One Pot and Facile Preparation of Pure ZnO and Cudoped Au-ZnO Nano-particles : Photocatalytic Properties

Anis FKIRI (anisfkiri9@gmail.com)
Lab of Hetero-Organic Compounds and Nanostructured Materials (LR18ES11) University of Carthage. Faculty of Sciences of Bizerte, 7021 - Zarzouna, Tunisia.

Mohamed Ali Saidani
Lab of Hetero-Organic Compounds and Nanostructured Materials (LR18ES11) University of Carthage. Faculty of Sciences of Bizerte, 7021 - Zarzouna, Tunisia.

Leila Samia Smiri
Lab of Hetero-Organic Compounds and Nanostructured Materials (LR18ES11) University of Carthage. Faculty of Sciences of Bizerte, 7021 - Zarzouna, Tunisia.

Research Article

Keywords: Au-ZnO, Nanoparticles, Hydrothermal method, methylene blue, Photocatalytic activities

DOI: https://doi.org/10.21203/rs.3.rs-552432/v1

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Abstract

In this present work, a new synthesis process, named hydrothermal method, of hybrid Au-ZnO nanoparticles (Au-Zn$_{1-x}$Cu$_x$O; where 0<x<1%) was presented and discussed in detail. Nanocrystals of copper doped zinc oxide in the presence of diethylene glycol (DEG) as solvent were synthesized using the One Pot and Facile new proposed synthesis process. The photocatalytic activities of the synthesized nanoparticles were tested and analyzed for the degradation of methylene blue (MB) under white light illumination. The performances of the synthesized Au-ZnO nanoparticles showed a pronounced enhancement compared to either pure ZnO nanoparticles or to undoped Au-ZnO nanocomposites. Various key parameters such as a photocatalyst loading, the MB concentration, and type current gas have been systematically investigated on the catalytic activities of the as-prepared.

Highlights

- Synthesis of pure ZnO and Cu doped Au-ZnO Nano-particles using a hydrothermal method
- Characterization of pure ZnO and Cu doped Au-ZnO Nano-particles by different techniques
- Degradation of Methylene Blue (M.B) by pure ZnO and Cu doped Au-ZnO Nano-particles under solar light irradiation

Introduction

During the last few years, organic contaminants have attracted great interest from the scientific and industrial community in all over the world as major pollutants, which noteworthy contributing to environmental degradation, especially water and the atmosphere.

To the best of our knowledge, because of they contain many dyes, the discharged wastes are considered to be poisonous to microorganisms, aquatic life, human beings, and so on [1]. In this regard, hybrid Metal (Au, Ag, Cu)/semi conductor (ZnO, TiO$_2$, ZnS) nanomaterial samples have received a great deal of attention [2-5] due to the synergetic interaction between the metal and semiconductor components [6,7]. Practically, among the wide variety of the hybrid samples based on metal-semiconductors nanomaterials, hybrid nanoparticles based on Au-ZnO have received considerable attention from academia as well as industry [8-12]. On the other hand, hybrid nanoparticles based on Au-ZnO are crucial samples for research and development of numerous applications such as solar energy conversion [13], biological detection [14,15] sensing fields [16-18], photo-catalysis field [19-21] and so on, due to its impressive properties. Consequently, a plethora of research groups have investigated the catalytic effect of Au-ZnO, which are synthesized using various methods like chemical vapor deposition [22], electrodeposition synthesis [23], wet-chemical synthesis [24], coprecipitation method [25], hydrothermal method [26] and Polyol method [27]. Bifunctional nanoparticle Au-ZnO has several advantages: low toxicity, biocompatibility and high chemical stability. The photocatalytic degradation test under UV irradiation of rhodamine B (RhB) deposited on Au-ZnO NPs shows that these NPs exhibit good catalytic performances compared to that of pure ZnO [28] with an increase in the degradation efficiency of a factor 10. This is
attributed to charge transfer between the Au and ZnO [29]. Hang Yu and al. [30] prepared Au-ZnO nanocomposites and ZnO nanowires by a simple chemical method and found that the Au-ZnO hybrids posses higher photocatalytic activity for degradation of benzene; Under UV irradiation and visible light, the degradation percentages reach 56.0% and 33.7% respectively. Yuanzhi Chen and al [31] synthesized Au-ZnO nanoflowers, nanomultipods and nanopyramids by a one-pot method. In comparison with pure ZnO nanocrystals, hybrid Au-ZnO nanoparticles exhibit very high photocatalytic activity during the degradation of Rhodamine B. The photocatalytic properties of hybrid nanowires Au-ZnO synthesized by Xue Zhao and al. [32] showed a photodegradation of dye methyl orange (MO) increased by a factor 3.

In this work, we report on the one pot and facile synthesis of pure ZnO and hybrid Au-ZnO nanoparticles (Au-Zn_{1-x}Cu_xO; where 0<x<1%) formed by hydrothermal method in diethylene-glycol (DEG) as a solvent, by the sole use of gold, zinc acetate and copper chloride precursors without the adding any other reagents. Furthermore, the as synthesized nanoparticles have improved photocatalytic properties which are uses in the photodegradation tests of MB under solar illumination.

**Experimental Procedure**

2.1. Synthesis of Au-Zn_{1-x}Cu_xO nanoparticles

The Cu doped hybrid Au-ZnO nanoparticles (Au-Zn_{1-x}Cu_xO; where 0<x<1%) was synthesized via one pot and facile hydrothermal method. Briefly, gold chloride (HAuCl$_4$.3H$_2$O) (15 mg), zinc acetate dehydrate Zn(OAc)$_2$.2H$_2$O (1.5g) and Copper chloride CuCl$_2$ (x g) were mixed together in 50 mL of diethylene-glycol (C$_4$H$_{10}$O$_3$) [33-36]. The prepared solution was heated to a temperature 160 ºC, magnetically stirred for about 60 minutes, cooled to room temperature, and kept undisturbed for 3 hours. The sequential reactions are thermally controlled. At the end of the reaction, the precipitate is centrifuged, washed several times with ethanol, and dried in vacuum at 100°C for 24 h to yield a white dry and purple Cu doped Au-ZnO powder.

2.2. Characterization

X- ray diffraction patterns (XRD) were collected using an INEL diffractometer with a cobalt anticathode ( = 1.79030 Å and 2ϴ = 20-80°) at room temperature. Morphological details of the synthesized of pure ZnO and (Au-Zn_{1-x}xCu_xO; where 0<x<1%) nanoparticles were characterized by transmission electron microscopy (TEM) (JEOL-JFC 1600). Energy-dispersive X-ray spectrograph (EDX) attached to the TEM was used for elemental analysis. The UV-visible spectra of pure ZnO and (Au-Zn_{1-x}xCu_xO; where 0<x<1%) nanoparticles dispersed in ethanol were performed on a Perkin-Elmer Lambda 11 UV/VIS spectrophotometer (wavelength range in 200-800 nm).

2.3. Photo degradation experiments

The photocatalytic activities of pure ZnO, pure Au-ZnO and Cu doped Au-ZnO (Au-Zn_{1-x}Cu_xO; where 0<x<1%) nanoparticles were evaluated by the degradation of MB under solar light irradiation [36,37]. In
each test, the evaluation of the photo-degradation performance of MB was prepared as follows: 30 mg of
the nanoparticles was dissolved in 0.1 L solution of methylene blue (MB) (3 mg / 0.1 L) at pH = 6. Using
UV-Visible Spectrophotometer Shimadzu 1650PC, the concentration of (MB) in each degraded sample
was determined. The percentage of degradation of (MB) was determined using the following formula:

\[
\text{Degradation rate} \, (\%) = \frac{(C_0 - C_t)}{C_0} \times 100
\]

Where $C_0$ is the initial concentration of MB and $C_t$ is the concentration at time t.

**Results And Discussion**

**3.1. Characterization of Au-Zn$_{1-x}$Cu$_x$O nanoparticles**

The diffractions of pure ZnO and Au-Zn$_{1-x}$Cu$_x$O (0<x<1%) are shown in Fig. 1. Three main peaks are
mentioned in the X-ray diffraction patterns of Au-Zn$_{1-x}$Cu$_x$O at $2\theta = 31.76, 34.41$ and 36, 30°, respectively,
are which very well correspond to the (100), (002) and (101) diffraction peaks of zinc oxide, ZnO (JCPDS
No. 36-1451). The diffractograms obtained reflect the formation of the pure hexagonal wurtzite ZnO
phase (space group P6$_3$mc, lattice constant $a = 3.249(2)$ Å, $c = 5.208(3)$ Å). In addition to ZnO diffraction
peaks, three diffraction peaks observed in the XRD patterns at $2\theta = 38.3^\circ, 44.2^\circ$ and 64.73°, respectively,
assigned to the lines (111), (200) and (220) of fcc gold nanoparticles (space group Fm-3m, lattice
constant $a = 4.070$ Å) (JCPDS No. 65-2870) [38]. The lines are particularly wide reflecting the nanometric
character of the Au-Zn$_{1-x}$Cu$_x$O nanoparticles produced. The diffractograms have shown that the
nanoparticles thus produced exhibit very high crystallinity without any heat treatment. We also note that,
the X-ray diffractions do not show any additional peak corresponding to the oxides mixed CuO, Cu2O, Cu-
Zn or to other phases containing copper. Obviously, this result is due to the small amount of Copper
incorporated in the materials. Tab.1. shows, the average size of the ZnO crystallites, determined using the
Debye-Scherrer formula [39]. The lattice parameters of the synthesized were refined by the Rietveld
method [40,41]. The variation of lattice parameters $a$ and $c$ as function Cu content (0<x<1%) with the
molar substitution of Zn$^{2+}$, is shown in table 1. It is seen that, the lattice parameters decrease with
increasing concentration of copper. Doping makes the ZnO volume slightly smaller, the radius of the
doped particles is very close, Zn$^{2+}$ (0.060 nm) >Cu$^{2+}$ (0.057 nm) so the lattice constant changes little and
the material does not have significant lattice distortion. This fact gives an indication of the substitution
of Zn$^{2+}$ with Cu in ZnO [42].

The determination of morphologies of pure ZnO, and Cu-doped Au-ZnO (Au-Zn$_{1-x}$Cu$_x$O; where 0<x<1%)
nanocomposites was undertaken by the means the transmission electron microscopy. Figure 2b displays
aggregates of spherical Au-ZnO NPs (with an average size of 150 nm). The TEM images (Fig. 2b-d) of Cu
doped Au-ZnO reveal also agglomerates of spherical Au-Zn$_{1-x}$Cu$_x$O nanoparticles. The average size of the
particles is about 150 nm. The EDX spectrum of the undoped Au-ZnO NPs presented in Fig. 3a, show that
only Au, O and Zn elements are detected. The presence of Ni is due to the grid used for the TEM/EDX
experiments. The EDX spectrum of the Au-Zn$_{1-x}$Cu$_x$O (x=0.001) (Fig. 3b) shows the existence of copper.
This result thus confirms the substitution of Zn$^{2+}$ by Cu$^{2+}$ ion. The presence of Ni results from the grid used for the TEM/EDX experiments.

The absorption spectra of the different samples Au-Zn$_{1-x}$Cu$_x$O show two absorption bands (Fig. 4a). The ZnO nanoparticles present a maximum absorption around 360 nm. A second broad absorption band centered at about 548 nm, which is assigned to the surface plasmon resonance of the gold nanoparticles (Fig. 4a). Using Tauc's plot method [43], the band gap of the as-synthesized can be calculated. Figure 4.b shows the so obtained bands gaps, they are respectively 3.17, 3.08 and 2.53 eV for x = 0, 0.1 and 1%. The blue shift in the band gap width with the increase in the copper doping content is certainly due to the decrease in the size and lattice parameters of the ZnO nanocrystals, obtained by measurement of X-ray diffraction (Tab. 1) [44].

### 3.2. Degradation of M.B

The catalytic tests of Au-Zn$_{1-x}$Cu$_x$O nanoparticles were evaluated for the degradation of MB in aqueous solutions exposed to sunlight. Figure 5a shows the UV-vis spectra of MB containing 0.1 g of suspended Au-ZnO at various irradiation times. The material exhibits an intense absorption peak centered on 663 nm which indicates the initial concentration of MB in the absence of any catalysts. It can clearly be seen that the maximum absorption of MB decreased considerably with increasing irradiation time. To compare the percentage of degradation of methylene blue according to the addition of different photocatalysts, the MB degradation process was investigated by the reaction kinetics. The given equation has been used to fit the experimental data:

$$\ln \left( \frac{C_0}{C_t} \right) = K_{ap} t$$

Where $k$ corresponds to the degradation constant, $C_0$ and $C_t$ are the concentration and MB and $t$ denotes the reaction time. The MB is not degradable at room temperature after 12 h under sun light, explicating that in the experimental conditions, we can neglect the photolysis of the MB molecule. Therefore, without the addition of the Au-Zn$_{1-x}$Cu$_x$O nanocomposies, the solution exhibits an intense blue color, which gradually decreases as a function of the irradiation time until it becomes colorless, in the presence of the Au-ZnO nanoparticles (Fig. 5a). The percentage of degradation is of the order of 62%.

The result of photocatalytic degradation of MB under solar light illumination in aqueous solution suggested that Cu doped Au-ZnO exhibited higher photodegradation towards MB than Au-ZnO nanoparticles. In order to compare the effect of copper doping for the Au-Zn$_{1-x}$Cu$_x$O (0<x<1%) hybrids on the percentage degradation of MB, all the tests were examined under the same conditions while keeping the other parameters unchanged. Figure 5b shows the $C_t / C_0$ versus time plot for different catalysts. We find that the catalytic performance of the photocatalysts is proportional with the increase in the level of copper incorporated in the zinc oxide material. The MB degradation efficiency increased from 62 % to 92% for Au-ZnO and Cu-doped Au-ZnO (1%) [36]. The following mechanism can explain the important result obtained for the degradation of MB in the presence of the Cu doped Au-ZnO catalyst (Fig. 6). ZnO can
generate holes in the valence band (VB) and electrons in the conduction band (CB) under solar irradiation. The photoinduced electrons in the CB of ZnO can transfer to Au since the empty conduction band energy levels of Au lie below the CB of ZnO [33, 36, 45]. The inhibition of recombination of photoinduced electrons and holes is significant due to the formation of the Schottky barrier at the Au-ZnO interface. Therefore, the metal domain can function as an electron sink to achieve enhanced separation of charge carriers. The ensuing electrons and holes can react with adsorbed oxygen and surface hydroxyl, respectively, and generate hydroxyl radicals which are have the ability to degrade MB molecules adsorbed on the surface of the catalyst.

Conclusions

To sum up, the preparation of ZnO and Cu doped Au-ZnO nanoparticles (Au-Zn\(_{1-x}\)Cu\(_x\)O where (0<x<1\%) were successfully achieved using a one pot and facile hydrothermal method, without the addition of any other reagents, template or intricate metal ligand. During these preparations the solvent has an important role, it is used both as solvent reducing agent and stabilizer. This hybrid nanoparticles show excellent catalytic results for the photodegradation of MB under solar light. Indeed, the degradation of MB is successfully by Au-Zn\(_{1-x}\)Cu\(_x\)O assisted photocatalysis in aqueous dispersion under Solar light. Miscellaneous parameters were tested such as solar energy’s effect, and the type of used catalyst.

Declarations

Acknowledgements

Anis Fkiri, gratefully acknowledges the support of the Ministry of Higher Education and Scientific Research of Tunisia.

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Tables

Tab.1. Crystallites average size, copper concentration, band gap and lattice parameters of substituted zinc oxide Zn$_{1-x}$Cu$_x$O deduced from the XRD data.
## Figures

![X-ray diffraction pattern of the ZnO, Au-ZnO and Cu doped Au-ZnO nanoparticles.](image)

**Figure 1**

X-ray diffraction pattern of the ZnO, Au-ZnO and Cu doped Au-ZnO nanoparticles.
Figure 2

Characterization of hybrid Au-ZnO nanocomposites using transmission electron microscopy (TEM): (a) images of pure ZnO; (b) pure Au-ZnO; (c) Au-ZnO (0.1% Cu) and (d) Au-ZnO (1% Cu) nanoparticles.
Figure 3

EDAX spectra of (a) Au-ZnO and (b) Cu doped Au-ZnO (1%Cu).
Figure 4

Absorption spectra (a) and Tauc plot for the absorption spectra (b) of pure Au-ZnO and Cu doped Au-ZnO nanoparticles.
Figure 5

UV-visible absorption spectra (a), Photocatalytic degradation of M.B over different Cu-doped Au-ZnO products under solar light irradiation (b).
Figure 6

The band structure of Au and ZnO junction with uniform Fermi level induced by electron transfer between Au and ZnO