Highly Efficient Photocatalytic and Antimicrobial AgGaCl Tri-Doped ZnO Nanorods for Water Treatment under Visible Light Irradiation

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Received: 29 January 2020; Accepted: 10 February 2020; Published: 7 July 2020

Abstract: The aim of the present study is to analyze the synergy of antimicrobial elements, such as Ga, Ag and Cl by incorporating them in ZnO nanorods and measuring their antimicrobial and photocatalytic activity under visible light irradiation for water treatment. AgGa-doped ZnO nanorods and AgGaCl-doped ZnO nanorods on polyethylene substrate were prepared by a simple and fast microwave assisted synthesis. HCl was used in order to lower the pH of the precursor solution and favor Ga and Cl incorporation in the ZnO nanorods. The synthesized undoped and doped ZnO nanorods were analyzed with SEM, EDX, XRD and CL. The photocatalytic properties of the nanorods were evaluated via methylene blue degradation under visible light irradiation. Antimicrobial activity of the nanorods was measured via growth kinetics of Vibrio parahaemolyticus. It was found that AgGaCl-doped ZnO nanorods improve the methylene blue photo-degradation and above all, the antimicrobial activity of the AgGaCl tri-doped ZnO nanorods showed a lethal effect on the bacteria’s growth. This work shows that AgGaCl NRs are an excellent alternative for the development of sustainable water treatment devices and antimicrobial applications.

Keywords: zinc oxide nanorods; antimicrobial activity; doped nanorods; photocatalytic activity; water treatment

1. Introduction

Water pollution is an increasing and concern issue mainly resulted from human activities, causing serious health, social and economic problem [1,2]. Among conventional water treatment methods, which focus on removing solid contaminants and killing pathogens, are chlorination, ozonation and ultraviolet irradiation, which have serious limitations. Chlorination is an ineffective method against some highly resistant waterborne pathogens, and tends to form carcinogenic disinfection by products when chlorine is added to water. Ozonation produces fewer byproducts but it is more expensive than chlorination. UV treatment does not leave residual products; however, it does not protect against future infections in the distribution network and it is unsuitable to treat turbid water as the light cannot penetrate [3,4].

In recent years, the use of nanomaterials as photocatalytic materials has gained much attention as an alternative active material in water treatment. Taking advantage of their large specific area and unique properties make them good candidates due to their ability to improve the degradation of organic pollutant molecules through oxidative processes [5–7]. A photocatalytic process initiates when the catalyst, generally metal oxide semiconductors such as TiO₂, ZnO, etc., absorbs a photon of greater energy than its energy band gap generating electron-hole pairs. Some of the photogenerated
electron-hole pairs recombine releasing their energy, while others are using it to participate in oxidation-reduction reactions on the surface of the catalyst producing reactive oxygen species (ROS), such as superoxide ions and hydroxide radicals (O$_2^-$, •OH). Conventional catalysts have limited capabilities as not being able to produce these radicals using visible light irradiation, missing the opportunity to use sunlight as a source of activation. In recent years, researchers have focused in the effort to synthesize improved visible light photocatalyst materials [8–10]. Metal-doped semiconductors are alternative materials to improve the visible light driven photocatalysts [11,12]. Another approach to further activate the photocatalysis process is by generating enough surfaces electronic states via microwave assisted [13].

There are many studies focused on the development of effective photocatalytic materials capable of removing organic contaminants from water but most of them do not consider the antimicrobial properties of the materials [14–16]. Ag nanoparticles (NPs) and some Ga, and Cl-based compounds exhibit great antimicrobial properties but cause human, animal and environmental health risks when used at high concentrations [17–19]. The antimicrobial properties of Ag-NPs have been attributed to the binding affinity of surface-Ag to important functional groups of enzymes [20]. Antimicrobial properties of Ga have been attributed hypothetically to the capture of Ga atoms by the bacteria through their siderophores molecules (Fe chelating agents) blocking multiple bioprocesses in the bacteria when Fe$^{2+}$ is oxidized to Fe$^{3+}$ [21,22]. In the case of Cl-compounds, the antimicrobial activity has been attributed to its oxidant power acting on peptide links and protein denaturation [23,24]. A viable alternative, taking advantage on the antimicrobial properties of both kind of materials, avoiding their health risks, is by incorporating them at low concentrations (doping) in a more secure nontoxic material network (e.g., ZnO) supported on a polymer membrane.

In a previous work, we presented the photocatalytic and antimicrobial properties of Ga-doped ZnO nanorods (NRs) and Ag-doped ZnO nanorods, separately [13]. Experiments showed that both Ga and Ag can improve the photocatalytic and antimicrobial properties of ZnO nanorods; as well as the relationship between doping concentrations, with both the toxicity effect of the NRs toward bacteria and the NRs photocatalytic performance. After this study, possibility arose of a synergy interaction between Ag and Ga or other antimicrobial elements incorporated simultaneously in the ZnO NRs that can improve their antimicrobial performance and photocatalytic activity. In this work, we synthesized AgGa-doped ZnO NRs and AgGaCl-doped ZnO NRs supported on polyethylene via fast microwave-assisted synthesis and evaluated their photocatalytic performance and antimicrobial activity. The outcome of this study presents a low cost, visible light-responsive material with high photocatalytic activity and an excellent toxicity toward pathogen bacteria. These results showed that the AgGaCl NRs are promising as a potential candidate for the development of sustainable water treatment devices and other antimicrobial applications.

2. Results and Discussion

2.1. NRs Characterization

2.1.1. Morphology

In a previous work [13], we synthesized 2 at.% Ga-doped ZnO NRs and 2 at.% Ag doped ZnO NRs with a diameter range of 300–500 nm and 500–800 nm, respectively. In the present work, we synthesized ZnO NRs doped with both Ag and Ga (ZnO_AgGa) and also tri-doped ZnO_AgGaCl NRs adding HCl to the precursor solution. Figure 1 illustrates the morphology of synthesized ZnO NRs. AgGa-doped ZnO NRs showed diameters of 200–250 nm and their diameter slightly reduces to 125–175 nm when doped with Cl at pH 6.0, meanwhile the NRs diameters increased when doping with Cl at pH values between of 5.5 and 5.0.
Figure 1. SEM images of the synthesized doped ZnO NRs: (a) AgGa-doped ZnO NRs, AgGaCl-doped ZnO NRs at pH 6 (b,e), pH 5.5 and (d,e) at pH 5.0 (f,g). (h) Samples of AgGaCl-doped ZnO NRs on PE substrate.

2.1.2. Chemical Composition
2.1.2. Chemical Composition

Figure 2 shows the EDX spectra and atomic percent’s of the AgGa-doped ZnO NRs and the AgGaCl-doped ZnO NRs. Figure 2a show that AgGa-doped ZnO NRs includes elements such as Zn, O, Ga and Ag. Meanwhile AgGaCl-doped ZnO NRs include elements such as Zn, O, Ga, Ag and Cl (Figure 2b–d). The S signal-peak present in spectrum arises from the thiolated substrate. According to these results, lowering the pH favored the incorporation of Ga in the ZnO network but decreases that of Ag. These results are consistent considering that both Ga and Ag tend to occupy Zn vacancies in the ZnO network and that the Ga precursor solubility is more suitable in acidic solutions. Cl was incorporated in the ZnO network at very similar concentrations at pH 6.0 and 5.5 being more remarkable at pH 5.0 with an atomic concentration above 1%.

**Figure 2.** EDX spectra and atomic percent’s of AgGa-doped ZnO NRs: (a) pH unmodified and (b–d) pH modified.

2.1.3. Structure

XRD results of PE, ZnO AgGa-doped and tri-doped ZnO_AgGaCl NRs are reported in Figure 3. The analysis in the range 30–80° (Figure 1a) showed three main peaks at 34.42°, 36.25° and 47.53°, respectively indexed to the (0 0 2), (1 0 1) and (1 0 2) planes, typical of the hexagonal ZnO crystal structure (JCPDS 00-036-1451). No trace of chlorine or Ag related phases was detected; which is consistent considering the low doping concentration used (2% at.). Only AgGa-doped ZnO NRs showed a weak peak corresponding to metallic Ga (JCPDS 00-027-0022).
2.1.4. Optical Properties

The optical properties of undoped ZnO NRs, AgGa-doped ZnO NRs and AgGaCl-doped ZnO NRs were studied by CL (Figure 4a). For all samples, it can be observed a UV emission band around 385 nm (3.22 eV) and a broad emission band from ~450 to 700 nm in the visible region, centered in 550 nm. In the literature, the ZnO UV emission is attributed to near band edge emission (NBE) resulted by irradiative recombination of excitons [25] and the broad visible emission band at 450 to 620 nm is often attributed to lattice-defects where the electrons transition into deep levels caused by intrinsic defects such as oxygen vacancies and/or zinc interstitials [26]. The intensity of defect-related light-emission, overpass that of the NBE emission in the AgGaCl-doped ZnO NRs at lower pH, indicating an increment in surface defects. A blue emission centered at ~430 nm appears with the incorporation of Cl as dopant material. A change of color between the AgGa-doped ZnO NRs and the AgGaCl-doped ZnO NRs could be observed on the samples (Figure 4b).
2.2. NRs Photocatalytic Activity

The photocatalytic performance of undoped ZnO NRs, Ag doped ZnO NRs, Ga-doped ZnO NRs, AgGa-doped ZnO NRs and AgGaCl-doped ZnO NRs was evaluated under visible light irradiation (Figure 5). It can be observed that all samples showed a very good photocatalytic activity with MB degradation between 50% and 75%. The AgGa-doped ZnO NRs resulted with the lower photocatalytic activity, meanwhile the AgGaCl-doped NRs (pH 5.5) degraded approximately 75% of MB solution in 5 h.

![Figure 5. MB photodegradation kinetics under visible light irradiation for undoped and Ga, Ag, AgGa and AgGaCl-doped ZnO NRs. Inset: MB photodegradation experiment.](image)

Some authors have indicated that Cl doping of ZnO causes an increment of the photogenerated electron concentration [27,28] and that chlorine atoms are incorporated into the ZnO lattice by occupying oxygen sites, creating an energy level (a shallow donor), inside the ZnO energy band gap. Our optical study suggests that blue emission shoulder at ~430 nm might be generated by electron transitions from Cl donor-levels to the valence band. Thus, under a photocatalytic experiment, a greater electron production must be occurred in Cl doped ZnO NRs, empowering more electrons to participate in their surface oxidation–reduction reactions, enhancing the MB degradation by ROS.

2.3. NRs Antimicrobial Activity

The antimicrobial activity of undoped ZnO NRs, Ag doped ZnO NRs, Ga-doped ZnO NRs, AgGa-doped ZnO NRs and AgGaCl-doped ZnO NRs it is shown in Figure 6. All samples showed an antimicrobial effect against *Vibrio parahaemolyticus*. As confirmed with our previous work the Ag doped ZnO NRs showed good antimicrobial activity. Meanwhile, the AgGaCl-doped ZnO NRs were lethal against the bacteria showing an antibiotic behavior during the 12 h of reaction time. Considering the elements and reaction conditions during the AgGaCl-doped ZnO NRs synthesis, it is possible the formation of chlorine dioxide (ClO$_2$) on the ZnO NRs. A mechanism of ClO$_2$ production is suggested in Equations (1)–(4). Also, during the NRs synthesis AgCl could be formed and when the photocatalytic-antimicrobial evaluation was carried on in the presence of visible light, the AgCl...
formed can be degraded to Ag$^+$ and Cl$^-$ (Equation (5)). Chlorine dioxide is a strong oxidant with good antibacterial properties [29,30]. In addition, some authors had proved that chlorine dioxide has a high oxidizing power on proteins [31,32].

$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$  \hspace{1cm} (1)

$$\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2$$  \hspace{1cm} (2)

$$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$$  \hspace{1cm} (3)

$$2\text{NaClO}_2 + \text{HOCl} + \text{HCl} \rightarrow 2\text{ClO}_2 + \text{H}_2\text{O} + 2\text{NaCl}$$  \hspace{1cm} (4)

$$\text{AgCl} \xrightarrow{\text{Light}} \text{Ag}^+ + \text{Cl}^-$$  \hspace{1cm} (5)

Figure 6. Vibrio parahaemolyticus cell culture growth kinetics for undoped, AgGa-doped and AgGaCl-doped ZnO NRs. Inset: growth kinetics experiment.

The sum of all the toxic properties of the AgGaCl-doped ZnO NRs toward the bacteria causes the bacteria instant death. All these toxic effects can involve: (a) size of NRs: the simple contact between the bacterial cell and the NRs can cause changes in microenvironment within the contact area of the organism and particle [33]. (b) The metal toxicity toward bacteria’s cells of Ag and Ga: metal particles can generate destabilization of the phospholipids bilayer of the cell. Ga can be captured by siderophores molecules of the bacteria interrupting metabolic process that can lead to the bacteria cell death. (c) The oxidative effect of ClO$_2$ can act denaturalizing bacteria’s cell proteins.

2.4. Comparative of Photocatalytic and Antimicrobial Properties

Table 1 resume some recent works related with the synthesis and evaluation of materials with photocatalytic and/or antimicrobial properties for water treatment. As can be observed AgGaCl-doped ZnO NRs can degrade a high concentration of MB compared with the concentration used in other
studies. This can be explained by considering that the incorporation of Ag, Ga and Cl in the ZnO NRs network gave the material a high density of photogenerated electrons that can initiate oxidation reduction processes for the MB degradation. Meanwhile on the antimicrobial activity performance, regardless of the antimicrobial evaluation method, none of the studies shows an immediate lethality against bacteria such as the AgGaCl-doped NRs synthesized in this work. This lethality can be attributed to the antimicrobial power of ZnO, Ag, Ga and Cl working together in a synergistic way. Further research could address the evaluation of the effectiveness of the AgGaCl-doped ZnO NRs incorporated in water treatment devices for the treatment of real contaminated water systems.

Table 1. Comparative results between other recent studies and the present study on the development of photocatalytic and/or antimicrobial materials for water treatment.

| Photocatalysts and/or Antimicrobial Materials | Suspended or Immobilized | Irradiation | Pollutant | Bacteria | % of Degraded Contaminant and Antimicrobial Activity | Ref. |
|---------------------------------------------|--------------------------|-------------|-----------|----------|-----------------------------------------------------|------|
| Transition metal doped ZnO NPs             | Suspended                | Visible     | MB        | E. coli  |                                                     | [34] |
| Ag NPs by crumpled GO–TiO$_2$              | Immobilized              | Visible     | None      | E. coli and B. subtilis |                                                   | [35] |
| Bismuth tungstate and titanium dioxide      | Immobilized              | Visible     | Rhodamine B| E. coli  | Reduced number of viable E. coli cells in suspension to below the limit of detection in the first 48 h of irradiation | [10] |
| coatings on glass                          | Immobilized              | UV          | Methyl Orange (5 mg/L) | -        | 96% of dye was degraded after 4 h of irradiation | [36] |
| ZnO nanowires on glass                     | Immobilized              | Visible     | MB (10$^{-5}$ M) | -        | 98% of dye was degraded by 0.5 mol% Ag-doped ZnO NPs in 180 min | [37] |
| ZnO and Ag doped ZnO nanoparticles         | Suspended                | Visible     | MB (6 mg/L) | E. coli  | 2 at% Ag-doped ZnO NRs degraded 40% dye in 5 h. 2 at% Ag doped ZnO NRs and 2 at% Ga-doped ZnO NRs reduced 50% of bacteria growth on both strain cultures. | [13] |
| Ag doped ZnO NRs and Ga-doped ZnO NRs on PE| Immobilized              | Visible     | MB (100 mg/L) | Vibrio spp. | AgGaCl-doped ZnO NRs (pH 5.5) degraded approximately 75% of MB solution in 5 h. AgGaCl-doped ZnO NRs completely inhibit the bacteria growth for 12 h. | This work |
| AgGaCl-doped ZnO NRs on PE                 | Immobilized              | Visible     | MB (100 mg/L) | Vibrio parahaemolyticus |                                                     |      |

3. Materials and Methods

3.1. Microwave Assisted Doped ZnO NRs Synthesis on Polyethylene Substrate

ZnO NRs synthesis was achieved as reported in a previous work [13]. Rectangular 0.4 × 1.0 in. polyethylene (PE) substrates were treated with a 1% dodecanolthiol solution in methanol using the water bath (100 °C for 15 min) in order to thiolate the substrates surface. Then the substrates were seeded by dipping the substrates into a colloidal solution of ZnO nanoparticles in 2-propanol and heated at 150 °C for 10 min to evaporate the solvent. After obtaining the PE with ZnO NPs, a ZnO NRs precursor solution were prepared with an 3.0 mM equimolar solution of zinc nitrate hexahydrated (Zn(NO$_3$)$_2$·6H$_2$O, Sigma 99% purity) and hexamethylenetetramine (C$_6$H$_{12}$N$_4$, Sigma 99.5%) in water.
Finally, the ZnO precursor solution was heated with a microwave oven (model WM1311DS, Whirlpool, Apodaca, México) at 300 W for 65 min. To synthesize 2% at. AgGa-doped ZnO NRs, gallium oxide (Ga$_2$O$_3$, Sigma 99.99%) and silver nitrate (AgNO$_3$, Jalmek 99% purity) were added to the precursor solution before heating at 300W in a microwave oven. To synthesize the AgGaCl-doped ZnO NRs the pH of the AgGa-doped ZnO NRs precursor solution was modified from the original pH at 6.5 to 6.0, 5.5 and 5 with a 1.0 N HCl solution (Figure 7). It is important to note that once obtaining the PE substrates with ZnO nanoparticles it is fast to synthesize the AgGaCl NRs lasting approximately 25 min per synthesized sample.

![Figure 7. AgGaCl-doped ZnO NRs general synthesis diagram.](image)

### 3.2. NRs Characterization

Morphology and NRs diameter of the synthesized AgGa-doped ZnO NRs and AgGaCl NRs were characterized by Scanning Electron Microscopy (SEM) using a JEOL-JIB 4500 microscope (Tokyo, Japan). The elemental analyses of the synthesized NRs were carried out in-situ in the SEM using an energy dispersive X-ray (EDS) microanalysis (OXFORD INCA Energy System) at an electron accelerating voltage of 15 kV. The crystal structure of the NRs were determined by XRD analysis carried out on PANalytical X’Pert PRO using monochromatic CuK$_\alpha$ radiation of wavelength $\lambda = 1.5418$ Å from a fixed source operated at 45 kV and 40 mA. The optical properties of the grown NRs were investigated through cathodoluminescence experiments in the SEM using a Gatan MonoCL4 cathodoluminescence detector (Pleasanton, CA, USA).

### 3.3. NRs Photocatalytic Performance

Photocatalytic performance experiments of doped and undoped ZnO NRs were carried out using NRs/PE in a 20 mL of 100 mg/L methylene blue (MB) solution. The samples were then exposed to a fluorescent Tecnolite lineal lamp (16W, Mexico City, Mexico). The variation of the concentration of MB was measured spectrophotometrically every hour in a N4S UV–VIS spectrophotometer (Zhejiang, China) at 664 nm wavelength. The photocatalytic performance was evaluated in triplicate.
3.4. Antimicrobial Evaluation

To determine the growth curve of *Vibrio parahaemolyticus* in presence of doped and undoped ZnO NRs, bacterial cells were cultured in 50 mL Mueller Hinton (MH) broth at 25 °C overnight. Growth kinetics were performed in 20 mL sample glass vials after adding 5% of inoculum from overnight cultures in MH broth supplemented with the doped and undoped ZnO NRs supported on PE under visible light irradiation. A control group with the strain without any NRs was also maintained but supplemented with oxytetracycline at 100 mg/mL. The absorbance at 600 nm was monitored every hour in a N4S UV–VIS spectrophotometer at 25 °C without shaking for 12 h. The antimicrobial activity was evaluated in triplicate.

4. Conclusions

This work shows the antimicrobial power of AgGaCl as dopant materials in ZnO NRs acting in a synergy form and causing a lethal effect against pathogen bacteria. It shows the improvement of its photocatalytic activity under visible light irradiation. The synthesized AgGaCl-doped ZnO NRs are potential candidates for the development of more efficient water treatment devices.

**Author Contributions:** Supervision, investigation and writing—original draft, M.N.C.-C.; investigation and writing—original draft, S.S.-S.; writing, fundamental concepts, discussing and editing, O.E.C. The manuscript was written through contributions of all of the authors. All authors have given approval to the final version of the manuscript.

**Funding:** This research work was supported by SEP through PRODEP UABC-PTC-644-511-6/17-8051 project, CONACYT-FORDECYT No. 272894 and UNAM through DGAPA-PAPIIT project IA103117.

**Acknowledgments:** We acknowledge SEP, CONACYT-FORDECYT and UNAM for their financial support. We are thankful to Natalie Millán for language and style corrections and to Israel Gradilla for technical assistance.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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