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Photocatalytic Activity of Cu Doped TiO_2 Films Deposited by Electrophoresis

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Abstract

On latest years, an emergency necessity for clean methods to improvement of environment quality has attracted attention in several researches fields. The use of films on photocatalysis process is one of the most interesting alternatives due to its easily on separation of residual water and recovery of photocatalyst. In this work, we synthesized bare and Cu doped TiO_2 powder samples, which were characterized by X ray diffraction, micro-Raman spectroscopy, optical spectroscopy in ultraviolet and visible region and photocatalytic experiments for degradation of Rhodamine B dye. TiO_2 doped with 0.5% at. Cu promoted anatase phase stabilization, local structural distortions and reduction of band gap energy due to formation of intermediate energy levels within band gap. Cu doped TiO_2 sample was deposited by electrophoresis on aluminum substrate and resulted in thickness of approximately 125 µm, and 3 films on experiments tests allowed 56.3% of degradation of Rhodamine B solution in 60 minutes of reaction. Therefore, electrophoretic deposition is an effective method to obtain photocatalytic films and has shown an attractive potential for technological applications.

Keywords: Photocatalytic activity; Electrophoresis; Photocatalysis

Introduction

On recent years, the search for environmentally clean and friendly methods for degradation of toxic organic compounds has been one of the most attractive researches areas. This necessity arises from the lack of control in waste disposal of industries and domestics effluents, which makes favorable a pre-treatment of such waste before discarding them. Herewith, heterogeneous photocatalysis has shown to be a powerful and attractive process due to its potentiality, such non-selective to target compounds, production of highly oxidizing species and possibility of using solar energy [1,2] . However, although the favorable characteristics of process and high photoactivity of several materials, technological applications on

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industries are still a hindrance due to difficulty of catalyst recovery and separation of residual water, since materials in nanoscale powder form are usually used [3-5].

In order to overcome these obstacles, the use of materials in films form has been a desirable option for application in several technological fields, since its applications allows recovery and reuse of photocatalyst, easy separation of residual water and possibility of higher concentration of photocatalyst on process. Hereupon, electrophoresis deposition (EPD) is an interesting and favorable method to obtain ceramic films on certain substrates due to easiness on obtainment, short time deposition and allow modulating the film shape. Furthermore, there is no chemical reaction between electrode and ceramic particles, maintaining its morphology, structural phase and surface charge [6,7]. Among several semiconductors, TiO_2 is one of the main materials researched due to it high photoactivity, low cost and chemical inertia on water, which makes it favorable to environmental applications [8,9]. Despite this fact, a wide range of modifications have been made to improvement of it photocatalytic performance and for it use with sunlight process [10,11]. Doping semiconductors with metal transition cations has proven to be an effective method to achieve desirable properties due to changes in structural and electronic characteristics of materials [12,13].

Therefore, in this work we reported the photocatalytic activity of films of TiO_2 doped with Cu deposited by electrophoresis technique for degradation of Rhodamine B (RhB). These materials in powder form of bare and doped TiO_2 were characterized by X ray diffraction, Raman scattering spectroscopy, optical spectroscopy in ultraviolet and visible region, photoluminescence spectroscopy and photocatalytic experiments. These measurements allow understanding the structural, optical and photocatalytic behavior of prepared materials. The powder sample with higher photocatalytic activity was deposited by electrophoresis and it photocatalytic performance was carried out.

Experimental

For preparation of powder samples and films, all chemical reagents used were of analytical grade and without any treatment process.

Synthesis

Powder samples were prepared by polymeric precursor method, which were used titanium isopropoxide, citric acid and ethylene glycol in a ratio of 1:4:16 moles. First, ethylene glycol (purity 99%, Synth) was heated to 70 ºC and later titanium isopropoxide (purity 95%, Alfa Aesar) was added to it and stirred for 20 minutes. Lastly, citric acid (purity 99.5%, Synth) was added and the mixed was heated to 90ºC and stirred for 2 hours to formation of polymeric solution of Ti. For Cu doped TiO_2 sample, stoichiometric contents of $Cu(NO_3)_2.3H_2O$ was added to polymeric solution of Ti in order to obtain 0.5% at of Cu in relation to Ti. The resulting solutions were annealed at 380 ºC for 4 hours in conventional oven to form the primary solid and later at 400 ºC for 10 hours to eliminate residual organic compounds. A final thermal treatment was employed at 500 ºC for 4 hours to crystallization of lattice.

Characterization

In order to understand the structural properties of bare and Cu doped TiO_2, powder samples were characterized by X ray diffraction (XRD, Rigaku-Rotalex Dmax/2500 PC) using Cu Kα radiation and micro-Raman spectroscopy (MR, Horiba Jobin Yvon LabRAM iHR550) using a laser of wavelength of 514 nm. For insights of optical properties, powder samples were characterized by optical spectroscopy in ultraviolet and visible region as diffuse reflectance mode (Perkin Elmer, Lambda 1050 UV/Vis/NIR). The obtained films were analyzed by scanning electron microscopy in a Topcon model SM300 (operating with 10 kV), in order to verify its surface and average thickness.

Electrophoretic deposition

The powder sample with highest photocatalytic activity was deposited by electrophoresis deposition on an aluminum substrate of 2×1 cm. For this, 25 mg of iodine was dissolved in 20 mL of isopropanol to form the liquid medium. Then, 100 mg of photocatalyst was added to prior solution, and this was kept for 80 in an ultrasonic probe to form the suspension. The substrate and a counter electrode of stainless steel were immersed on the suspension with a distance separation of 1 cm to each other, and then a potential difference of 2 kV and 6.5 mA of current were applied during 15 seconds for deposition. For this process, the power supply used was a FUG Elektronik GmbH. After deposition, the films were heat treated at 400ºC for 1 hour in conventional oven to remove organic compounds and iodine traces.

Photocatalytic experiments

Photocatalytic experiments of powder samples were carried out for degradation of Rhodamine B dye solutions. The reactor was a Philips Ouro, which was fitted with a quartz tube and an inner UV germicide lamp ($\lambda = 254$ nm, 11 W, Osram, Puritec HNS 2G7). The reactor was 9.4 cm of inside diameter and 17.2 cm of height, the quartz tube was 4.1 cm of the inside diameter and 22 cm of height which was sustained by a support. The UV germicide lamp was inside the quartz tube and has dimensions of 1.2×2.6×19 cm. The experiments were conducted with 700 mL of Rhodamine B dye (RhB) solutions (10^{-5} mol L^{-1}), 70 mg of catalyst and under constant agitation and pumping air to saturation of O_2 dissolved. At certain times, aliquots were withdrawal and centrifuged for absorbance measurements in a Perkin Elmer spectrophotometer (Lambda 1050 UV/Vis/NIR). The photocatalytic experiments of films were performed on same reactor and same experimental conditions described above, however 3 films of photocatalyst were used to tests, which each film has approximately 18 mg of powder deposited.

Results and Discussion

X ray diffraction (XRD)

FIG. 1 shows XRD patterns of bare and Cu doped TiO_2 samples annealed at 500ºC. Both materials presented mixed phases of anatase and rutile for TiO_2 structures, with majority of anatase phase due to it thermodynamic stability on this temperature [14,15]. In addition, another feature that plays a more important role in majority of anatase phase is it thermodynamic stability in spherical particle size around 14 nm [16,17], but there may be variations in this size depending on the morphology and surface characteristics of particles [18,19]. No peaks related to any structural phase of Cu have been observed, indicating the introduction of dopant as solid solution on TiO_2 lattice. On XRD patterns, it was clearly observed a reduction in peak intensity related to rutile phase and increase of peak intensity related to anatase phase with introduction of 0.5% Cu on TiO_2 lattice, which indicates a stabilization of anatase phase on TiO_2 with Cu doping. Due to large difference in ionic radii of Cu^{2+} (0.870 Å) related to Ti^{4+} (0.745 Å), both occupying octahedral positions [20], Cu^{2+} ions tends to segregates on surface of TiO_2 particles [21,22]. This segregation process occurs due to electrostatic interactions and distortion energy of lattice due to difference in ionic radii [21-23]. Since Cu^{2+} are segregated on surface particles, these cations tends to reduces the surface energy, hence reducing the rate of grain growth, promoting a stabilization of anatase phase [16,22,24,25]. The average crystallite sizes of bare and Cu doped TiO_2 samples were calculated by Scherrer equation [26], being these, 19.2 nm and 18.7 nm, respectively. Therefore, a slight reduction on average crystallite size was observed, which corroborates the anatase phase stabilization with Cu doping on TiO_2.

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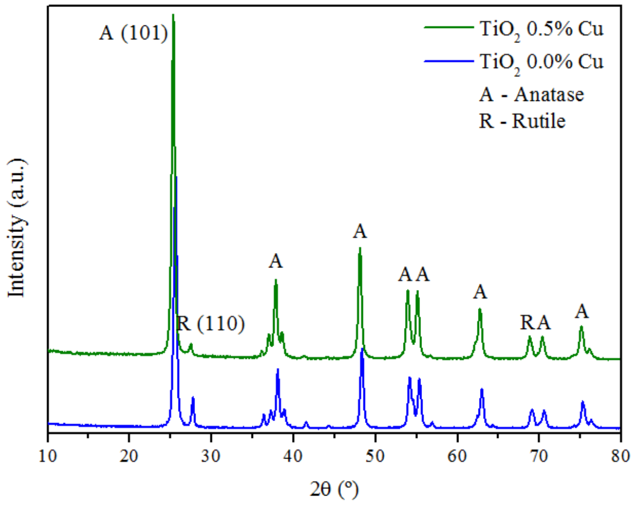

FIG. 1. XRD patterns of bare and Cu doped TiO_2 powder samples.

Micro-Raman spectroscopy

FIG. 2 shows Raman spectra of bare and Cu doped TiO_2 samples. All scattering bands exhibited for both samples has related to vibrational modes of anatase structure of TiO_2, not detecting vibrational modes related to rutile phase. No band related to vibrational modes of any structure of Cu was observed, corroborating the introduction of dopant as solid solution on TiO_2 lattice, as observed by XRD results. Raman bands observed on spectra were related to five vibrational modes of anatase structure, being these located at approximately 144, 197 and 639 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}) and 513 cm^{-1} (A_{1g}), which are in well agreement with literature data [27,28]. The Raman bands exhibited intense and sharp profile, indicating a well organization of structure as anatase phase. However, with introduction of Cu on TiO_2 lattice, a slight displacement of Raman band related to E_g vibrational mode near of 144 cm^{-1} was observed. Such displacement was approximately at 3.5 cm^{-1} to higher energy, which indicates a local lattice distortion on $[TiO_6]$ clusters caused by modifications on coordination parameters by Cu^{2+} insertion [29-31].

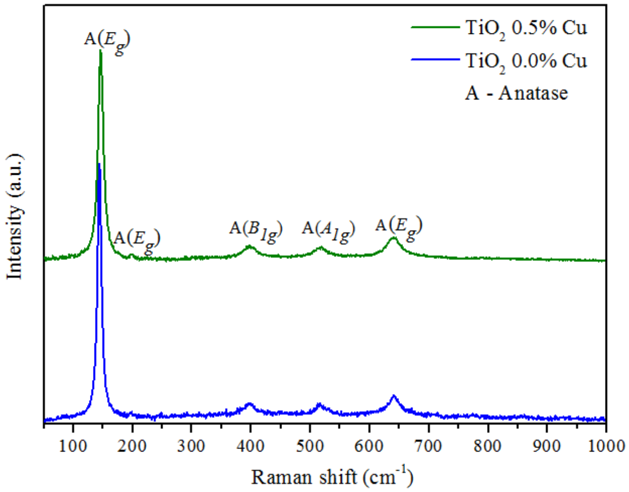

FIG. 2. Raman spectra of bare and Cu doped TiO_2 powder samples.

Optical spectroscopy in ultraviolet and visible region (UV-Vis)

The optical absorption behavior of bare and Cu doped TiO_2 samples were analyzed by its absorption on ultraviolet and visible region, from 250 to 700 nm. Measurements were performed by diffuse reflectance mode and the absorbance were correlated through Kubelka-Munk remission function, which $f(R) = (1-R)^2 / 2R$. On this equation, f(R) has correlated to absorbance of material and R is the reflectance [32]. **FIG.3a** shows absorption spectra by remission function of Kubelka-Munk of bare and Cu doped TiO_2 samples. Optical band gap of both samples were obtained by Tauc plot [33], and its values were estimated to 2.98 and 2.53 eV, for bare and Cu doped TiO_2, respectively, as shown in **FIG.3b**. It was clearly observed a large reduction on optical band gap energy with Cu doping on TiO_2, indicating the introduction of its dopant on lattice. The insertion of Cu^{2+} on TiO_2 structure generates intermediate energy levels within band gap primarily due to formation of oxygen vacancies and energy levels of 3d orbitals of Cu [9]. Hereupon, the formation of intermediate energy levels within band gap reduces energy required to excites an electron to a higher and unoccupied energy level, hence decreasing its optical band gap [34,35].

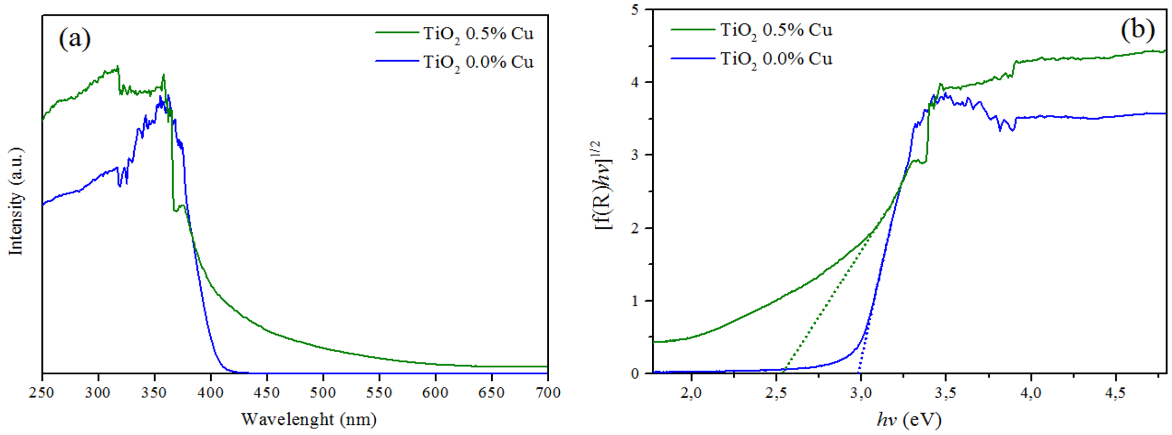

FIG. 3. (a) Absorption spectra and (b) Tauc plot of bare and Cu doped TiO_2 powder samples.

Photocatalytic experiments

Photocatalytic tests were performed to verify the photocatalytic activity of bare and Cu doped TiO_2 samples, in order to determine the most photoactive material. The experiments were conducted for degradation of organic dye Rhodamine B (RhB) and its results are shown in **FIG. 4**. As can be observed, Cu doping on TiO_2 with 0.5% at. related to Ti resulted in an significant improvement on photocatalytic activity of TiO_2. Photolysis test was performed without any photocatalyst in order to compare the contribution of materials on process. As indicated on **FIG. 4**, photolysis test allowed 34.1% of degradation of RhB in 60 minutes of reaction, while bare TiO_2 powder allowed 63.9% and Cu doped TiO_2 powder allowed 98.3% of degradation on same reaction time. The introduction of Cu^{2+} on TiO_2 lattice generates intermediate energy levels within band gap due to formation of oxygen vacancies and presence of 3d orbitals of Cu, as observed in optical spectroscopy analysis. In addition, Cu doping on TiO_2 led to local structural distortions on $[TiO_6]$ clusters, altering its coordination parameter, as observed in Raman spectra. This structural distortion arises from variations on bonds angle and lengths, hence altering the electronic structure of material. Therefore, oxygen vacancies, Cu 3d orbitals and local structural distortions generates intermediate energy levels within band gap on TiO_2 that act as electron trap on recombination process of electron/hole pair. Since these energy levels can trap electron, the recombination rate of electron/hole pair tends to decrease, and hence increase the lifetime of electron/hole pair. Due to lower recombination rate and higher lifetime of electron/hole pair, both electron and hole have greater availability for reduction and oxidation reactions, respectively, increasing the photoactivity performance of material. Due to higher photocatalytic activity of Cu doped TiO_2, this sample was chosen for deposition as film by electrophoresis. **FIG.4** shows results of photocatalytic experiments using 3 films of Cu doped TiO_2. As can be seen, the tests with films allowed 56.3% of degradation of RhB solution in 60 minutes of reaction. The reduction on process yield was clearly expected compared to same sample as powder form, since lower surface area for contact is available and the mass of photocatalyst used in films was approximately 54 mg, instead 70 mg as used in powder form. Due to photoactivity of Cu doped TiO_2 films, this procedures presents advantages compared to powder form and has attractive potential for technological applications.

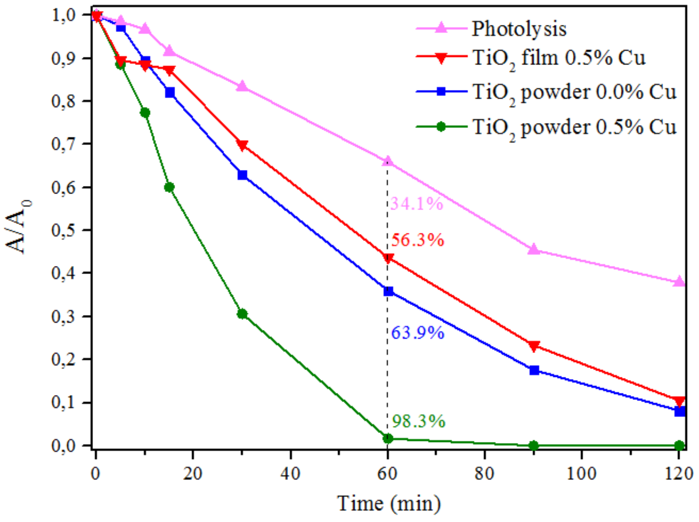

FIG. 4. Photocatalytic tests of all prepared samples.

Scanning Electron Microscopy (SEM)

FIG. 5 shows micrographs obtained by scanning electron microscopy of Cu doped TiO_2 film, in 100x and 200x of magnification on (a) and (b), respectively. The lower part of micrograph is the aluminum substrate and upper part is the Cu doped TiO_2 sample deposited. As observed, the obtained film has a high roughness on surface, being these favorable for photocatalytic activity due to higher area available to adsorption of water and organic species on surface, compared to films of flat surface. The average thickness of sample deposited was observed as 125 µm.

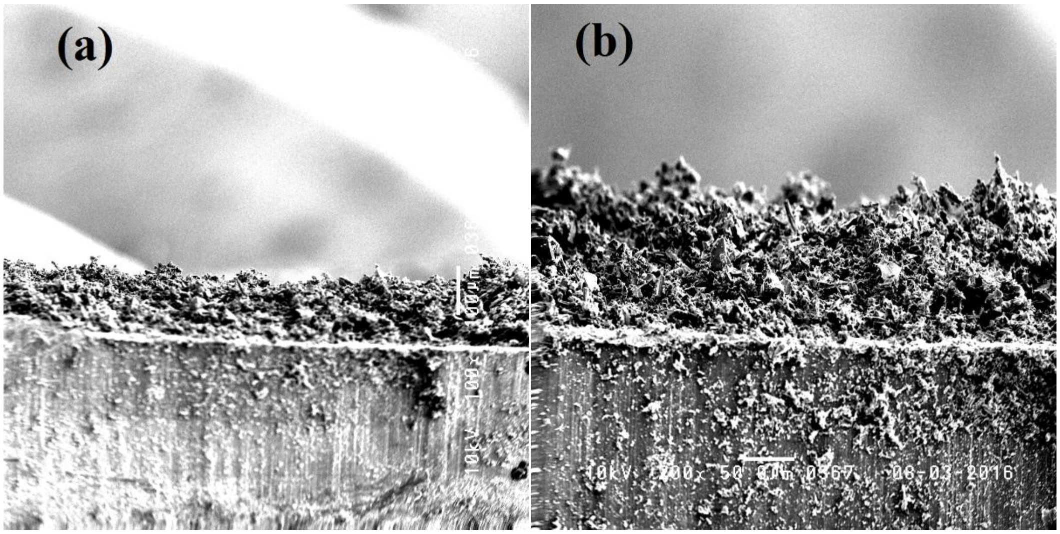

FIG.5. Scanning electron microscopy of Cu doped TiO_2 film with (a) 100x and (b) 200x of magnification.

Conclusion

The introduction of Cu on TiO_2 resulted in anatase phase stabilization in long-range order, local structural distortions and formation of intermediate energy levels within band gap, which favored the photocatalytic activity of TiO_2 due to reduced recombination rate and increased lifetime of electron/hole pair. Electrophoresis deposition was an efficient method to obtain films with photocatalytic activity for degradation of organic dye and rough surface, showing to be an interest alternative to technological application due to easily in photocatalyst recovery and reuse, separation of residual water and easy deposition of powders.

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