/ml and seeded on Müller agar Hinton for 24 to 37 °C. The colonies were then counted and the results were reported as log10 CFU/ml expressed.

**RESULTS AND DISCUSSION**

Fig. 1 shows XRD pattern of prepared Au:SnO$_2$/carbon dots. As can be seen in XRD pattern, the noisy broad weak peak in 2θ=21° have corresponded to carbon dots. Other observed peaks confirmed the formation of tetragonal SnO$_2$ with space group P42/mnm (reference code 01-077-0450). The high intensity of peaks confirms a good crystallinity of the synthesized tin oxide nanoparticles, and large width of the full width at half maximum (FWHM) of the peaks leads to the small grain size of the tin oxide nanoparticles. For the calculation of crystalline size, the Scherer equation can be applied:

$$D_c = \frac{K\lambda}{\beta \cos \theta}$$

that β is defined as the width of the provided diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (CuKα radiation, equals to 0.154 nm). The average crystallite size was calculated 23.2 nm. It was predictable that the Au-related peak would not be seen in the XRD pattern because the amount of doped Au was very low.

The EDS analysis was applied for the chemical characterization of samples. As well as shown in Fig. 2, the EDX profile virtually proves the presence of C, Sn, O, and Au elements, which might be a part of the authentic synthesized Au:SnO$_2$/carbon dots. Percentage compositions of the elements present in Au:SnO$_2$/carbon dots are presented in a Table inserted under Fig. 2. It is clear that no other dominated peak was observed in the EDS spectrum that confirmed that the as-prepared Au:SnO$_2$/carbon dots is formed with any impurity.

FT-IR analysis was used for the investigation surface functional group of the product. Fig. 3 shows FT-IR spectrum of Au:SnO$_2$/carbon dots. As-showed broad peak in 3412 and sharp peak...
Fig. 2. EDS analysis of as-prepared Au:SnO$_2$/carbon dots nanocomposites.

Fig. 3. FTIR spectra of prepared Au:SnO$_2$/carbon dots nanocomposites.
at 1744 cm\(^{-1}\) in the FT-IR spectrum of products confirm hydroxyl group stretching vibrations and bending mode vibrations associated with the absorption of a few molecules of water. The bonds in the wavenumber range of 1000-1500 cm\(^{-1}\) are related to the C-C in carbon dots and Sn-OH stretching vibration. The main characteristic peaks at low wavenumbers, including 685 cm\(^{-1}\) and 606 cm\(^{-1}\) can be attributed to the antisymmetric and symmetric tin-oxygen-tin vibration, which is derived from the active IR modes \(E_u\) (TO) mode and the \(A_{2u}\) (TO) mode.

Morphological properties of as-prepared Au:SnO\(_2\)/carbon dots nanocomposites were investigated via scanning electron microscope (SEM). SEM images of Au:SnO\(_2\)/carbon dots is shown in Fig. 4 at two different magnifications. It can be concluded that the regular morphology of
SnO$_2$ nanoparticles are formed in 50 nm diameter. It should be noted that SEM images could not distinguish the Au nanoparticles and carbon dots. Carbon dots could not be investigated via the SEM analysis for their very tiny size. For further investigation of prepared Au:SnO$_2$/carbon dots transmission electron microscopes (TEM) analysis was applied. It is clear in Fig. 5 that very tiny carbon quantum dots are formed with tin oxide nanoparticles. From TEM images, it can be...
revealed that carbon dots have been distributed in Au:SnO$_2$ homogenously.

The optical properties of prepared Au:SnO$_2$/carbon dots nanocomposites was investigated via UV-Vis and PL spectroscopy. Fig. 6a shows the UV-Vis absorption spectrum of as-prepared Au:SnO$_2$/carbon dots in the wavelength range of 200-600 nm. The strong absorption peak is observed at 278 nm. This can be attributed to the direct band gap of SnO$_2$ nanoparticles that confirms absorption for the electronic transitions from the valence band to the conduction band. The energy band gap ($E_g$) is calculated from the optical absorption spectra using Tauc relation:

\[
(\alpha h\nu) = C (h\nu - E_g)^{1/2}
\]

where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, and $E_g$ is the band gap. As well as illustrated in Fig. 6b, the band gap was determined 2.2 and 3.3 eV for the synthesized Au:SnO$_2$ and carbon dots respectively. Compared to the previously reported band gaps for SnO$_2$ and carbon dots, it is found that the calculated band gap is considerable [34, 35]. PL is known as an appropriate technique to investigate optical properties of nanoparticles, the active sites on the surface of metal oxides, the crystalline quality, and also the presence of impurities within the materials further as exciton fine structures. Fig. 7 shows the emission spectrum of prepared Au:SnO$_2$/carbon dots nanocomposites. The PL spectra of product show the broad luminescence band at 438 and 547 nm. The observed band can be related to the all Sn and oxygen vacancies, Sn interstitials, and defects on the surface of product.

In this study, the antibacterial activity of Au:SnO$_2$/carbon dots nanocomposites was examined against Gram-positive and Gram-negative bacteria. The broth microdilution procedure were used to determine the MIC and MBC values. Table 1. The Minimum Inhibitory Concentration (MIC), Minimum Bactericidal Concentration (MBC), and diameter of inhibition zone of the Au:SnO$_2$/carbon dots nanocomposites against tested microorganisms.

<table>
<thead>
<tr>
<th>Test microorganism</th>
<th>SnO$_2$Au</th>
<th>SnO$_2$:Au/Cdot</th>
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<tbody>
<tr>
<td></td>
<td>MIC</td>
<td>MBC</td>
</tr>
<tr>
<td>Aspergillus niger (ATCC 9029)</td>
<td>125</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Bacillus subtilis (ATCC 6633)</td>
<td>62.50</td>
<td>250</td>
</tr>
<tr>
<td>Candida albicans (ATCC 10231)</td>
<td>62.50</td>
<td>250</td>
</tr>
<tr>
<td>Escherichia coli (ATCC 25922)</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Klebsiella pneumonia (ATCC 10031)</td>
<td>125</td>
<td>1000</td>
</tr>
<tr>
<td>pseudomonas aeruginosa (ATCC 27853)</td>
<td>62.50</td>
<td>250</td>
</tr>
<tr>
<td>Salmonella paratyphi-A serotype (ATCC 5702)</td>
<td>62.50</td>
<td>1000</td>
</tr>
<tr>
<td>Shigella dysenteriae (PTCC 1188)</td>
<td>125</td>
<td>250</td>
</tr>
<tr>
<td>Staphylococcus aureus (ATCC 29737)</td>
<td>250</td>
<td>1000</td>
</tr>
<tr>
<td>Staphylococcus epidermidis (CIP 81.55)</td>
<td>250</td>
<td>16</td>
</tr>
<tr>
<td>Streptococcus pyogenes ATCC 19615</td>
<td>62.50</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 1. The Minimum Inhibitory Concentration (MIC), Minimum Bactericidal Concentration (MBC), and diameter of inhibition zone of the Au:SnO$_2$/carbon dots nanocomposites against tested microorganisms.
pyogenes (ATCC 19615) with an inhibition zone of 16 mm. The improvement of antibacterial activity via introducing carbon dots can be related to the carbon dots-related optical properties. For its semiconductor properties, carbon dots improve optical properties of Au:SnO$_2$ and this lead to increase the photocatalytic activity of Au:SnO$_2$/carbon dots nanocomposites. The presence of carbon dots produced more reactive oxygen species (ROS) and this species lead to increase antibacterial activity. The antibacterial activity of some antibiotics against tested microorganisms is provided in Table 2.

**CONCLUSION**

In this study Au:SnO$_2$/carbon dots nanocomposites were synthesized via a simple and novel chemical route. The crystalline structure,
purity, and morphological properties of samples were characterized via XRD, EDS, SEM, and TEM analysis. The results confirmed that Au:SnO₂/carbon dots nanocomposites were formed in pure and regular morphology. The optical properties of products were investigated via UV-Vis and PL analysis. The band gap of as-prepared Au:SnO₂/carbon dots nanocomposites was calculated 2.8 eV. The biological activity of synthesized Au:SnO₂/carbon dots nanocomposites was examined against the Gram-negative and Gram-positive microorganisms. It was found that Au:SnO₂/carbon dots nanocomposites has higher antibacterial activity than Au:SnO₂. The results revealed that Streptococcus pyogenes (ATCC 19615) has the highest sensitivity since the lowest concentration of Au:SnO₂/carbon dots nanocomposites was applied via MIC and MBC value 62.5 and 62.5 μg/ml.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES


