Photocatalytic Activity of Ag-ZnO Nanocomposites Integrated Essential Ginger Oil Fabricated by Green Synthesis Method

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Abstract. Facile and eco-friendly green synthesis route was used to fabricate pure ZnO nanoparticles (NPs) and silver doped ZnO nanocomposites (Ag-ZnO NCPs) using essential ginger oil (EGO) as reduction agent. These Ag-ZnO NCPs were determined and characterized via various analytical tools such as X-ray diffraction, FESEM, and UV-Vis spectrophotometer. X-ray diffraction patterns confirmed the crystallinity of single ZnO that showed a hexagonal wurtizite (HW) structure with preferential orientation in the (100) direction and the Ag NPs verified face center cubic (FCC) structure with preferred orientation in the (111) direction. The FESEM images exposed uniformly distributed triangle cages of ZnO NPs and nanowires shape of Ag-ZnO NCPs. The UV-Vis absorption band of as-synthesized Ag-ZnO NCPs showed sharp and minor peaks at 395 nm and 550 nm. Photocatalytic activity of Ag-ZnO NCPs was obtained through methylene orange (MO) dye degradation tests, which exhibited remarkable photodegradation efficiency around ≈ 90% after 150 min under UV light. In contrast, single ZnO revealed photodegradation efficiency ≈ 84% at 150 min UV light exposure. These Ag-ZnO NCPs can offer a great potential for large demands of semiconductor applications.

1. Introduction
Recent advances in the field of nanotechnology applications which rely on metals and semiconductors materials are of interest due to their distinctive electrical, optical, and catalytic characteristics. Particularly, the ability of nanocomposites (NCPs) synthesis with diverse shapes and aspect ratios have led to the production of a wide range of photocatalyst agents such as ZnO, SnO₂, TiO₂ etc. [1-3]. Zinc oxide (ZnO) is considered to be one of the most commonly observed semiconductor photocatalysts because of its high photocatalytic activity. In addition, its abundant natural resources, non-toxicity, low cost, high efficient generation of photon induced carriers (electron-hole pairs) and physical and chemical stability have made them exportable [4, 5]. However, rapid recombination of photo-excited electron-hole pairs weakens the photocatalytic efficiency of ZnO NCPs. Hence, numerous attention have been focused on the modification of semiconductors structures (ZnO, TiO₂, etc.) with noble metal (Ag, Au, Pd etc.). The promising effect of the noble metal photocatalytic activity is to enhance the process of reduction and thus improve efficiency of light harvesting [6-11].

Recently, sundry reports have revealed that the noble metal nanoparticles (NPs) exhibit an unusual redox activity via readily accepting electrons from a suitable donor [12, 13]. If these metal NPs come into contact with a charged semiconductor NCPs, they can undergo Fermi-level equilibration. The literatures have proved that the modification of ZnO doped noble metal such as Ag NPs is an efficient way to enhance photocatalytic performance [9, 14-16]. Ghosh et al.,[17] reported that when Ag NPs are attached to ZnO, it will perform as an electron sink to allow interface from ZnO to Ag NPs structure chins. This will increase the rate of electron transfer and keep holes remaining on the surface of ZnO NCPs.
In the current report, ZnO-doped Ag NCPs were successfully synthesized at room temperature via a simple process of green synthesis method using essential ginger oil (EGO). This green method plays two important roles in production process. It could be act as a reaction agent for ZnO NCPs formation and reduce (Ag⁺) to (Ag⁰) structure. Depend on our knowledge; the literatures have not paid attention in the area of novel green synthesis technique to preform Ag-ZnO NCPs toward photocatalytic applications. A systematic study is presented to the structure and phase characterization, as well as the optical properties of the as-synthesized Ag-ZnO NCPs. Finally, the photocatalytic activity of pure ZnO and Ag-ZnO NCPs were determined and discussed.

2. Experimental Procedures

2.1. Extraction of essential ginger oil (EGO)
Ginger oil was extracted via hydro-distillation as explained in a literature [2]. Fresh ginger was washed several times via deionized water (DW) and then crushed. The as-prepared precursor was boiled with DW in a distillation hydration device in atmospheric pressure to gain the necessary oil. Figure 1 shows the synthetization process of Ag-ZnO NCPs.

Figure 1. Experimental work, (a) Fresh ginger, (b) Oil extraction, (c) Ginger oil, and (d) Ag-ZnO NCPs.

2.2. Synthesis of Ag-ZnO NCPs
Ag-ZnO NCPs was produced by one-pot route in EGO. This precursor of EGO processed as 40 ml) was dissolved in ethanol (100 ml) under stirring at room temperature. Then, zinc acetate dehydrates (Zn (Ac)₂. 2H₂O, (0.5 mM)) was added to the as-prepared precursor solution in an aqueous bath system at 80 °C with continuous stirring. Light cream color suspension was obtained after temperature treatment and continued stirring for (3 h). Followed, AgNO₃ (0.1 mM) was added into suspension and the reaction was further preceded for 30 min. Finally, the as-synthesized product was collected by centrifugation and then washed by ethanol to remove extra EGO and dried at 100 °C for 3 h. Likewise, pure ZnO NP was synthesized to compare with the Ag-ZnO NCPs. The surface morphology and structural properties of as-synthesized Ag-ZnO NCPs were determined using FESEM (Hitachi 4100-SU8020) and XRD (Rigaku, 2100)
measurements. The UV–Vis absorption spectra in the wavelength range of 300-800 nm were measured using a PerkinElmer Lambda-2 spectrometer. All the characterizations are performed at room temperature.

2.3. Photocatalysis sample preparation
Methyl orange (MO) employed as a representative dye pollutant to study the photocatalytic act of pure ZnO and Ag-ZnO NCPs under UV light at room temperature. The photocatalysts (20 mg) was stirred in 40 ml of (1 x 10^{-4}) M aqueous solution of MO. Before irradiation process, the solution was stirred in the dark for 4 h to achieve an adsorption/desorption equilibrium process. For each irradiation time intervals, the solution absorbance was measured using UV-Vis spectrophotometer. The photocatalytic activity of pure ZnO and Ag-ZnO NCPs was estimated using the following equation [6]:

$$D(\%) = \frac{A_o - A_t}{A_o} \times 100$$  

(1)

Where \((A_o)\) represents the initial absorbance after the equilibrium adsorption of (MO) and \((A_t)\) the absorbance after a time interval of irradiation \((t)\).

3. Results and Discussion

3.1. X-ray diffraction (XRD) analysis
The crystalline structures studies of pure ZnO NPs and Ag-ZnO NCPs were confirmed by the XRD analysis. Figure 2 shows that the X-ray pattern of pure ZnO NPs was distinguished with a hexagonal wurtzite (HW) structure according to (JCPDS card no. 36-1451) [5]. This spectrum showed 5 diffraction peaks labeled at (31.8\(^\circ\), 34.1\(^\circ\), 36.1\(^\circ\), 56.6\(^\circ\), and 67.7\(^\circ\)), were indexed to the (100), (002), (101), (110), and (112) planes, respectively. Clearly, the (100) direction was represented the preferential orientation of ZnO NPs. Moreover, XRD pattern in Figure 2 referred to the growth of Ag-ZnO NCPs according with characteristic diffractions of face-centered-cubic (FCC) structured based on (JCPDS Card no. 04-0783) [18]. This XRD spectrum exhibited different diffraction peaks placed at (38.1\(^\circ\), 44.3\(^\circ\), 64.6\(^\circ\), and 77.4\(^\circ\)) indexed to the (111), (200), (220), and (311) planes, respectively with preferred orientation in the (111) direction. Thus, the XRD diffraction peaks confirmed that the synthesis NCPs consist of Ag and ZnO. However, the diffraction peaks corresponding to the Ag-ZnO NCPs was broader and weaker in intensity in comparison with the pure ZnO NPs as displayed in Figure 2.
3.2. Morphology analysis

Figures 3 illustrates the FESEM images of green synthesis method produced Ag-ZnO NCPs. Inspection of the FESEM image in Figure 3a displayed the formation of agglomerate ZnO NPs with nanorod shape. In contrast, loose and few agglomerates of NPs have grown bigger by creating clusters as well as nanorod-like Ag-ZnO NCPs form as can be seen in Figure 3b. Obviously, the agglomerations of Ag-ZnO NCPs unlike pure ZnO NPs were shown much larger in size. These results confirmed that the morphology of as-synthesized samples in this study have been importantly changing compared with the previous report due to the changes in the concentration of precursor materials [5]. Azizi et. al., [2] reported that the synthesis of Ag-ZnO NCPs as agglomerate structure only Ag-NPs embedded in ZnO NPs via a ‘‘one-pot’’ process in EGO solution under growth time of 3 hours.
3.3. UV-Visible spectra

At room temperature, Figure 4 exemplifies the UV-Vis absorption spectra of pure ZnO NPs and Ag-ZnO NCPs. Two distinguish absorption spectra were perceived, compared with the absorption edge of pure ZnO NPs at 409 nm, while the Ag-ZnO NCPs showed higher intensity and blue-shift of the surface plasmon absorption band around (395 nm ??) and minor absorption peaks around 550 nm. These results have strongly consistent with the previous study [2]; and could be ascribed to the strong interfacial coupling between ZnO NPs and the Ag NPs. This occurs due to electron deficiency on the surface of Ag NPs, and then that deficiency arises because of transfer of electrons from Ag NPs with higher Fermi-energy level to ZnO NPs with lower Fermi-energy level. Furthermore, these blue-shift and high intensity in absorption edge of as-synthesis Ag-ZnO NCPs could be strongly attributed to the changes in the size of particle and surface morphologies [2,19].

Furthermore, optical absorbance features of pure ZnO NPs and Ag-ZnO NCPs on their the bandgap measurements were estimated by plot of \((\alpha h\nu)^2\) with photon energy \((h\nu)\) as shown in Figures 5 (a-b). Where, \((h)\) is Plank constant, \((\alpha)\) the absorption coefficient, \((\nu)\) the photon frequency, and the energy bandgap \((E_g)\). Figures 5 (a-b) revealed that the optical bandgap of pure ZnO NPs was found around \(\approx 3.37\) eV which
slightly increased for Ag-ZnO NCPs approximately ≈ 3.45 eV. This indicates the addition of Ag NPs in the as-synthesis structure led to enhance their crystallinity through reduce defect sites [5, 20].

Figure 5: Optical energy bandgap of (a) pure ZnO NPs and (b) Ag-ZnO NCPs

3.4. Photocatalytic activity
The photocatalytic performances of the pure ZnO NPs and Ag-ZnO NCPs were evaluated via assessing the absorbance band in range of 300-600 nm with methylene orange (MO) dye under UV light irradiation (Figure 6). Irradiation time as a function of degradation efficiency was presented in Figure (7). It was evident that the increase of photo irradiation time from 0-150 min for time interval 30 min in the presence of Ag-ZnO NCPs led to gradually decrease in the (MO) concentration. The photodegradation efficiency reached nearly 90% after illumination time of 150 min via UV light (Figure 7). These findings confirmed that the photocatalytic activity dependent Ag-ZnO NCPs can be meaningfully enhanced through doping an suitable amount of Ag NPs, which consistent with previous studies [7, 20]. Due to the essential role of Ag NPs on the surface of ZnO NPs, it was act as a sink for the electrons. The enhancement of photocatalytic activity can be attributed to increase the separation of photogenerated electron-hole pairs via endorses interfacial charge-transfer kinetics between the semiconductor and the metal NPs [7, 20-25].

Furthermore, Liu et al., [7] reported that the structural defects may serve as the recombination centers for photo-generated electron-hole pairs during photocatalysis process. This can be leading to decrease the photocatalytic performance. Thus, the present green method which used to synthesis of Ag-ZnO NCPs will be beneficial to photocatalytic reaction because the improvement of crystallinity properties as established by analysis results of XRD (Figures 2).
4. Conclusions

In summary, the pure ZnO NPs and Ag-ZnO NCPs were synthesized by a green method using EGO solution. This is an advantage for ginger and other plants extract containing similar functional groups which can potentially contribute in fabricating NCPs and be converted into valuable nanomaterial. Pure ZnO NPs revealed photodegradation efficiency about $\approx 84\%$ at 150 min UV light exposure. While Ag-ZnO NCPs was
showed great photocatalytic activity with that the MO dye degraded around ≈ 90% after 150 min under UV light irradiation. It is an obvious that after the illumination time of 150 min, the initial MO solution can be totally decolorized. It can be concluded that small crystal sizes with larger specific surface areas and high crystallinity of the Ag-ZnO NCPs may play important roles in the enhancement of photocatalytic activities.

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