Research Article

One-Pot Synthesis of Ru-Doped ZnO Oxides for Photodegradation of 4-Chlorophenol

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The photocatalytic degradation of 4-chlorophenol in water using Ru-doped ZnO mixed oxides (0, 0.5, 1, and 3 wt% RuO₂) synthesized by the one-pot homogeneous coprecipitation method is reported. ZnO with wurtzite structure was present in the mixed oxide as corroborated by Raman spectroscopy and X-ray diffraction analysis. All the samples showed nanorod morphological features. The presence of Ru⁶⁺/Ru⁴⁺ couples on ZnO modified the band gap of the mixed oxides and led to a shift of the band gap energy from 3.20 eV to 3.07 eV. Ru addition increased the surface area and significantly promoted the formation of active surface oxygen species such as hydroradicals evidenced by the fluorescence spectroscopy measurement. In the photodegradation of 4-chlorophenol solution under UV irradiation, a notable increase in photoactivity was obtained as the amount of RuO₂ in the mixed oxides increased to 3 wt%. The charge transfer between Ru⁶⁺/Ru⁴⁺ couples and ZnO nanoparticles together with the formation of free radical oxidant species effectively inhibits electron-hole recombination rate, thus favoring the photodegradation of 4-chlorophenol.

1. Introduction

Although most water effluents are effectively treated by traditional biological and/or physicochemical methods, the presence of chlorinated compounds represents an increasing problem, since these compounds, for example, chlorinated phenol derivatives, are often mutagenic or carcinogenic. 4-Chlorophenol is one of the most dangerous substances as far as toxicity is concerned. Therefore, it is highly necessary to develop more effective processes for the destruction of such contaminants. Actually, the expanding demand for efficient and economical techniques for wastewater treatment is the origin of a wide spectrum of investigations and technological innovation [1–5]. Some new technologies such as the advanced oxidation process (AOP) have been applied for the elimination of organic compounds in water systems. In AOPs, the oxidation of organic compounds by the very reactive free radicals takes place on the surface of heterogeneous catalysts which has been proven to be of interest due to the efficient degradation of recalcitrant organic compounds in water [6–8].

Developed in the 1970s, photocatalytic oxidation has attracted considerable attention, and in recent years, numerous studies have been carried out on the applications of photocatalytic oxidation in the presence of a semiconductor oxide [9–13]. As a good candidate of photocatalyst, ZnO
has a band gap energy ($E_g$) of 3.37 eV, which corresponds to light absorption in the UV region [14]; this $E_g$ value indicates that its photocatalytic properties are almost comparable with TiO$_2$. Li et al. reported that the total photodegradation of chlorophenol and dichlorobenzene can be realized by using ZnO nanoparticles [15]. On the other hand, RuO$_2$ has been studied as a photocatalyst showing strong oxidation properties [16]. The catalytic role in the N$_2$O decomposition over Ru-doped FAU zeolite was also investigated [17]. Zhuiykov et al. reported that the electrocatalytic activity of ZnO-RuO$_2$ catalysts appears to be governed by the redox behavior of the active surface sites [18].

In the present work, we report the one-pot homogeneous coprecipitation method for the synthesis of a set of Ru-doped ZnO oxides with different Ru contents (0.5, 1, and 3 wt% of RuO$_2$). These catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron, and UV-Vis spectroscopic techniques. The textural properties including the surface area and pore volume were determined by the N$_2$ adsorption-desorption isotherms method. The crystalline structure of the samples was refined by the Rietveld refinement method, and the surface chemical composition was analyzed by the electron dispersive spectroscopic (EDS) technique. The formation of the surface *OH radicals was monitored by using fluorescence emission spectroscopy. The photocatalytic performance of the RuO$_x$-ZnO catalysts with various RuO$_2$ contents for the degradation of 4-chlorophenol was investigated, and the surface photoreaction mechanism was discussed.

2. Experimental

2.1. Sample Preparation. The RuO$_x$-ZnO semiconductors were synthesized by the one-pot homogeneous coprecipitation method as follows: appropriate amounts of Zn(CH$_3$COO)$_2$ (Baker, 99.99%) and RuCl$_3$·3H$_2$O (Aldrich, 99.9%) solutions were mixed at a pH of ~8.5 adjusted with an ammonia solution. The amount of RuCl$_3$·3H$_2$O was calculated in order to obtain final solids with 0, 0.5, 1.0, and 3.0 wt% of RuO$_2$. Afterwards, the mixture containing both metallic precursors was heated at 80°C under constant stirring for 2 h. The resultant precipitate was collected by filtration and washed with deionized water until a neutral pH in the effluent was reached, and finally, the wet solid was dried at 100°C in air for 6 h and calcined at 400°C in a muffle furnace for 12 h. These solids will be hereinafter referred to as xwt% RuO$_2$-ZnO, where x = 0, 0.5, 1, and 3.

2.2. Characterization. X-ray diffraction (XRD) patterns of the RuO$_2$-ZnO solids were obtained by an Empyrean multipurpose research X-ray diffractometer (PANalytical) with a Cu-Kα radiation (1.5418 Å) source. Diffraction intensity was measured between 4° and 70° with a 2θ step of 0.02°. The crystalline structures of the catalysts were refined using the Rietveld method. The JAVA-based software named Materials Analysis Using Diffraction (MAUD) was employed for refining each XRD pattern [19]. The atomic fraction coordinates for ZnO are reported in Table 1.

The textural properties of the samples were obtained by nitrogen adsorption-desorption isotherms at ~196°C in a Quantachrome Autosorb-1C instrument. The surface area was calculated by the Brunauer–Emmett–Teller (BET) equation. All samples were degassed at 300°C for 6 h before N$_2$ adsorption.

Raman spectra were recorded at room temperature on previously calcined samples using an ISA Labram micro-Raman apparatus. The excitation line of a He-Ne laser was 632 nm. To avoid thermal effects, the laser power on the samples was kept at ~1 mW.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface metal oxidation state of the samples. The XPS spectra were acquired with a THERMO Scientific K-Alpha spectrometer, equipped with a hemispherical electron analyzer and Al Kα X-ray source (1486.6 eV).

Scanning electron microscopy analysis (SEM) was carried out on a Quanta 3D FEG microscope. The microscope has detectors for surface chemical analysis by X-ray energy dispersive spectroscopy (EDS).

The band gap energy ($E_g$) of the catalysts was measured using a Cary 100 spectrophotometer with an integration sphere, and MgO was used as 100% reflectance patron. The band gap energy values were determined using the Kubelka–Munk function by the method.

Fluorescence emission spectra of 2-hydroxyterephthalic acid were measured on a SCINCO fluorescence spectrometer FS-2. The *OH radicals generated by the semiconductor material in the absence of 4-chlorophenol were measured with the following procedure: terephthalic acid (TA) (5 × 10$^{-4}$ M) was dissolved in a water/NaOH solution (2 × 10$^{-3}$ M). Then 200 mg of the photocatalysts was added and the suspension was stirred for 60 min under dark conditions. Afterwards, it was irradiated by a UV light Pen-Ray lamp with a wavelength of 254 nm ($I_0 = 4.4$ mW cm$^{-2}$), during 60 min, and aliquots were taken each 5 min. The fluorescence emission spectra of the irradiated solution were analyzed by PL (excited at 320 nm).

2.3. Photocatalytic Activity. The photocatalytic degradation of 4-chlorophenol in water was performed at room temperature (~25°C) using a solution of 4-chlorophenol in water (80 ppm) employing a Pyrex reactor (500 mL). 200 mg of the catalyst with particle size 60–80 meshes was used for the photodegradation reaction. The mixture was under stirring and bubbling with air (1 mL/s) generated by a magnetic stirring and electric pump at room temperature (approximately 30°C). The mixture prepared was exposed to UV radiation for 6 h. The irradiation source was a UV Pen-Ray lamp ($λ = 254$ nm and intensity = 4400 μW/cm$^2$), protected with a

| Atom | Site | x   | y   | z    |
|------|------|-----|-----|------|
| Zn   | 2b   | 0.3333 | 0.6667 | 0   |
| O    | 2b   | 0.3333 | 0.6667 | 0.3825 |

Table 1: Atomic fractional coordinates in the crystalline structure of ZnO. Space group: P63mc; SG number: 186; crystal system: hexagonal.
quartz tube whose outer and inner diameters were 0.5 and 0.35 in nm, respectively. The 4-chlorophenol photooxidation reaction procedure was monitored via following the variation of the characteristic absorption band at 221 nm using the UV-Vis spectrophotometer (Varian Cary 100 UV-Vis). The 4-chlorophenol concentration was monitored by taking aliquots of 3 mL every 15 min of reaction. The aliquots were filtered with a 0.45 µm nylon filter to eliminate any suspended solids.

3. Results and Discussion

3.1. Crystalline Structure and Rietveld Refinements. The XRD patterns of the samples calcined at 400°C are shown in Figure 1. All the diffraction peaks can be indexed to the hexagonal Wurtzite structure of ZnO (ICPDS card 36-1451) [20, 21]. XRD peaks corresponding to RuO2 and changes in the crystalline structure of ZnO are not observed; thus, it can be assumed that the ruthenium oxide like RuO2 is not detectable since its quantity is very small; perhaps, it is dispersed uniformly on the surface of ZnO with a crystallite size smaller than 4 nm.

The crystalline structures of the solids were refined with the Rietveld refinement technique. A plot of the Rietveld refinement for the 3 wt% RuO2-ZnO catalyst is shown in Figure 2. The crystallite size, lattice cell parameters, and Rwp are reported in Table 2. The crystallite sizes determined by Scherrer’s equation and obtained by the Rietveld refinement were 60.6, 75.9, 69.5, and 61.8 nm for the 0RuO2-ZnO, 0.5RuO2-ZnO, 1RuO2-ZnO, and 3RuO2-ZnO samples, respectively. It seems that Ru addition led to a slightly greater ZnO crystallite size, even if this effect becomes weak for the higher Ru content sample. Ru doping probably promotes the formation of surface hydroxyls which may gain linkage degree with the hydroxide units during the synthesis, leading to a slight enlargement of the crystallite size. The lattice cell parameters of ZnO with a hexagonal wurtzite structure varied: a = b from 3.2903 to 3.4098 Å and c from 5.2219 to 5.4039 Å, depending on the Ru content.

3.2. Raman Spectroscopy. The Raman spectra of the samples were obtained in the wavelength interval 300–550 cm⁻¹, and they are shown in Figure 3(a). The Raman bands at 330, 380, and 437 cm⁻¹ are assigned to ZnO with a wurtzite (hexagonal) structure belonging to the P63mc space group. The dominant and sharp peak at 332 cm⁻¹ is due to the second-order Raman spectrum, and the peak labeled as E₁ at 437 cm⁻¹ is known as the Raman active phonon mode, which is a characteristic of the Wurtzite hexagonal phase of ZnO.

In Figure 3(b), the Raman modes of E₂g, A₁g, and B₁g at 528, 646, and 716 cm⁻¹, respectively, are shown, corresponding to RuO2 in 1RuO2-ZnO and 3RuO2-ZnO samples. The intensity of Raman peaks increases with the increasing of the RuO2 content [22, 23]. Although Ru oxides were not detectable by XRD analysis, Ru-O bonds are clearly present in the surface of the catalysts. Therefore, the Raman spectroscopy is more sensitive for identifying the surface Ru-O bonds.

3.3. XPS Characterization. The chemical oxidation states of Ru and Zn in the Ru-doped ZnO samples were analyzed by the XPS technique. The Ru 3d core levels in the XPS spectra of all samples are presented in Figure 4. By deconvoluting with software (XPS PEAK 4.1), two doublets in XPS spectra were determined: the peaks at 280.9 and 285.0 eV are assigned to Ru 3d 5/2 and Ru 3d 3/2, respectively, indicating that Ru is in the oxidation state Ru⁴⁺ (RuO₂) [24]. The other two small peaks at 282.5 and 286.3 eV correspond to Ru⁵⁺ (ReO₃). The intensity of these peaks increases with increasing content of RuO₂.

The XPS spectra of Zn 2p core levels are shown in Figure 5, and they exhibited two symmetric peaks centered at 1022.0 and 1044.7 eV, which are attributed to Zn 2p 3/2 and Zn 2p 1/2, respectively, indicating the Zn²⁺ oxidation state [25].

Figure 6 shows the asymmetric O1s spectra on the surface of 0RuO2-ZnO, 0.5RuO2-ZnO, 1RuO2-ZnO, and 3RuO2-ZnO samples. For the pure ZnO sample, the O1s signal was deconvoluted into two peaks at 530.6 eV and 532.6 eV, corresponding to the lattice O²⁻ in the Zn-O bond and surface oxygen in hydroxyls (OH) [26]. For the other three Ru-doped samples, four peaks at approximately 529.0, 530.3, 530.6, and 532.6 eV were observed. These are assigned to lattice oxygen in RuO₂ (529.0 eV, Ru⁴⁺-O) and RuO₃ (530.3 eV, Ru⁵⁺-O), lattice oxygen in ZnO (530.6 eV, Zn-O), and surface oxygen in the hydroxyl group (532.6 eV, O-H) in the RuO₂ and ZnO solids, respectively [27]. The XPS analyses confirm that different kinds of oxygen species exist on the surface of the RuO₂-ZnO solids and Ru ions have two oxidation states: Ru⁴⁺ (major) and Ru⁵⁺ (minor).

The surface elemental composition analysis of each sample was performed by the EDS technique. Signals belonging
to Zn, Ru, C, and O elements are observed (see Figures 7(b), 7(d), 7(f), and 7(h)). Figure 7(b) only shows the signals of Zn and O with carbon traces. Carbon was probably formed from the acetate precursor used in the ZnO synthesis. Figures 7(d), 7(f), and 7(h) show the chemical composition of the $\text{RuO}_2$-$\text{ZnO}$. A small peak for Ru appears which increases in intensity as the content of $\text{RuO}_2$ increases. It is also noted that as the $\text{RuO}_2$ content increases, the peak corresponding to oxygen increases in agreement with the results of XPS analysis. The increment of the surface oxygen content is important as the oxygen species usually take part in the oxidation reactions.

3.5. Textural Properties. The textural properties of the $\text{RuO}_2$-$\text{ZnO}$ samples are reported in Table 4. The surface area of the samples with different $\text{RuO}_2$ loadings varies in the range of...

![Figure 1: XRD patterns of the xwt% RuO$_2$-ZnO samples. $x = 0$, $x = 0.5$, $x = 1$, and $x = 3$.](image1)

![Figure 2: A plot of Rietveld refinement of 3 wt% RuO$_2$-ZnO. The black line corresponds to the experimental data, the red line corresponds to the calculated data, and the grey line indicates residuals between experimental and calculation data.](image2)
11–38 m²/g. When the RuO₂ content is greater, the specific surface area is bigger. The 3 wt% RuO₂-ZnO sample shows the biggest specific surface area, three times greater than that obtained for pure ZnO. According to the above results, we can assume that the variations on the BET surface area are due to the changes of the structure resulted from the modification of RuO₂ doping.

3.6. Band-Gap Energy Measurement. Figure 8 shows the plots of the Kubelk-Munk function (\(F(R_1)E^{1/2}\)) against the absorbed light energy (\(E\)). The optical band gap energies (\(E_g\)) of each sample can be estimated by extrapolating the slope to cut the abscissa axis [28–30]. The presence of RuO₂ (0.5, 1, and 3 wt %) produces to a red-shift of the absorption band towards the visible region. The band gap energy for pure ZnO was approximately 3.20 eV, which is close to report in the literature [31, 32]. Several previous investigations suggest that the visible emission is due to the surface defects and oxygen vacancies in the crystalline structure of the ZnO nanomaterials [33, 34]. These RuO₂-ZnO catalysts show a continuous absorption in the visible range and the absorption is stronger when the RuO₂ content is greater. The estimated band gap energies decrease from 3.20 eV for pure ZnO to 3.07 eV for 3 wt% RuO₂-ZnO. The \(E_g\) data obtained from Figure 8 are reported in Table 4.

3.7. Photocatalytic Activity Test. To investigate the photocatalytic activity, the RuO₂-ZnO samples were evaluated in the photocatalytic degradation of 4-chlorophenol in aqueous solution. Figure 9 illustrates a set of UV-Vis absorption spectra of 4-chlorophenol molecule at different intervals of reaction time for the 3 wt% RuO₂-ZnO catalyst. The maximum absorption bands of 4-chlorophenol appear at 221 and 277 nm under UV irradiation. These absorption bands gradually decrease in intensity within 150 min, indicating that 4-chlorophenol was photodegraded.

The influence of the content of RuO₂ on the photodegradation efficiency (noted as \(C/C_0\)) of 4-chlorophenol is presented in Figure 10. The Ru-doped ZnO catalysts exhibit an increased photocatalytic activity compared to pure ZnO. After 225 min of reaction time, the photodegradation efficiency of 4-chlorophenol pollutant is about 46%, 61%, 70%, and 92% for 0RuO₂-ZnO, 0.5RuO₂-ZnO, 1RuO₂-ZnO, and 3RuO₂-ZnO, respectively.

3.8. Determination of \(^{1}OH\) Radical Generation and Reaction Mechanism. In order to understand the mechanism of the photodegradation of 4-chlorophenol, it is important to obtain information about the formation of free radicals, especially the formation of \(^{1}OH\) radicals, which have a high oxidative power and great capacity for degradation of organic contaminants in an aqueous medium. The \(^{1}OH\) radicals can be monitored by the fluorescence spectrum resulting from the formation of 2-hydroxy terephthalic acid by the \(^{1}OH\) radicals reacting with terephthalic acid when the solid was irradiated with ultraviolet light [35, 36]. The most active catalyst 3 wt%RuO₂ was measured by comparison with TiO₂-P25 in the absence of 4-chlorophenol.
photolysis performance was also obtained in the absence of any catalyst. Figure 11(a) shows the fluorescence spectra obtained with the 3RuO₂-ZnO and TiO₂ P25 catalysts. The peak at 454 nm indicated the amount of produced 2-hydroxy terephthalic acid or the amount of OH radicals produced. The peak intensity clearly increases as a function of irradiation time. Both 3RuO₂-ZnO and TiO₂ P25 show almost the linear relationship between the band intensity and the irradiation time, but 3RuO₂-ZnO exhibits a greater concentration of OH radicals on the surface in comparison with TiO₂ P25 during the irradiation procedure. Without the catalyst, the photolysis produces a rather low concentration of hydroxyl terephthalic acid, indicating the low concentration of OH radicals.

The reaction mechanism considered for heterogeneous photocatalysis usually consists of two steps: the fast adsorption of the reactants on the photocatalyst surface, followed by the slow surface reaction of the adsorbed reactants with photo-generated radicals (e.g., O₂, OH) to generate the...
photooxidized active species. In the presence of dissolved oxygen in aqueous solution and the surface hydroxyl radicals in the solid catalysts, oxygen species may exist in several forms such as $\text{O}_2$, $\cdot\text{OH}$, $\text{O}_2^-$, and $\text{O}_2^{2-}$, depending on the adsorption capability of the structure and temperature. The formation of surface oxygen species in the RuO$_2$-ZnO catalysts can be explained by the following reactions on the surface of the catalysts:

$$\text{RuO}_2 - \text{ZnO} + h\nu \rightarrow e^- (\text{ZnO}) + h^+ (\text{RuO}_2)$$

$$\text{O}_2 + e^- \rightarrow \text{O}_2^-$$  \text{and/or}  $$\text{O}_2 + 2e^- \rightarrow \text{O}_2^{2-}$$  \quad (1)

$$\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \cdot\text{OH}$$

The surface of RuO$_2$-ZnO solids presents a high degree of surface hydroxylation. For instance, the catalyst with 3 wt%RuO$_2$ presents a high concentration of surface hydroxyl species as evidenced by the XPS spectra in Figure 6 and by the fluorescence spectroscopy in Figure 11, and therefore, it shows the highest concentration of surface active oxygen.
Figure 7: SEM images and EDS spectra of the x wt% RuO$_2$-ZnO samples. (a, b) $x = 0$; (c, d) $x = 0.5$; (e, f) $x = 1$; and (g, h) $x = 3$. 
species and thus the best photoactivity. All catalysts with RuO₂ exhibit higher reaction rates than the pure ZnO. Perhaps, there is a synergistic interaction between RuO₂ and ZnO that favors the improvement of photocatalytic activity. It is assumed that a heterojunction structure was created in the interface of the ZnO and RuO₂ nanoparticles. Ru doping strongly affects the surface properties of semiconductors by generating a “barrier” in the ZnO which acts as an electron trap of the Ru metal in contact with the ZnO semiconductor surface. The electrons in the Ru conduction band (CB) transferred to the ZnO CB under the force of the electronic field of the heterojunction structure [37]. Thus, the surface of the ZnO was more negative and favors the formation of more hydroradicals. Therefore, Ru doping promotes the active surface oxygen formation via electron transfer. All these may inhibit the recombination rate of the electron-holes and promote the Ru⁶+/Ru⁴⁺ ox-red cycles due to the electron transfer from the RuO₂ (RuO₃ and RuO₂) nanoparticles to the Zn-O bond. These results show that the one-pot homogeneous coprecipitation synthesis reported herein is a simple but very effective method for obtaining RuO₂-ZnO nanocatalysts with high photocatalytic activity in the photodegradation of 4-chlorophenol.

### 4. Conclusions

This work showed that Ru doping for ZnO reduced the band gap energy of ZnO solid, generated more surface active oxygen species such as hydroxyls, O₂⁻, and O₂⁻, and increased the surface area by modification of the crystalline structure and morphological features. In the photodegradation of 4-chlorophenol solution, the RuO₂-ZnO catalysts could effectively photodegrade the 4-chlorophenol contaminant with a much faster reaction rate than the pure ZnO. This can be explained by rich active oxygen species and high concentration of free radicals on the surface of the Ru-doped catalyst that may inhibit the electron-hole recombination rate and promotes the Ru⁶+/Ru⁴⁺ ox-red cycles due to the electron transfer from the RuO₂ (RuO₃ and RuO₂) nanoparticles to the Zn-O bond. These results show that the one-pot homogeneous coprecipitation synthesis reported herein is a simple but very effective method for obtaining RuO₂-ZnO nanocatalysts with high photocatalytic activity in the photodegradation of 4-chlorophenol.

| Sample          | \(S_{BET}\) (m²/g) | Pore volume (cm³/g) | \(E_g\) (eV) |
|-----------------|---------------------|---------------------|--------------|
| 0RuO₂-ZnO       | 11                  | 0.38                | 3.20         |
| 0.5RuO₂-ZnO     | 19                  | 0.16                | 3.12         |
| 1RuO₂-ZnO       | 32                  | 0.15                | 3.11         |
| 3RuO₂-ZnO       | 38                  | 0.22                | 3.07         |

**Figure 8:** A plot of the Kubelka-Munk function versus energy \((h\nu)\) for the \(x\) wt% RuO₂-ZnO samples. \(x = 0\), \(x = 0.5\), \(x = 1\), and \(x = 3\).

**Figure 9:** A set of UV-Vis spectra of 4-chlorophenol solution recorded in the presence of the 3 wt% RuO₂-ZnO sample at different irradiation times.

| Wavelength (nm) | Absorbance (a.u.) |
|-----------------|-------------------|
|                 |                   |
|                 |                   |
| 221 nm          |                   |
| 283 nm          |                   |

**Figure 10:** Photodegradation of 4-chlorophenol with \(x\) wt% RuO₂-ZnO and in 350 min of reaction. The activity of TiO₂ P25 was evaluated as reference.
Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare herein that this article currently has no conflict of interests.

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