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Structural and optical properties of Cu-doped ZnAl$_2$O$_4$ and its application as photocatalyst for Cr(VI) reduction under sunlight

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Abstract

Cu-doped ZnAl$_2$O$_4$ spinel oxides (Zn$_{(1-x)}$Cu$_x$Al$_2$O$_4$, 0.0 ≤ x ≤ 1.0) were synthesized by co-precipitation method at 800 °C. The X-ray diffraction analysis of the as-prepared powders confirmed a spinel structure with a space group Fd-3m. XPS was used to investigate the state of the material surface and the elemental composition. The SEM image confirmed the presence of nano spherical particles. The optical properties were characterized by UV-Vis diffuse reflectance and all band gap values, in the range of 1.71 to 3.54 eV, indicate a semiconductor character of our compounds. The energy bandgap (E$_g$) values of Zn$_{(1-x)}$Cu$_x$Al$_2$O$_4$ decreased with increasing of the copper content. The photocatalytic activity were evaluated for Cr(VI) reduction under sunlight irradiation. The highest photoreduction efficiency was obtained for Zn$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ with a removal ratio of 75% after 150 min. The increase of surface area increase the photocatalytic activity as it implies larger contact surfaces exposed to Cr(VI). High surface area and pore volume is useful in the formation of photogenerated electron and hole pairs. The kinetics of photoreduction follows the modified Langmuir-Hinshelwood model. The obtained results indicate a good
photocatalytic activity, in particular for compounds with a high content of Cu.

**Key Words:** Cu-doped ZnAl$_2$O$_4$, sunlight, Optical gap, XPS, Photocatalytic reduction, Cr(VI).

1. Introduction

Semiconductor nanoparticles have been generated great interest for photocatalytic, photolysis, photoredox, photovoltaic, and optoelectronic applications due to their electrical, optical, electronic, and optoelectronic properties [1-8]. ZnAl$_2$O$_4$ compounds have been studied for their dielectric properties, chemical and thermal stability, mechanical resistance, and photocatalytic properties [9-11]. The particles size and preparation methods have a great influence on the optical, electrical and fluorescence properties of these compounds. It has been noticed that the nanoparticles of ZnAl$_2$O$_4$ presents a large specific surface area and have significant effect on their high performances [11-12]. ZnAl$_2$O$_4$ presents a spinel structure where the Zn$^{2+}$ and Al$^{3+}$ cations occupying tetrahedral and octahedral sites. This distribution of cations is not always thermodynamically stable, since Zn$^{2+}$ and Al$^{3+}$ cations can exchange interstices, eventually leading to inverted spinel, where all the Zn$^{2+}$ cations occupy the octahedral interstices [13]. ZnAl$_2$O$_4$ compounds are extensively used as refractory materials, magnetic field, ceramic pigments and as catalyst for chemical reactions [4,14].

The spinel oxides are usually synthesized by different synthetic routes, such as solid state reactions at high temperature [15-17], combustion synthesis route, sol gel method, co-precipitation method, solvothermal approach; polymeric precursor method and microwave-assisted hydrothermal methods are also used to prepare pure spinel oxides at low temperature [18-21]. Solid state reactions suffer from a large particles size and inhomogeneity of particles distribution. The high temperature treatment implies compounds with low surface area. The synthesis by co-precipitation method allows the production of very pure powders, with a homogeneous and nano-metric particles size with high surface area. This attractive technique is also faster and much less costly in energy than solid synthesis.
A large family of spinels can be used in photocatalysis process for the elimination of several pollutants which are discharged into the environment (soil, water and air). Chrome is widely used by several industries, including dyes, electroplating, tannery and textile. Chrome exists in two oxidation states, Cr(VI) and Cr(III), Cr(VI) form is the most dangerous and toxic to human health. Several methods are used to remove it from wastewater such as chemical precipitation, ion exchange, adsorption, electrochemical precipitation, membrane separation and bacterial reduction.

In the last decades, significant progress has been made on the use of photocatalysis for degradation of organic and inorganic pollutants. The use of semiconductors such as TiO$_2$, SnO$_2$, CuCr$_2$O$_4$, CuBi$_2$O$_4$, ZnO, CdS has been largely studied [3, 6, 7, 10]. TiO$_2$ photocatalyst is one of the most used products due to its chemical stability and non-toxicity, optical properties, low cost and high photocatalytic activity. Nevertheless, it can be only activated by the UV irradiation. Therefore, much attention has been devoted to the search for new catalysts which can adsorb in the visible region.

In this work, we are interested by the photocatalytic reduction of the toxic chromate by Zn$_{(1-x)}$Cu$_x$Al$_2$O$_4$ (0.0 ≤ x ≤ 1.0) photocatalysts under sunlight irradiation. ZnAl$_2$O$_4$ presents a wide band gap and absorbs only UV light. In order to improve its photocatalytic properties, ZnAl$_2$O$_4$ is doped by different Cu-content. Thus decreases the band gap and shifts the absorption toward the visible light region. To our knowledge, Zn$_{(1-x)}$Cu$_x$Al$_2$O$_4$ (0.0 ≤ x ≤ 1.0) has the subject of several studies but its photoelectrochemical and photocatalytic properties for Cr(VI) have not been exploited yet. The effect of Cu-substitution of ZnAl$_2$O$_4$ on the structural, physical and photocatalytic reduction of Cr(VI) will be investigated and the energy band diagram will be constructed to support the proposed mechanism of Cr(VI) reduction.

2. Experimental

Stoichiometric quantities of Zn(NO$_3$)$_2$6H$_2$O, Cu(NO$_3$)$_2$3H$_2$O and Al(NO$_3$)$_2$9H$_2$O were dissolved in distilled water and magnetically stirred for a few minutes. The obtained solution was diluted in order to adjust the solution pH. Then, ammonia solution (24%) was gently added until the solution became neutral and a chelate was formed. The obtained precipitate
was heated after filtration at 115 °C for 24 h. The resulting powders were ground and calcined at 400 °C for 8 h, in order to remove the nitrates, then at 800 °C for 5 h until the formation of brown-black fine powders.

The X-ray powder diffraction (XRD) patterns have been collected at room temperature, with Cu Kα monochromatic radiation (λ = 1.54056 Å) of a D8 Advance Bruker diffractometer. The Fullprof program package was used to determine cell parameters by refining the diffractogramms [22]. The FT-IR spectra of samples were recorded in the 400-4000 cm⁻¹ region using KBr pellets method on SHIMADZU 8400 s spectrometer. The morphology and the particles size were characterized using Zeiss EVO40 SEM model. The surface area measurement was performed via Tristar 300 equipment, after outgassing all the powders at 350 °C for 2 h, using N₂ gas for the adsorption/desorption at 77 K. UV-Vis spectra were recorded from 200 to 1800 nm using JASCO V-670 spectrophotometer.

XPS analyses were conducted using a Kratos 300 spectrometer equipped with a monochromatic Mg Kα source (1253.6 eV). The samples were out gassed before the analysis for 12 h under vacuum at 10⁻⁸ torr. The XPS spectra were calibrated by using the C 1s peak fixed at 284.6 eV of the surface trace contaminants [23]. The photoemission peaks were fitted using a home-developed least squares curve-fitting program (Winspec) and a Shirley background subtraction was used for all the spectra [24]. The surface atomic composition was determined by the integration of the peak areas according to the scolfield’s sensitivity factors [25].

The electrochemical measurement was recorded in a standard cell containing the working aqueous solution by a Solartron 1287 potentiostat and a frequency response analyzer Solartron 1260. The swept rate of 5 mV s⁻¹ was used. The data of the interfacial capacitance were recorded at 10 kHz in 0.1 M Na₂SO₄ electrolyte.

The photocatalytic tests were conducted between 10 am and 3 pm outside our laboratory. The sunlight irradiation was evaluated as 700 W/m², while the temperature averaged 30 °C. Lux meter is used to measure the sun light intensity. The evaluation of the photocatalytic efficiency was performed in a Pyrex cell. 100 mg of catalyst were suspended in 100 mL of (HCrO₄⁻, pH ~ 4) solution in presence of H₂C₂O₄ (10⁻⁵ M). According to our previous work, the
high photocatalytic degradation of Cr(VI) is obtained at pH=4. The stock of Cr(VI) ions solution at concentration of 1000 mg/L was prepared by using potassium dichromate (K₂Cr₂O₇, Merck) as a source of Cr(VI) ions. Experimental solutions of the desired concentrations were obtained by successive dilution in deionized water. H₂SO₄ was used for pH adjustment. The amount of adsorbed HCrO₄⁻ is evaluated by titration after the dark adsorption (2 h). Then, the reactor was exposed to solar irradiation. The UV–visible absorption spectra of the aliquots were collected using a Shimadzu1800 UV–visible spectrophotometer. The changes in the HCrO₄⁻ concentrations with irradiation time were monitored by the measure of the UV–visible absorption spectra (λ_max = 350 nm). The removal efficiency was calculated by the expression:

\[
\text{Removal efficiency} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100
\]

C₀ and Cₜ are the initial concentration and at various time intervals, respectively.

3. Results and discussion

3.1. XRD, FT-IR and XPS analyses

The XRD patterns of Zn_{(1-x)}CuₓAl₂O₄ (x = 0.0-1.0) obtained after calcination at 800 °C shown in Fig. 1 revealed a single phase with a spinel structure. Zn_{(1-x)}CuₓAl₂O₄ (x = 0.0-1.0) compounds present a cubic symmetry with the Fd-3m space group. The XRD peaks observed are in agreement with JCPDS card of ZnAl₂O₄ No. 05–0669. Nevertheless, the intensities of the peaks indexed as (400) and (331) are different according to the compositions. Indeed, these peaks are very sensitive to the inversion phenomena observed in the spinel structures [13].

The cell parameters and reliability factors (χ², Rp, Rwp) of the refinement using the software Fullprof are reported in Table 1. The experimental, calculated and difference profiles for XRD data are shown in Fig. 2. A good fit between calculated and experimental data is obtained as highlighted by the low values of χ² and R. In general, the a lattice parameter (Table 1) decreased as function of the copper rate x in Zn_{(1-x)}CuₓAl₂O₄ compounds from 8.0817(5) Å for x=0 to 8.0476(8) for x=1. However, the evolution was not monotonous, the lattice contraction is more pronounced above x = 0.60. This variation is related to the relative
difference of ionic radii of Zn$^{2+}$ and Cu$^{2+}$, the evolution of Cu valence state as the copper content increases and also the inversion in the spinel structure. This inversion was confirmed by XPS analysis performed on our samples. According to the literature, ZnAl$_2$O$_4$ presents a direct spinel where Zn$^{2+}$ occupies tetrahedral site and Al$^{3+}$ the octahedral sites with slightly inverted spinel whatever the synthesis methods [13, 26]. Cu$^{2+}$ and Al$^{3+}$ cations are known to be preferentially stabilized in octahedral coordination than in tetrahedral one, whereas Zn$^{2+}$ cations occupy preferentially the tetrahedral sites and partially inverted structures were expected for Zn$_{1-x}$Cu$_x$Al$_2$O$_4$. The cell parameter (a) remains lower than obtained by the solid-state route which can be explained by the mixed Cu valence states stabilized in the spinel network and the creation of defects associated with oxygen vacancies [26-27]. The crystallite size $d_{\text{XRD}}$ was calculated, using the full-width at half-maximum (FWHM) from the XRD lines broadening ($\beta$) [28] and the results are reported in Table 1.

XPS was used to examine elemental composition, state of the material surface, nature of bonding, and acid-base properties of oxides. Fig. 3a shows the survey XPS spectrum of the Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ surface powders calcined at 800 °C for $x = 0.2$ and 0.8. The calculated surface atomic composition for the samples $x=0.2$ and $x=0.8$ expressed in atomic percent (at. %), and the binding energy of their respective regions are summarized in Table 2. The spin-orbit coupling for Zn$^{2+}$ and Cu$^{2+}$ cations respectively for theses compositions is also calculated. These values obtained confirm those of the literature [29].

The photoelectron spectra of the most important elements, Al 2p, Zn 2p, Cu 2p and O1s, present on the surface of the compositions $x=0.2$ and 0.8 are shown in Fig. 3a. The impurities of carbon (Table 2) can be introduced at the stage of sample preparation or as a result of hydrocarbon adsorption during the sample evacuation inside the spectrometer.

Fig. 3b shows Al 2p photoelectron peak fitting. All peaks are attributed to Al$^{3+}$ cations bonded with oxygen [30-31]. Peaks observed at 73.33 and 73.57 eV were attributed to Al-O bonds in oxides spinel, while those located at 74.41 and 75.87 eV characterize hydroxides environment [32]. The Zn 2p photoelectron peak is characterized by two components, their appearance is due to the spin-orbit splitting between Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$. For example, the observed value of the spin-orbit splitting for the composition $x=0.2$ is 23.11 eV (Fig. 3c). Zn 2p$_{3/2}$ peak observed at $\approx 1022$ eV is the most intense and it can give more information on the
chemical state of zinc. The Zn 2p 3/2 photoelectron peaks shown in Fig. 3d are decomposed into two peaks. The most intense peak at 1021.56 eV for x=0.2 and 1021.58 eV for x=0.8 is ascribed Zn$^{2+}$ chemical state with the zinc atom occupying tetrahedral site; while the peak at high binding energy, 1022.33 eV for x=0.2 and 1022.55 eV for x=0.8, is due to the incorporation of Zn$^{2+}$ ions at the octahedral site and confirm the inversion phenomena of peaks observed in XRD, which can appear in the spinel structures [13]. These values are in agreement with the literature where the binding energy of ZnO is located between 1021.6 and 1023 eV [32].

Fig. 3e reports the curve fitting of the Cu 2p 3/2 region. It can be decomposed in three principal peaks: the first one at 932.234 eV is attributed to copper metal (Cu$^0$) and/or Cu$^+$ of Cu$_2$O oxide, because it is so difficult to distinguish between them. The presence of Cu$^+$ and/or Cu$^0$ ions results from a partial reduction of Cu$^{2+}$ surface. The second peak at 934.763 eV characterizes the Cu$^{2+}$ environment of spinel; this peak is sensibly large, so we cannot exclude the presence of hydroxides Cu(OH)$_2$ on the surface. Finally, the peak at high energy (933.533 eV) is attributed to CuO oxide [33-34]. The XPS spectra of O1s shown in Fig. 3f was decomposed into three peaks. The large peak observed at 532.529 eV for x=0.2 and 532.737 for x=0.8 are associated with oxygen of organic compounds and adsorbed water [35-36]. The two other peaks observed at low binding energies, 530.12 and 531.238 eV for x=0.2 and 529.931 and 530.767 eV for x=0.8, are attributed to the oxygen of the crystal lattice. Zn-O and Cu-O bonds in Zn$_{(1-x)}$Cu$_x$Al$_2$O$_4$ present a normal ionic character and it’s easier to eject the electron from the oxygen core level; the XPS signal is observed at lower energies. Al-O presents a semi-covalent bond and it is more difficult to eject it: therefore, the signal is observed at higher energies. As a result, the energies observed at 530.12 and 529.931 eV can be attributed to the Zn-O and Cu-O bonds while those at 531.238 and 530.767 eV are assigned to the Al-O bonds [37].

The percentage of the deconvoluted peaks of the O 1s region for both samples (x=0.2 and x=0.8) are given in Table 3. Based on these results the percentage of oxygen atoms involved in the crystal lattice can be calculated, 63.14% and 74.77% for x=0.2 and x=0.8 respectively. The percentage for the sample x=0.8 at 530.77 eV is very important (52.43%) which is due to an accumulation of Cu$^{2+}$ and Al$^{3+}$ ions in the octahedral sites, the copper aluminate spinel
CuAl₂O₄ is partially inversed with the copper ions preferentially distributed over the octahedral according to the crystal field theory [13]. To estimate the character of the materials surface, carbon and oxygen of H₂O and CO₂ have been excluded. It is shown (Table 3) that the ratio of sum of fractions of Al³⁺, Zn²⁺, Cu²⁺ and that of the oxygen for the two samples (x=0.2 and 0.8) are very important: 0.957 and 0.857 respectively. This suggest that the surface had a moderate character of a Lewis acid, and pronounced anionic character, which could predicts an interesting photocatalytic properties for these materials.

Fig. 4 shows the FT-IR spectra of Zn₁₋ₓCuₓAl₂O₄ (x = 0.0-1.0). A series of absorption peaks in the range of 500–4000 cm⁻¹ are shown. Some bands are common to the different contents of Cu. The band centered at ~ 3400 cm⁻¹ can be attributed to the O-H longitudinal H₂O vibration, and the bands around 1650 cm⁻¹ to the bending vibration of H-O-H. These bands are related to chemical adsorption phenomenon due to the high surface areas of the material. The bands observed below 800 cm⁻¹ can be assigned to the metal-oxide groups [23, 15]. The most important bands are around 690 and 545 cm⁻¹, and can be related to bonds of tetrahedral and octahedral sites of the spinel.

3.2. Scanning electron microscopy (SEM) and BET measurement

The SEM images (Fig. 5) for x = 0.2 and 0.8 indicate that the morphology of the particles is somewhat homogenous and present quasi-spherical grains with a nanometric scale. The nanoparticles sizes have been estimated between 50 and 100 nm. These values deviate strongly from those calculated from DRX (Table 1) mainly for the composition x = 0.8, indicating that the particles are more agglomerated on the surface.

The values of surface area (S_BET) and the most frequent pore volume (Vp) were estimated by the BET method, the results are reported in Table 4. The obtained surface area is very interesting, suggesting that this type of spinel could be used as catalysts in several reactions. The average diameter of crystallites (d_BET), assuming spherical forms (Table 4), was also calculated. The calculated values are in agreement with those obtained by SEM analysis. The average particle sizes found by chemisorption are systematically higher than the corresponding diameters estimated from XRD data. The obtained values present an irregular profile. Indeed, the surface area S_BET decreases from x=0 to x=0.6 then gets back to x=1. This
can be related to the powder agglomeration. Therefore, nano sized powders have a greater surface/volume ratio, so in order to minimize the total interfacial energy of the system, there is a formation of Van Der Waals links between the particles; consequently, most of nano crystalline powders form agglomerates.

Fig. 6 shows the adsorption-desorption isotherms of N$_2$ on the oxides prepared at 800 °C. The two samples reported here (x=0.2 and 0.8) present the IV and V adsorption type isotherms (Fig. 6a) [38]. This adsorption behavior is a characteristic of mesoporous structure, and the desorption branches present A type hysteresis [39]. The corresponding pore size distribution curves were presented in Fig. 6b. All samples display a similar unimodal distribution, with peaks in the range (2-12 nm), centered in the mesoporous region (between 20 and 500 Å) according to the classification established by De boer et al. [39].

3.3. UV-Visible spectroscopy and Optical gap measurement

The optical property of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ oxides can be observed by the UV-Vis spectroscopy. Fig. 7a shows the UV-Vis absorbance spectra of the compounds calcined at 800°C. All samples have an intense absorption peak in the interval (228 – 233 nm), characteristic of semi-conductor materials and can be related to ligand (oxygen)-to-metal (copper) charge transfer transition (LMCT). Others bands appear in the visible region and become intense and large when Cu-content increases; they are at 410 nm, 458 nm and 503 nm, and can be assigned to inter-atomic charge transfer d-d of Cu$^{2+}$ cations.

The diffuse reflectance data of each sample of the system Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ were measured in the spectral range: 200 to 900 nm, then converted into absorptivity, using the Kubelka–Munk function [36]. Thus, the band gap energy was estimated from the intercept of the straight lines at (αhv)$^2$ = 0:

$$(αhv)^n = A (hν - E_g) \quad (2)$$

A is a constant and n is equal to 2 or $\frac{1}{2}$ for direct and indirect transition, respectively. The spinel oxides present a direct allowed transition (n =2) and can be attributed to inter-band d-d transitions. The obtained values for the optical gap are reported in Fig. 7b. All the obtained values, in the range 1.71-3.54 eV, indicate a semiconductor character. In this case, it is clear
that the optical gap decreases with the increase of the copper content, because of the conductive character of the copper and to the induced defects levels following the Cu substitution [40]. Thus, this property in addition to the BET results could suggest good semiconductor materials for the photocatalytic reactions compared to the unsubstituted compounds (ZnAl$_2$O$_4$, CuAl$_2$O$_4$). The values of the optical gap obtained in this study are in good agreement with those reported in the literature for ZnAl$_2$O$_4$ and CuAl$_2$O$_4$ [40-42].

### 3.4. Photocatalytic activity

The photocatalytic property of the as-prepared powders are evaluated for Cr(VI) reduction under sunlight irradiation. In this part, we will present only the best results obtained for the compositions $x=0.8$. The results for $x=0.2$ are added for comparison. In industrial effluents, chromate concentrations can reach 100 mg/L or more. It is therefore interesting to study the effect of the initial concentration ($C_0$). The influences of initial solution concentration (from 30 to 90 mg/L) on the photocatalytic removal of Cr(VI) by the as-prepared catalysts are shown in Fig. 8.

It is clear that the Cr(VI) concentration in the solution remained constant in the dark and little adsorption ($< 10\%$) of Cr(VI) on catalyst is observed after 60 min. Moreover, the removal ratio of Cr(VI) from the solution decreases proportionally with the increases of the initial concentration of Cr(VI). The decrease of the removal ratio of Cr(VI) obtained after 180 min is illustrated in Fig. 8c. At low concentrations, the number of accessible photocatalytic sites is higher than that of HCrO$_4^-$ ions and the photocatalysis activity increases with the increase of $C_0$. The saturation of active sites of the catalyst is obtained when the initial concentration of Cr(VI) is higher compared to the mass of catalyst used and the active sites will be unable to reduce all Cr(VI) ions present in the solution. The decrease of the photoactivity of the catalysts can be also attributed to the blocking of photocatalytic sites by the compound Cr(OH)$_3$ with low solubility ($K_s = 5.4 \times 10^{-31}$). The color of the powder turns green after the photocatalytic process due to the adsorption of Cr(III) ions and Cr(OH)$_3$ compound [43-44]. In addition, HCrO$_4^-$ can be competitively reduced with water.

The highest removal ratio of Cr(VI) is shown for an initial Cr(VI) concentration of 30 mg/L and the removal ratio of Cr(VI) by Zn$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Al$_2$O$_4$ photocatalysts
reached 75% and 55% after 180 min under visible light irradiation, respectively. This difference is due to the behavior and properties of copper over zinc. The photocatalytic reduction of Cr(VI) in Zn_{1-x}Cu_xAl_2O_4 suspensions is favored at high content of Cu (x=0.8). These results demonstrate that Zn_{0.2}Cu_{0.8}Al_2O_4 exhibits better photocatalytic activity towards Cr(VI) reduction. Therefore, it is interesting to work at high concentrations because the rate of reduction does not change significantly (70% for 70 mg/L under Zn_{0.2}Cu_{0.8}Al_2O_4). Furthermore, our results are better than reported in the literature with other photocatalysts under the same condition [6, 45-47].

The photocatalytic efficiency of Cr(VI) reduction increases in the presence of oxalic acid with efficient separation of (e^-/h^+) pairs. The oxalic acid can be adsorbed on the surface of catalyst and is oxidized by the photogenerated holes, thus reduce the recombination of holes and electrons. Moreover, the formed holes are not used to reduce Cr(VI) and can produce 'OH radicals from water oxidation. In addition, the formed Cr(III) can be re-oxidized to Cr(VI). To avoid these effects, several organic agents are often added as sacrificial agents, reacting with the 'OH radicals or holes and suppress the electron-hole recombination with an enhancement of the Cr(VI) reduction.

The photocatalytic reduction rate obeys to the pseudo-first order kinetics.

\[
\frac{dC}{dt} = k_{app}C
\]  

(3)

Where \( k_{app} \) (min\(^{-1}\)) is the apparent rate constant and t is the irradiation time. The integration of Eq. (3) gives:

\[
Ln \left( \frac{C_0}{C} \right) = k_{app} t
\]  

(4)

Where \( C_0 \) is the initial concentration and C is the concentration of Cr(VI) at the specific time.

The plot of \( Ln \left( \frac{C_0}{C} \right) \) as a function of time (t) for different initial Cr(VI) concentrations in the presence of Zn_{0.2}Cu_{0.8}Al_2O_4 and Zn_{0.8}Cu_{0.2}Al_2O_4 photocatalysts are illustrated in Fig. 9a and b. Obviously, the decrease of initial Cr(VI) concentration was able to increase the
apparent rate constant and the removal ratio of Cr(VI). The kinetics of photoreduction follows
the modified Langmuir-Hinshelwood model (inset Fig. 9a and b).

\[
\frac{1}{k_{app}} = \frac{1}{k_r k_s} + \frac{C}{k_r}
\]

(5)

Where \(k_r\) is the reaction constant and \(k_s\) is the adsorption constant.

The mechanism of the photocatalytic reduction of Cr(VI) by Zn\(_{0.2}\)Cu\(_{0.8}\)Al\(_2\)O\(_4\) is illustrated in
Fig. 9c. Under visible light irradiation, the electrons of the conduction band and the holes of
the valence band are generated when the energy is higher than the energy of the band gap (\(> E_g = 1.99\) eV). Thus, the photogenerated electrons from Zn\(_{0.2}\)Cu\(_{0.8}\)Al\(_2\)O\(_4\)-CB reduce the
Cr(VI) through the adsorbed HCrO\(_4^-\) on the catalyst surface. The photogenerated holes are
captured by oxalic acid which avoids the recombination of the photogenerated holes and
electrons and enhances widely the photocatalytic activity. The relevant reactions are
summarized as follows:

\[
Zn_{0.2}Cu_{0.8}Al_{2}O_{4} + h\nu \rightarrow Zn_{0.2}Cu_{0.8}Al_{2}O_{4} (e^-CB, h^+VB)
\]

(6)

\[
Zn_{0.2}Cu_{0.8}Al_{2}O_{4} + h\nu \rightarrow CB^- Zn_{0.2}Cu_{0.8}Al_{2}O_{4} (e^-) + VB^- Zn_{0.2}Cu_{0.8}Al_{2}O_{4} (h^+)
\]

(7)

\[
Zn_{0.2}Cu_{0.8}Al_{2}O_{4} (3e^-) + HCrO_4^- + 7 H^+ \rightarrow Cr^{3+} + 4 H_2O + Zn_{0.2}Cu_{0.8}Al_{2}O_{4}
\]

(8)

\[
Zn_{0.2}Cu_{0.8}Al_{2}O_{4} (3e^-) + 2 H_2O \rightarrow Zn_{0.2}Cu_{0.8}Al_{2}O_{4} + H_2 + 2 OH^-\]

(9)

\[
HCrO_4^- + 7 H_2O^+ + 3 e^- \rightarrow Cr^{3+} + 11 H_2O
\]

(10)

\[
2H_2O + 2 e^- \rightarrow H_2 + 2 OH^-
\]

(11)

\[
C_2H_2O_4 + 0.5 O_2 + 4 h^+ \rightarrow 2 CO_2 + H_2O + 4 H^+
\]

(12)

4. Conclusion

In summary, a new family of ZnAl\(_2\)O\(_4\) nanoparticles zinc aluminates compounds was
developed by substitution of zinc by copper using the co-precipitation route. The preparation
through this method with low annealing temperature allowed the stabilization of nanoparticles
of pure zinc-copper aluminates in the spinel structure (Fd-3m). All Zn_{1-x}Cu_xAl_2O_4 (x = 0.0-1.0) spinel oxides presented a pure single phase after calcinations at 800 °C. The SEM images revealed the presence of quasi-spherical particles with homogeneous particle size distribution. The increased of copper content decreases the cell parameter of the spinel structure, influence the particles size (50-100 nm) and optical properties. The high specific surface areas determined by BET measurement and the surface analysis carried out by X-ray photoelectron (XPS), show that the surface is presented a moderate Lewis acid character, and pronounced anionic character. The optical gap values indicate a semiconductor character and the values decrease with increasing copper content. The photocatalytic activity for the as prepared powders are evaluated for Cr(VI) reduction under solar light irradiation. The photoreduction reaction follows pseudo-first order kinetics according to the modified Langmuir-Hinshelwood model. The highest photoreduction efficiency for the powders synthesized with different content of Cu was observed for x=0.2 (Zn_{0.2}Cu_{0.8}Al_2O_4) for an initial Cr(VI) concentration of 30 mg/L. The removal ratio of Cr(VI) reached 75% after 150 min exposure to sunlight.

Conflicts of Interest

None.

Acknowledgments

The authors are thankful to Hikmet Sezen for assisting in the XPS measurements and to Eda Özkaraoglu for SEM images and EDAX analysis (Bilkent University, Ankara, Turkey). The authors are thankful to the Directorate General for Scientific Research and Technological Development (DGRSDT) of Algeria, project with Socio-economic Impact No°06/Univ Jijel/DGRSDT.
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Tables captions:

**Table 1.** Refined structural parameters of Zn\(_{(1-x)}\)Cu\(_x\)Al\(_2\)O\(_4\) powders synthesized through the co-precipitation route.

**Table 2.** XPS analysis of the surface composition At (%) and binding energy (eV) for Zn\(_{(1-x)}\)Ni\(_x\)Al\(_2\)O\(_4\) (x = 0.2 and 0.8) samples.

**Table 3.** Percentage of deconvoluted peaks of O 1s region for Zn\(_{(1-x)}\)Cu\(_x\)Al\(_2\)O\(_4\) samples, x = 0.2 and x = 0.8.

**Table 4.** The results of BET measurements: the surface area (S\(_{BET}\)), the pore volume (V\(_p\)) and the particle size (d\(_{BET}\)).

Figures captions:

**Fig. 1.** Powder XRD patterns of Zn\(_{(1-x)}\)Cu\(_x\)Al\(_2\)O\(_4\) oxides calcined at 800 °C.

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**Fig. 4.** FTIR spectra of Zn\(_{(1-x)}\)Cu\(_x\)Al\(_2\)O\(_4\) oxides (x=0.0-1.0) calcined at 800 °C for 5h.

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Fig. 9. Kinetics of the HCrO\(_4\)\(^-\) photoreduction (pH \~ 4, T = 25 °C and catalyst dose = 1 mg/mL) under a) Zn\(_{0.8}\)Cu\(_{0.2}\)Al\(_2\)O\(_4\), b) Zn\(_{0.2}\)Cu\(_{0.8}\)Al\(_2\)O\(_4\). Inset: Plot of 1/k\(_{app}\) as a function of C\(_0\), c) Proposed mechanism for photocatalytic reduction of Cr(VI).
Tables:

Table 1

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<thead>
<tr>
<th>Zn$_{1-x}$Cu$_x$Al$_2$O$_4$</th>
<th>Space group</th>
<th>Crystallite size (nm)</th>
<th>Cell parameters a (Å)</th>
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Table 2

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Table 3

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\[\text{[Zn]} + \text{[Al]} + \frac{\text{[Cu]}}{\text{[O]}}^a\]

\[
\begin{align*}
    & x = 0.2 & 0.957 \\
    & x = 0.8 & 0.857 \\
\end{align*}
\]

\(^a\text{[O]} \text{ represents the percentage of oxygen of the lattice; the contaminants O and C are not considered.}\)

Table 4

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<td>Vp (cm}^3\text{/g})</td>
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<td>439.85</td>
<td>225.47</td>
<td>472.34</td>
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</table>
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In the dark | Under illumination

(a) $\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Al}_2\text{O}_4$

- HCrO$_4$ 30 mg/L
- HCrO$_4$ 50 mg/L
- HCrO$_4$ 70 mg/L
- HCrO$_4$ 90 mg/L

(b) $\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$

- HCrO$_4$ 30 mg/L
- HCrO$_4$ 50 mg/L
- HCrO$_4$ 70 mg/L
- HCrO$_4$ 90 mg/L

(c) % Reduction of Cr(VI)

$C_0$ (mg/L)

- $\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$
- $\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$
Fig. 8. a) The removal of Cr (VI) by a) Zn$_{0.8}$Cu$_{0.2}$Al$_2$O$_4$, b) Zn$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$; (pH ~ 4, T = 25 °C, [catalyst] =1 mg /mL), c) The rate of Cr (VI) photoreduction after 180 min, [HCrO$_4^-$] =30-90 mg /L.
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