Research Article


**Green synthesis and studies on citrus medica leaf extract-mediated Au–ZnO nanocomposites: A sustainable approach for efficient photocatalytic degradation of rhodamine B dye in aqueous media**

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**Abstract:** Incorporating narrow band gap oxide semiconductors and metals into zinc oxide (ZnO) nanostructures broadens the range of light sensitivity to include visible wavelengths. In this study, the photocatalytic degradation of rhodamine B (RhB) dye was studied as a model for environmental pollution in aqueous media. This study describes the use of photodegradation catalysts, including gold (Au), ZnO, and Au–ZnO nanocomposites (prepared in ratios of 90:10 and 95:5) using the extract of Citrus medica leaves. X-ray diffraction (XRD) findings have shown that ZnO nanoparticles (NPs) have a hexagonal wurtzite structure. Field emission-scanning electron microscopy findings have depicted that ZnO NPs have diverse shapes, including spherical, quasi-spherical, hexagonal, and anisotropic, with some clumping. Au exhibits consistent spherical shapes and sizes with even distribution. Au–ZnO (90:10) shows quasi-spherical NPs with interconnected spherical Au, forming a porous and uneven surface. Au–ZnO (95:5) has spherical gold nanoparticles (Au NPs) dispersed on a textured ZnO surface, with some clustering and size variation as evident from the transmission electron microscopy, atomic force microscopy, and diffuse reflectance UV-visible spectroscopy analysis. The characterization results have demonstrated the uniform distribution of Au across the ZnO lattice. Additionally, the XRD patterns confirmed the hexagonal wurtzite structure of ZnO. Furthermore, energy-dispersive analysis of X-ray (EDX)-mapping verified the inclusion of zinc, oxygen, and Au in the hybrid Au–ZnO nanocomposites and their effective distribution. The topological analysis revealed a rough surface for the generated nanostructures. By comparing the results of various techniques, EDX analysis using atomic and weight ratios confirmed the presence of oxygen and Au in the nanocomposite and their effective distribution. The surface area analysis (BET) test has reported that the adsorption and desorption of nitrogen follow a Type III isotherm. The presence of an H3-type hysteresis loop further confirms the mesoporous nature of the composites, which reports the presence of wedge-shaped pores. The Au–ZnO (90:10) nanocomposite exhibits a higher surface roughness compared to...
other composites. In addition, this UV-visible diffuse reflectance spectroscopy has enumerated the band gaps of various nanomaterials using UV-visible spectroscopy. Moreover, the analysis has unveiled that combining ZnO with Au NPs (doping) improved the photocatalytic performance of ZnO. This improvement is attributed to the formation of additional energy levels within the ZnO band gap due to the presence of Au ions. Experimental investigation of the breakdown of RhB dye under visible light irradiation revealed superior photocatalytic activity for the Au–ZnO (90:10) nanocomposite compared to both Au–ZnO (95:5) and pure ZnO and Au counterparts. Multiple experiments confirmed the effective photodegradation and removal of RhB dye from the aqueous medium using the nanocatalyst under visible light irradiation. Under optimal conditions (1.0 g·L\(^{-1}\) photocatalyst, 10 ppm RhB, and pH 10), 99% photodegradation efficiency was reached within 50 min of irradiation. Investigation of reactive species revealed that the increased effectiveness of photodegradation in Au–ZnO (90:10) stems from the presence of photogenerated holes and hydroxyl radicals. The study also analyzed the reaction kinetics and order, and the reusability of the best photocatalyst Au–ZnO (90:10) was confirmed through five consecutive cycles, demonstrating its sustained effectiveness in photodegradation. These findings highlight the potential of Au–ZnO (90:10) nanocomposite as a promising material for photocatalytic degradation of organic dyes.

**Keywords:** Au, ZnO nanocomposite, eco-friendly, photodegradation, rhodamine B dye

1 Introduction

Environmental pollution and its cleanup have garnered significant attention worldwide due to the severe damage it inflicts on aquatic environments, humans, and other animals. Industrial effluent, posing a major threat, is one of the key contributors to this problem [1]. While increasing pollution and population remain pressing global issues, the escalating need for water, particularly within the developing industrial sector, is further exacerbating water source contamination and creating significant environmental challenges [2].

The discharge of pigmented waste materials poses a highly perilous ecological threat, escalating the contamination of aquatic ecosystems. Textile dye pollution, a prevalent issue, has detrimental effects on both the aquatic environment and the health of animals and humans. This contamination primarily stems from the rise in chemical and biochemical oxygen demand (COD and BOD), leading to a decline in photosynthesis, stunted plant growth, and bioaccumulation throughout the aquatic food chain [3]. New paths for developing advanced pharmaceutical treatments and analytical procedures have emerged thanks to advancements in wastewater treatment. Combinatorial therapies targeting both organic and biological toxins are crucial to prevent natural resource depletion, particularly water, caused by various industries like agriculture, paper, and leather [4]. Notably, industrial dyes (e.g., rhodamine 6G, methyl orange, methylene blue) and infectious microorganisms (e.g., Corynebacterium glutamicum, Escherichia coli, Bacillus subtilis) can exacerbate the impact of these pollutants, potentially increasing carcinogenicity and life-threatening effects.

Photocatalysis has emerged as a highly effective method for wastewater cleanup due to its advantages over alternative approaches [5]. It is recognized for its ability to completely mineralize various non-biodegradable organic contaminants found in aquatic environments, making it a viable strategy for removing several pollutants from wastewater. Zinc oxide (ZnO) is a well-researched photocatalyst due to its exceptional physical and chemical properties. It is widely recognized as an n-type oxide semiconductor with a significant band gap energy (\(E_g\)) of 3.35 eV [6]. The band gap energy of ZnO varies between 3.1 and 3.4 electron volts (eV), showing sensitivity to factors like synthesis methods and crystal size/morphology. This versatility makes ZnO a highly valuable material, thanks to its rapid oxidation potential, resistance to biological and chemical interactions, strong redox capacity, non-toxicity, affordability, and environmental friendliness.

The escalating contamination of aquatic ecosystems by pigmented waste materials, particularly textile dyes, poses a significant environmental threat. These pollutants have detrimental effects on the aquatic environment and can lead to various diseases in animals and humans. Increased COD and BOD caused by these contaminants disrupts photosynthesis, hinders plant growth, and leads to bioaccumulation throughout the food chain [7].

ZnO has seen widespread adoption in diverse fields, including biosensing, adsorption, solar cells, photocatalysis, and various medical and biological applications. However, its wide band gap typically limits its photocatalytic activity to ultraviolet (UV) light. While bare ZnO exhibits limited activity in the visible light range, specific modifications like self-sensitization and vacuum deoxidation can unlock its potential to harness solar radiation for photocatalysis [8,9].

ZnO can be modified through various techniques, including the addition of metal nanoparticles (NPs) like silver (Ag), iron (Fe), gold (Au), palladium (Pd), and copper (Cu). These modifications aim to address ZnO’s large band
gap energy, which limits its photocatalytic activity [10]. Notably, gold nanoparticles (Au NPs) are valuable in bioimaging, biomedical treatments, and diagnostics due to their biocompatibility, low toxicity, and ease of detection. When combined with oxide semiconductors, Au NPs enhance visible light absorption and charge separation, ultimately improving photocatalytic efficacy [11,12].

Another strategy involves mixing ZnO with semiconductors with narrower band gaps, such as Au, Ag, or Cu, or carbon nanomaterials like graphene oxide (GO), reduced GO (rGO), or carbon dots. This approach effectively adjusts the ZnO band gap, creating materials that are highly active under visible light. Additional methods like heat treatment, dye sensitization, and plasma treatment can also modify the optical band gap of ZnO [13].

Incorporating narrow-band gap oxide semiconductors and metals into ZnO nanostructures broadens the range of light sensitivity to include visible wavelengths. For example, Au undergoes a triple oxidation process, transitioning from its elemental form (Au) to a +3-oxidation state with a smaller band gap compared to ZnO [14]. Integrating Au NPs with zinc oxide nanoparticles (ZnO NPs) facilitates efficient charge carrier separation and band alignment, thereby influencing the band structure of ZnO and enhancing photoelectron transfer [15,16]. Recent research findings have revealed that the introduction of photogenerated electrons from Au into ZnO leads to a notable enhancement in photocatalytic performance for several applications, including wastewater treatment, organic dye degradation, and dye-sensitized solar cells [17].

When comparing the previous method of preparing nanomaterials with the modern method, we find that the traditional chemical-based method for preparing nanomaterials is considered hazardous and harmful to the environment, toxic, and economically costly. A global movement has recently emerged towards producing nanocatalysts using more environmentally friendly methods.

Botanical extracts, employed in environmentally safe processes, have been used to biosynthesize ZnO NPs using bacteria, fungi, and algae. Plant extracts from various parts, such as roots, flowers, leaves, stems, seeds, and fruits, have also been utilized. Green synthesis allows for large-scale production of ZnO NPs with fewer undesired impurities.

A binary Au–ZnO nanocomposite was created using Citrus medica leaf extract as an easy, safe, environmentally friendly, harmless, and non-toxic method. This biological method is also economically inexpensive.

These nanomaterials were used as catalysts for the photodegradation of rhodamine B (RhB) dyes, a model for environmental pollution in the aqueous medium. This process purifies water from pollutants and contributes to the degradation of wastewater pollutants.

Only a few publications have been published on the environmentally friendly production of hybrid Au–ZnO nanocomposites utilizing plant extracts.

To analyze the as-fabricated nanomaterials, the main technique used was X-ray diffraction (XRD). XRD analysis revealed the angles for each prepared sample, as well as Miller’s coefficients for these angles, confirming the success of the preparation process.

2 Experimentation

2.1 Materials

All materials used are highly purified and can be used without further purification due to their high purity. The following substances were bought from B.D.H.: zinc(II) nitrate hexahydrate (Zn(NO₃)₂·6H₂O; purity, 99.5%), hydrogen tetra-chlorocuprate(III) hydrate (HAuCl₄·3H₂O; purity, 99.9%), and hydrochloric acid (HCl, 37% purity, 97%; maximum wavelength of 553 nm) was purchased from Sigma-Aldrich, and hydrochloric acid (HCl, 37%) was purchased from B.D.H. and sodium hydroxide (NaOH, 99%) from Scharlau. Deionized (DI) water was used to prepare all the solutions.

2.2 Preparation of the aqueous extract of Citrus medica

The study utilized Citrus medica leaves that were freshly harvested from an open field located in Babylon, Iraq. The leaves were subjected to a thorough washing process using DI water. Subsequently, the specimen was allowed to remain undisturbed at ambient temperature within a controlled atmosphere devoid of particulate matter, with the aim of mitigating the potential evaporation of volatile organic compounds. The leaves were thereafter severed and immersed in 75 mL of DI water prior to being subjected to a temperature of 80°C for a duration of 30 min, accompanied by intense agitation. The extract was further subjected to filtration using Whatman No.1 filter paper and centrifugation at a speed of 6,000 rpm for a duration of 10 min, aiming to eliminate minute suspended particles. The final volume was adjusted to 100 mL by the addition of DI water. Subsequently, in order to facilitate the
utilization of the clear extract in the process of synthesizing nanomaterials, it was stored at a temperature of 4°C.

2.3 Synthesis of ZnO and Au NPs

ZnO NPs were synthesized using a leaf extract in an environmentally friendly approach. A 50 mL aqueous extract of *Citrus medica* was used to dissolve 0.5 g of Zn(NO$_3$)$_2$·6H$_2$O under continuous magnetic stirring at 80°C for 4 h, reducing it to Zn$^{2+}$ ions. The solution was centrifuged at 6,000 rpm for 20 min to remove residual reactants and prevent photoreactions. Wrapped in aluminum foil, it then rested at room temperature for 24 h. The resulting dark precipitate was repeatedly washed with DI water and ethanol to remove impurities. Finally, it was dried at 80°C for 4 h, yielding a pale white solid. The color change from yellow to white confirmed the conversion of zinc nitrate to zinc ions and the formation of ZnO NPs. For comparison, Zn(NO$_3$)$_2$·6H$_2$O dissolved in only DI water failed to precipitate ZnO under the same conditions.

Au NPs were synthesized similarly. However, 0.5 g of HAuCl$_4$·3H$_2$O (99.9%) was dissolved in the *Citrus medica* extract and then calcined to form yellow-colored Au NPs.

2.4 Synthesis of Au–ZnO (90:10) and Au–ZnO (95:5) nanocomposites

The nanocomposite Au–ZnO (90:10) was prepared in a typical experiment where 50 mL of the aqueous *Citrus medica* extract was dissolved in 4.09 g·L$^{-1}$ Zn(NO$_3$)$_2$·6H$_2$O and 0.19 g·L$^{-1}$ hydrogen tetrachlorocuprate (m) hydrate (HAuCl$_4$·3H$_2$O 99.9%), which was then subjected to 4 h of continuous magnetic stirring at 80°C. The mixture was next covered with a heavy metal foil and allowed to sit at room temperature for 24 h to avoid any photoreactions. At 6,000 rpm, the reaction mixture was centrifuged for 20 min. The resultant precipitate was thoroughly cleaned of any adsorptive impurities using DI and ethanol before being dried for 4 h at 80°C to produce a light blue solid. The powder was then calcined at 500°C for 4 h. The same procedures as above were used to create conjugated Au–ZnO (95:5) in various ratios by altering the proportions of the initial substances involved in the reaction. This was done by adding 0.09 g·L$^{-1}$ of hydrogen tetrachlorocuprate(m) hydrate (HAuCl$_4$·3H$_2$O 99.9%) to a plant extract solution that contained 4.32 g·L$^{-1}$ of Zn(NO)$_2$·6H$_2$O.

3 Results and discussion

3.1 XRD

The XRD peaks of ZnO NPs match the hexagonal wurtzite phase of ZnO (JCPDS 21-1732). Specific peaks at 31.5020° (100 planes), 34.2340° (002 planes), and 36.2716° (101 planes) confirm ZnO synthesis, consistent with previous studies [18]. As shown in Figure 1, the monoclinic XRD pattern of Au NPs indicates pure Au (JCPDS 73-1839). The peaks at 38.1733°, 44.3202°, and 64.5334° correspond to Au NP lattice planes (111), (200), and (220), respectively, aligning with previous reports [19].

The XRD pattern of the Au–ZnO (90:10) nanocomposite aligns with the expected Au–ZnO structure based on the data (JCPDS 92-1793). Prominent peaks at 38.540° and 44.743° correspond to the (111) and (200) planes of Au, respectively, indicating the growth of Au nanoparticles on ZnO surfaces. Notably, Au incorporation alters diffraction intensities and reduces crystallite sizes of ZnO NP. Nonetheless, ZnO NPs maintain their structural integrity.

Similar diffraction intensity changes and decreased crystallite sizes are observed in Au–ZnO (95:5) (JCPDS 27-1375).
nanocomposites. Again, the XRD pattern confirms the structural integrity of ZnO NPs after Au incorporation. Interestingly, a singular, low-intensity peak at 38.708° (111) suggests the presence of some Au [20,21]. The crystallite sizes calculated using the Debye–Scherrer equation are presented in Table 1.

\[
D = \frac{K\lambda}{\beta \times \cos \theta}
\]

The full width at half-maximum (FWHM) of the XRD peaks and the diffraction angle are all constants, while \(D\) is the size of the crystallite, and \(K\) is a constant of 0.9.

### 3.2 Field-emission scanning electron microscopy (FE-SEM)

FE-SEM analysis revealed diverse surface morphologies for ZnO, Au, and their Au–ZnO nanocomposite (Figure 2). ZnO NPs exhibited a variety of shapes, including spherical, quasi-spherical, hexagonal, and anisotropic, with some particle agglomeration. The biosynthesized Au displayed consistent spherical shapes and sizes with uniform distribution.

Au incorporation modified ZnO morphology. The resulting Au–ZnO nanocomposite showed quasi-spherical NPs with interconnected spherical Au NPs, creating a porous and uneven surface according to FE-SEM micrographs.

For the Au–ZnO (95:5) nanocomposite, FE-SEM images revealed favorably dispersed spherical Au NPs on a textured ZnO surface, with some clustering and uneven size distribution. The presence of spherical particles on the Au–ZnO surface confirmed the formation of the nanocomposite [22] (Figure 3).

### 3.3 Energy dispersive X-ray (EDX) spectroscopy

EDX spectroscopy was used to examine the tiny particles (NPs) within a specially designed structure (hybrid nanostructure). Figure 4 shows the EDX results for these NPs. The analysis confirmed that ZnO NPs were pure, as there were no extra peaks in the spectrum. The Au NPs, as expected, only contained Au atoms. Similarly, the EDX spectra of the gold–zinc oxide (Au–ZnO) mixture (in a 9:1 ratio) showed the presence of zinc, oxygen, and Au. The analysis confirmed that the Au–ZnO mixture had the same basic elements as the individual components. Interestingly, the Au peaks were easily visible in the spectrum, while the zinc signal was also strong. This suggests a good distribution of both elements. In all the structures except pure Au, the presence of oxygen confirmed the successful formation of metal oxides. Furthermore, detailed maps obtained using EDX revealed a uniform spread of Au atoms across the ZnO surface. The researchers believe that the uneven distribution of Au on ZnO in another mixture (5:95 ratio) can significantly enhance its ability to break down pollutants using light (photocatalytic activity). This is because the uneven distribution creates numerous areas where Au and ZnO come into close contact, which is beneficial for this process. The specific percentages of each element in the different mixtures are given in Table 2 [23,24].

### Table 1: Calculated nanocrystallite sizes of synthesized nanomaterials from XRD analysis (in nm)

<table>
<thead>
<tr>
<th>Material</th>
<th>2θ</th>
<th>Miller indices</th>
<th>Lattice strain</th>
<th>Intensity</th>
<th>d-spacing (Å)</th>
<th>Average size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>31.502</td>
<td>100</td>
<td>0.0019</td>
<td>61</td>
<td>2.72011</td>
<td>16.30</td>
</tr>
<tr>
<td></td>
<td>34.234</td>
<td>002</td>
<td>0.0075</td>
<td>43</td>
<td>2.61966</td>
<td></td>
</tr>
<tr>
<td></td>
<td>36.271</td>
<td>101</td>
<td>0.0054</td>
<td>100</td>
<td>2.43120</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>38.173</td>
<td>111</td>
<td>0.0046</td>
<td>95</td>
<td>2.3217</td>
<td>24.34</td>
</tr>
<tr>
<td></td>
<td>44.320</td>
<td>200</td>
<td>0.0027</td>
<td>100</td>
<td>2.2171</td>
<td></td>
</tr>
<tr>
<td></td>
<td>64.533</td>
<td>220</td>
<td>0.0067</td>
<td>23</td>
<td>1.7675</td>
<td></td>
</tr>
<tr>
<td>Au–ZnO (90:10)</td>
<td>31.776</td>
<td>100</td>
<td>0.0061</td>
<td>63</td>
<td>2.83272</td>
<td>35.07</td>
</tr>
<tr>
<td></td>
<td>35.547</td>
<td>002</td>
<td>0.0053</td>
<td>46</td>
<td>2.51244</td>
<td></td>
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<tr>
<td></td>
<td>36.839</td>
<td>102</td>
<td>0.006</td>
<td>100</td>
<td>2.49182</td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.540</td>
<td>111</td>
<td>0.0051</td>
<td>70</td>
<td>2.7438</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.825</td>
<td>100</td>
<td>0.0058</td>
<td>60</td>
<td>2.28732</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.680</td>
<td>022</td>
<td>0.0043</td>
<td>48</td>
<td>2.24514</td>
<td></td>
</tr>
<tr>
<td>Au–ZnO (95:5)</td>
<td>36.973</td>
<td>102</td>
<td>0.0045</td>
<td>100</td>
<td>2.18492</td>
<td>32.6</td>
</tr>
<tr>
<td></td>
<td>38.708</td>
<td>111</td>
<td>0.0065</td>
<td>86</td>
<td>2.4378</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.894</td>
<td>220</td>
<td>0.0061</td>
<td>97</td>
<td>2.4783</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Transmission electron microscopy (TEM)

The dimensions and morphologies of the synthesized nanomaterials were analyzed using TEM. Figures 5 and 6 display TEM micrographs of the nanomaterials produced for this study, providing a more comprehensive visualization of the particles’ morphology and dimensions. The TEM images of ZnO NPs demonstrate that the particles have a predominantly hexagonal shape with limited aggregation, aligning with the findings of the FE-SEM.
The mean particle size was determined to range from 20 to 200 nm [25].

The TEM images of Au NPs exhibit the presence of spherical Au NPs, characterized by an average particle size of 25 nm Figure 5. This observation aligns with the findings obtained from the FE-SEM analysis. The TEM image provides unambiguous evidence of their predominantly spherical shape, with average particle sizes ranging from 20 to 80 nm [26].

The TEM images of ZnO doped with Au reveal an increase in particle size, accompanied by noticeable

### Table 2: Ratios of each of the elements zinc, Au, and oxygen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>O</td>
<td>76.71</td>
<td>89.86</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>20.19</td>
<td>13.24</td>
</tr>
<tr>
<td>Au</td>
<td>Au</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Au–ZnO (95:5)</td>
<td>O</td>
<td>32.19</td>
<td>74.16</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>64.3</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>3.51</td>
<td>1.34</td>
</tr>
<tr>
<td>Au–ZnO (90:10)</td>
<td>O</td>
<td>34.32</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>60.41</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>5.27</td>
<td>2.3</td>
</tr>
</tbody>
</table>

*Figure 5: Average particle size of synthesized Au NPs.*

The Au–ZnO (95:5) nanocomposite displays equally distributed Au NPs with effective capping and stabilizing characteristics attributed to the *Citrus medica* leaf extract.

The TEM images of ZnO doped with Au reveal an increase in particle size, accompanied by noticeable
agglomeration and a non-uniform distribution of Au and ZnO (ZnO) NPs. The NPs appear agglomerated with a virtually spherical form, and the average size falls within the range of 25–45 nm.

The TEM images of the Au–ZnO (90:10) nanocomposite clearly show the presence of NPs with various morphologies. Additionally, it indicates substantial aggregation in the anisotropic nanostructure [27].

3.5 Atomic force microscopy (AFM)

The topographic properties of the as-synthesized nanomaterials were investigated using AFM analysis. The 3D image of the Au–ZnO nanocomposite described by the AFM in tapping mode is shown in Figure 7. The topographic features of the as-synthesized nanomaterials are summarized. The average roughness values ($R_a$) of ZnO and Au NPs surfaces were 3.21 and 6.13 nm, respectively. The roughness value increases to 12.13 for ZnO NPs and 26.00 for Au NPs after coupling and doping with Au NPs, respectively. When compared to other ZnO nanostructures, the Au–ZnO (90:10) nanocomposite has a larger surface roughness (105.07 nm), indicating that this sample has a higher surface/volume ratio, which may enhance electron–hole pair formation when light is applied to the surface. The thickness of ZnO and Au NPs is calculated to be 15.12 and 105 nm, respectively, and it increases for Au–ZnO NPs (53.1 nm). The variation in the nanostructure thickness obtained from AFM is almost identical to the variation trend in the grain size. Agglomeration increases as a result of the high concentration of Au NPs, resulting in an increase in the thickness and surface roughness of ZnO nanocomposites. Table 3 summarizes the topographic properties of the as-synthesized nanomaterials. From Table 3, the average roughness values ($R_a$) of surfaces were 23.4 for the Au–ZnO (95:5) nanocomposite. Upon coupling and doping with Au NPs, the roughness increases to 50.9. The variation in the nanostructure thickness obtained from AFM analysis is almost like the variation trend in the grain size, as displayed in Table 3. Furthermore, the heightened roughness of as-produced nanomaterial surfaces is defined by the observed negative values of skewness ($R_{sk}$), indicating a surface with more deep and steep valleys, as seen. Additionally, a statistical measure known as the kurtosis parameter ($R_{ku}$) describes the asymmetry and flatness of a surface distribution. All generated nanostructures
Figure 7: (a–h) 3D and 2D images of AFM for Au–ZnO (95:5) and Au–ZnO (90:10) nanocomposites.
may be categorized as having spiky surfaces, and $R_{kv3}$ is one of them [28,29].

### 3.6 Surface area analysis (BET)

Based on Figure 8 and the data, the adsorption and desorption of nitrogen follow a Type III isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification. This indicates that all the prepared composites exhibit mesoporous characteristics, further confirmed by the H3-type hysteresis loop observed. Notably, the Au–ZnO (90:10) nanocomposite displayed a higher surface roughness attributed to the combined effects of increased pore diameter and smaller particle size [30].

### 3.7 UV-visible diffuse reflectance spectroscopy (DRS)

The band gaps of the synthesized nanomaterials were determined using UV-visible DRS. As previously reported, combining ZnO with Au through doping can improve its photocatalytic performance. This enhancement may be attributed to the formation of additional energy levels within the ZnO band gap due to the presence of Au ions. The band gap energy ($E_g$) can be calculated using the following equation:

$$(ahv)^2 = B(hv - E_g)^\gamma$$

where $a$ is the absorption coefficient, $h$ is the Planck constant, $v$ is the frequency of incident photons, and $B$ is a constant representing the band tailing parameter. Eq. 2 displays the diffuse reflectance spectra (DRS) of the synthesized nanomaterials. The direct optical band gap of each material was estimated from the corresponding plot of $hv$ versus $(ahv)^2$. Figure 2 shows the calculated $E_g$ values for ZnO, Au, Au–ZnO (95:5), and Au–nO (90:10) to be 3.28, 2.93, 3.60, and 3.87 eV, respectively. Notably, the absorption edge shifts towards longer wavelengths with increased Au doping in ZnO. These results confirm that doping ZnO with Au NPs enhances its absorption of visible light and narrows its band gap, consistent with the findings reported in previous studies [31,32] (Figures 9 and 10).

### 3.8 Photocatalytic degradation of RhB dye

Scientists used a special dye called RhB to simulate organic pollutants in the environment. They tested whether light could break down this dye (photodegradation) by shining visible light on it without any additional help (photocatalyst). This did not work very well. Next, they tried adding different materials (photocatalysts) to the dye solution and

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**Table 3: AFM parameter values of the prepared samples**

<table>
<thead>
<tr>
<th>Amplitude Factors</th>
<th>ZnO</th>
<th>Au</th>
<th>Au–ZnO (95:5)</th>
<th>Au–ZnO (90:10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_a$ (nm)</td>
<td>3.21</td>
<td>6.13</td>
<td>23.4</td>
<td>25.7</td>
</tr>
<tr>
<td>$R_q$ (nm)</td>
<td>3.33</td>
<td>8.32</td>
<td>22.1</td>
<td>30.9</td>
</tr>
<tr>
<td>$R_{ku}$ (nm)</td>
<td>0.0184</td>
<td>0.0328</td>
<td>−3.19</td>
<td>−3.3</td>
</tr>
<tr>
<td>Thickness</td>
<td>12.32</td>
<td>26.00</td>
<td>50.9</td>
<td>105.07</td>
</tr>
</tbody>
</table>

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**Figure 8:** BET of the prepared particles.

**Figure 9:** UV-Vis absorption spectra of Au, ZnO, Au–ZnO (95:5), and Au–ZnO (90:10).
shining light on it again. This time, the dye broke down more, but still not very efficiently.

Figure 11 shows how long it took to break down the dye using light and tiny, specially made particles (nanomaterials) at a certain concentration. The longer the light shone, the more dye broke down, but the effect slowed down over time. Interestingly, a mixture of Au and ZnO nanoparticles (Au–ZnO) in a specific ratio (90:10) worked much better than other materials tested before. With this mixture, almost all the dye broke down (92.1%) within 2 h of light exposure. In comparison, using plain ZnO as the photocatalyst was much less effective, only breaking down about half the dye [33].

3.8.1 Effects of the dosage of photocatalyst

The optimal dosage of the photocatalyst was determined through a series of experiments, with the aim of achieving effective absorption of transmitted visible light. The concentration of the Au–ZnO (90:10) nanocomposite was systematically altered within the range of 0.2 to 1.4 g L\(^{-1}\) under certain fixed conditions. These parameters included a fixed concentration of RhB at 20 ppm, a pH value of 7, an irradiation time of 120 min, and a temperature of 298 K. The efficiency of photodegradation exhibited a significant increase from 78.95 to 99.1%, as the dosage of the photocatalyst was increased from 0.2 to 1.0 g L\(^{-1}\), respectively, as depicted in Figure 12. The increase in the dosage of the photocatalyst results in a greater number of surface-active sites, which in turn enhances the production of highly reactive radical species responsible for driving the photodegradation reaction. A notable decline in the effectiveness of photodegradation was seen at a concentration of 1.0 g L\(^{-1}\). This phenomenon can be attributed to the excessive loading of the photocatalyst, resulting in unfavorable light scattering and the creation of an impermeable suspension. The phenomenon of agglomeration, resulting from the interaction between particles, becomes more pronounced as the dosage of the photocatalyst increases. This agglomeration is a significant factor contributing to the reduced light absorption capacity of the photocatalyst. Consequently, for the following investigations, a concentration of 1.0 g L\(^{-1}\) of the Au–ZnO (90:10) nanocomposite was employed as the photocatalyst [34].

Figure 10: A Tauc plot equation for the nanostructures Au, ZnO, Au–ZnO (95:5), Au–ZnO (90:10).

Figure 11: Efficiency of the optical degradation process of the rhodamine dye in the presence of nanomaterials.

Figure 12: The catalytic activity of various photocatalysts.
3.8.2 Effect of initial dye concentration

The concentrations of colors in wastewater effluents released from different phases of dyeing operations exhibit variability, which is influenced by the quantity of dyes utilized during the coloring procedure, as shown in Figure 13. The extent of light penetration in the reaction solution, in order to reach the surface of the photocatalyst, is subject to modification by altering the initial concentration of the dye. Therefore, it is imperative to examine the influence of the initial dye concentration on the efficacy of photodegradation. Figure 13 illustrates the impact of varying concentrations of dye RhB on the effectiveness of photodegradation. The experiment involved adjusting the initial dye concentration from 5 to 25 ppm, utilizing a catalyst consisting of the Au–ZnO (90:10) nanocomposite at a concentration of 1.0 g·L⁻¹. The experiment was conducted under certain conditions, including a pH value of 7, a temperature of 298 K, and a duration of 120 min of visible light exposure. The maximal effectiveness of photodegradation (100%) was attained at a concentration of 5 parts per million (ppm). A correlation has been shown whereby an increase in RhB concentration leads to a decrease in photodegradation efficiency. The reason for this phenomenon is that when the concentration of dye increases, a greater number of dye molecules are adsorbed onto the surface-active sites, so impeding the ability of photons to reach the surface of the photocatalyst. Consequently, the elevation in the dye concentration leads to a decrease in the accessibility of photoactive sites as a result of enhanced physical adsorption of dye molecules onto the surface of the photocatalyst. This, in turn, leads to a reduction in the generation of OH radicals [35].

Figure 13: The effect of dye concentration on the photocatalyst.

3.8.3 Effect of initial pH

The influence of solution pH on the surface charge properties of the photocatalyst is widely recognized, making it a crucial operational parameter. Consequently, solution pH plays a substantial role in the adsorption and photocatalytic degradation of water pollutants. The impact of solution pH on the photodegradation efficiency of the Au–ZnO (90:10) nanocomposite photocatalyst against RhB dye is illustrated in Figure 14. The increase in pH from 2 to 12 resulted in a corresponding enhancement in the photodegradation efficiency, with values from 76.3% to 99.1%. The results can be explained by the zero-point charges of the Au–ZnO (90:10) nanocomposite (pHzpc 8.47), as depicted in Figure 14. Consequently, it is anticipated that a change in the pH towards an alkaline environment may facilitate an increase in the concentration of hydroxide (OH⁻) anions within the solution, thereby promoting a more effective generation of hydroxyl (OH) radicals. The primary reactive oxygen species (ROS) responsible for initiating the photodegradation reaction are hydroxyl (OH) radicals. The enhanced effectiveness of RhB dye degradation in alkaline environments can be primarily attributed to the increased generation of OH radicals from the hydroxyl group (OH⁻) rather than water (H₂O). The positive charge on the surface of the Au–ZnO (90:10) nanocomposite at acidic pH levels, caused by functional protonation, leads to competition with positively charged RhB molecules for binding to active sites. As a consequence, the photodegradation efficiency is reduced. At pH values higher than the point of zero charge (pHzpc), the surface of the photocatalyst becomes negatively charged due to the presence of hydroxyl anions. This negative charge facilitates the adsorption of RhB molecules onto the surface of the Au–ZnO (90:10) nanocomposite through electrostatic attraction forces. As a result, there is a significant enhancement in the efficiency of photodegradation [36].

Figure 14: Effect of pH solution on the degradation of RhB dye.
3.9 Kinetic study

The present study investigated the photocatalytic performance of a nanocomposite consisting of Au–ZnO (90:10) under visible light irradiation. The RhB dye was employed as an organic pollutant for analysis. The UV/Vis absorption spectra of RhB solutions over the Au–ZnO (90:10) nanocomposite under visible light exposure are depicted in Figure 15. The spectra are presented as a function of irradiation time. The findings indicated that there was an inverse relationship between the duration of UV exposure and the magnitude of UV-Vis absorption spectra for RhB. The observed decrease in absorbance can be attributed to a reduction in concentration, potentially resulting from the degradation of the dye chromogen. This suggests that the catalyst effectively breaks down the conjugated xanthene ring in RhB. No new absorption peaks were seen after 50 min of irradiation, suggesting that the dye underwent full mineralization. Figure 15 illustrates the utilization of the first-order kinetic model, as represented by Eq. 3, for the investigation of the photodegradation process of the Au–ZnO (90:10) nanocomposite photocatalyst. The relationship between the natural logarithm of the ratio \( C_0/C \) and the duration of irradiation is depicted in Figure 15. This graph provides evidence in favor of the hypothesis that the degradation of dye follows a kinetic model known as pseudo-first-order kinetics [37,38]. The RhB photodegradation process on the Au–ZnO (90:10) nanocomposite photocatalysts was seen to exhibit a pseudo-first-order kinetic constant of \( 1.67 \times 10^{-3} \text{ s}^{-1} \).

\[
\ln \left( \frac{C_0}{C_t} \right) = k \times t
\]

(3)

3.10 Recycling of photocatalyst

The study conducted a series of degradation experiments on RhB using a five-cycle approach. The experiments were conducted under consistent reaction conditions, with the only variation being the replacement of the RhB dye solution after each cycle. No washing or drying treatments were applied to the catalyst particles between successive runs. The objective of these experiments was to examine the photostability and reusability of the Au–ZnO (90:10) nanocomposite, which was synthesized using a green method. Figure 16 illustrates that the catalytic activity of the Au–ZnO nanocomposite has had a marginal drop, but with a modest decline observed after three cycles. Consequently, the nanocomposite composed of Au–ZnO (90:10) exhibits remarkable photostability, as evidenced by the high destruction efficiency of RhB of 99.1%, 91.1%, and 87.4% during the initial, subsequent, and third cycles, respectively, following a 50-min irradiation period. Nevertheless, during four successive cycles, the catalyst photocatalytic activity remains above 82.4% of its initial value. This observation provides evidence for the favorable photostability of the Au–ZnO (90:10) nanocomposite and lends credence to the notion that the photocatalyst can be reused for the degradation of RhB in an aqueous solution. Following a mere five experimental iterations, the photodegradation efficacy exhibited a decline, reaching a value of 74.9%. The decrease in photodegradation efficiency can be attributed to multiple factors. First, the active sites of the catalyst become occupied by dye molecules and reaction intermediates. This results in a decrease in the available catalytic surface area, which in turn hinders the photodegradation process. Additionally, at high concentrations, the particles of the catalyst tend to agglomerate, further reducing the effective surface area for catalysis. Furthermore, the adsorptive occupation of active sites by various substances can lead to the blocking of these sites, thereby lowering the overall photodegradation efficiency.

3.11 Effect of radical scavengers

The two main ROS, OH• and O2•, are known to contribute significantly to the surface reaction. The hydroxyl radical is a non-selective, extremely powerful oxidant that causes partial or total mineralization of a variety of organic compounds. These species are the most important in the decolorization process, and raising their numbers increases the
pace of decolorization. Different scavengers can be used to determine the number of these species and their effects. Several scavengers were utilized in this investigation, including para-benzoquinone for O$_2$. For both h$^+$ and OH$^-$, potassium iodide (KI) and tert-butanol are used, respectively. As exhibited in Figure 17, the RhB decolorization efficiency is 99% without scavengers after 120 min of irradiation. The degradation efficiency was reduced to 32% under the same circumstances when tert-butanol was added and to 61% when para-benzoquinone was added. Because the iodide ion is a powerful scavenger that reacts with the valence band hole and adsorbed OH$^-$ radicals, the addition of KI, on the other hand, caused a 17% reduction in the degrading efficiency. The major species are hydroxyl radicals, while the second species is O$_2^-$, according to these investigations. All tests used a catalyst concentration of 1 g L$^{-1}$, a dye concentration of 15 ppm, a pH of 9, a scavenger, and a temperature of 25°C [39].

### 3.12 Mechanism for photodegradation of RhB

Photocatalysis involves three main processes: charge carrier separation, migration, and surface redox reactions. Applications of bare ZnO are limited due to its wide band gap (3.3 eV), resulting in poor charge separation and low visible light absorption [40–42]. Doping or decorating ZnO with noble metals like Au can enhance its photoactivity [43,44].

When exposed to visible light, the Au–ZnO catalyst generates electron–hole pairs. Au acts as an electron sink, preventing recombination due to its lower conduction band edge compared to ZnO [45,46]. Photogenerated electrons move from Au to ZnO, while holes move from ZnO to Au. These charge carriers then participate in redox reactions at the surface [47–49].

Electrons in the conduction band can reduce adsorbed oxygen (O$_2$) to superoxide radicals (O$_2^-$), while holes in the valence band can oxidize hydroxyl ions (OH$^-$) to hydroxyl radicals (OH$^-$). These highly reactive radicals degrade organic pollutants into harmless species like CO$_2$ and H$_2$O [50–52].

Understanding the dominant reactive species responsible for RhB degradation over Au–ZnO is crucial [53,54]. During the photodegradation process, scavengers like tert-butanol (OH trap), potassium iodide (OH and h$^+$ trap), and para-benzoquinone (O$_2$ trap) were added to suppress specific reactive species.

The inclusion of tert-butanol and para-benzoquinone had minimal impact on RhB degradation, indicating that O$_2^-$ radicals play a minor role. However, potassium iodide...
significantly reduced RhB degradation, suggesting that both holes (h+) and hydroxyl radicals (OH−) are critical contributors [49,55]. Photodegradation efficiency follows the order: KI > tert-butanol > THF, confirming that h+ and OH− are the main reactive species responsible for RhB degradation under visible light on Au–ZnO:

\[
\begin{align*}
\text{ZnO} + h\nu &\rightarrow \text{ZnO}(h_{\text{VB}}^+ + e_{\text{CB}}^-) \quad (4) \\
\text{O}_2 + e_{\text{CB}}^- &\rightarrow \text{O}_2^- \quad (5) \\
\text{OH}_2^- + h_{\text{VB}}^+ &\rightarrow \cdot\text{OH} \quad (6) \\
\cdot\text{O}_2^- + \text{RhB} &\rightarrow \text{Dye degradation} \quad (7) \\
\cdot\text{OH} + \text{RhB} &\rightarrow \text{Dye degradation} \quad (8) \\
\text{RhB} + h_{\text{VB}}^+ &\rightarrow \text{Dye degradation} \quad (9)
\end{align*}
\]

4 Conclusions

Citrus medica leaf extract was successfully used to prepare various nanomaterials, including ZnO, Au, and Au–ZnO composites (95:5 and 90:10), for photodegradation applications in water purification. Characterization techniques like XRD, FE-SEM, TEM, EDX, and AFM confirmed the structural, morphological, optical, elemental, topographical, and chemical properties of these nanomaterials.

Decoration of ZnO with Au shifted its absorption peak towards the visible light range, leading to significantly improved photodegradation efficiency. The Au–ZnO (90:10) composite achieved the highest efficiency, reaching 99.1% compared to 52.32% for bare ZnO. Under optimal conditions (pH 12, 50 min irradiation), this composite proved to be a viable photocatalyst for degrading RhB dye under visible light.

Experiments confirmed the effectiveness of the nanocatalysts in removing RhB dye from water under visible light. The optimal conditions for Au–ZnO (90:10) were 1.0 g L−1 catalyst, 20 ppm RhB solution, pH 10, and 50 min irradiation, achieving 99% photodegradation.

Enhanced photodegradation efficiency in Au–ZnO (90:10) was attributed to photogenerated holes and hydroxyl radicals. Reaction kinetics and reusability of the best catalyst were also studied, confirming its sustained effectiveness over multiple cycles.

In conclusion, this study demonstrates the successful synthesis of Au–ZnO nanocomposites using Citrus medica extract and their potential as promising photocatalysts for organic dye degradation and water.

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