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Research Article

TiO_2:Ce_x onto Al Clays for Photocatalytic Solar Water Disinfection

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A novel methodology was employed to prepare new nanocomposites with photocatalytic properties based on Ce-doped TiO_2 nanoparticles arranged over a layered silicate. The catalysts were porous materials formed by exfoliated silicate layers surrounded by anatase nanoparticles. In this way, the anatase was doped by different amounts of Ce, yielding to catalysts with light absorption properties on the visible region. The photocatalytic behavior was tested for different reactions: adsorption and photocatalysis, showing outstanding and promising results for the removal of bacteria by using solar light as an energy source. The influence of the physicochemical properties of the catalyst and the reaction parameters will be studied in detail to manage new catalysts for the disinfection of drinking water.

1. Introduction

Removing pollutants from wastewaters is becoming an important area of research as the amount and quality of freshwater available in the world continues to decrease. Every year, two million people die due to chronic diseases caused by unhealthy water [1]. In this sense, the idea to regenerate and reuse polluted water is a necessity that yields to develop new technologies, which application depends on the geographic location and the economy of the country.

Heterogeneous photocatalysis could be a promising technology to be used in rural areas and urban slums. The idea to use solar light as the energy source to achieve the disinfection of drinking water is the main hypothesis of many researchers. Many efforts are currently focused on the development of reliable catalysts that can be activated by visible and solar light [2] but also to generate a system that first adsorbs the bacteria and then disinfects it utilizing of the photocatalysis. Several initiatives have been implemented to enlarge absorption of the TiO_2, because it exhibits, for their anatase structure, an optical bandgap of 3.2 eV, which only covers about 5% of the solar spectra [3, 4]. In order to address this problem, doping with Ce has been recently reported [3–6]. Cerium (Ce) as a dope influences the electronic structure of TiO_2 with $Ce3^+$ and $Ce4^+$ with $4f^15d^0$ and $4f^05d^0$, respectively [4], making a red shift absorption within the range 400–800 nm and reducing charge carrier recombination [5, 6]. There are some studies that explore the Ti-Ce as a photocatalytic material for visible light applications [4–12]. In one paper of us [6], we explore that possibility with one inorganic contaminant in a matrix of AC-TiO_2, this time we will create nanocomposites of Ce-doped TiO_2 nanoparticles over a layered silicate. In our case, the synthesis pathway is based on a sol-gel methodology that allows the generation of new porous materials [13]. This process causes the exfoliation/delamination of the silicate layers while creates oxide nanoparticles that are arranged between the silicate sheets, giving rise to new titania/silicate nanocomposites. Results implying its good efficiency for the photocatalytic degradation of different contaminants have been recently published [14]. Now, we are testing its ability to adsorb and degrade bacteria under solar irradiation using photocatalysis.

2. Experimental

Several Ce-doped TiO_2/silicate nanocomposites were prepared, using Cloisite30B organoclay (Southern Clay Products) as the starting silicate. The silicate dispersed in alcohol was treated with a mixture of Ti^{4+} alkoxide and Ce^{4+} nitrate, controlling their hydrolysis with the addition of water. The suspension was stirred at 50°C until a viscous gel is formed, due to the Ti^{4+} alkoxide hydrolysis. The resulting gels were first dried at 50°C and heated at 500°C in air. Several Ti/Ce and TiO_2/silicate ratios were evaluated in this work.

X-ray diffraction (XRD) was performed using a Bruker D8 diffractometer, with Cu K_α emission, the 2θ angle was within the range from 2° to 70°. The nitrogen adsorption–desorption isotherms were performed with a Micrometrics Tristar 123 at −196°C. The surface area was calculated by the Brunauer Emmett Teller (BET) surface area analysis, while the De Boer's method was used to calculate the external and micropore surface areas. The morphology was obtained with a NOVA NANOSEM 230 from FEI, equipped with EDAX Genesis XM2i. The elemental analysis was performed with a Perkin-Elmer ICP-MS NexION 300XX.

3. Photocalytic Setup

The photocatalytic reactor implemented is described elsewhere [15]. The bacteria used as a model for this work was *E. coli* ATCC 25922. An incident radiation intensity of 40 W/m^2 in the UV A/B range was measured with a UV Light Meter model YK-34 UV. Reference [15] shows a typical irradiation spectrum. An aqueous solution with an initial volume of 40 ml was prepared with a bacteria concentration of about 10^9 CFU/ml and placed in the photocatalytic reactor. It is necessary to point out that under real conditions, no contamination of such a high concentration has been founded [16].

Stirring at 100-120 rpm was implemented to ensure the homogeneous concentration of catalyst and bacteria in the solution. Samples were immersed at the shown weights; then, 1 ml of solution was collected, in the middle of the vessel, at different intervals of time (0, 30, 60, and 90 minutes) with or without illumination. After collection, samples were incubating at 40°C during 16 h. Each experiment was performed in duplicate.

4. Results and Discussion

Physicochemical characterization of the prepared catalysts was studied using various techniques (XRD, N_2-Isotherms, UV-vis, ICP-MS). The photocatalytic behavior was evaluated for adsorption and the removal of *E. coli* from water by using solar photocatalysis. All the XRD patterns evidence the exfoliation of the silicate layers with the absence of the (001) peak of the pristine Cloisite30B organoclay [13, 14], remaining the structural properties of the sheets without the creation of titania pillars between layers. At the same time, titania crystallizes as anatase phase, with crystal size values ca. 20 nm. In Figure 1, symbols (+) and (∗) correspond to Si peaks and TiO_2 anatase crystalline peaks, respectively.

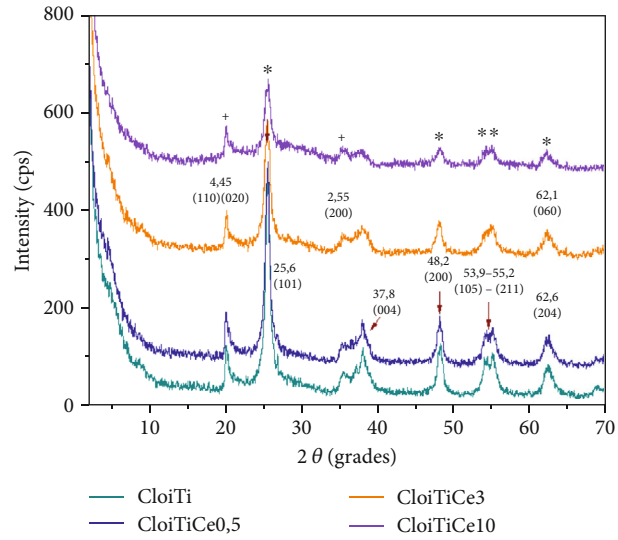

Figure 1: XRD patterns for TiO_2/silicate ratio of 1/1, symbols (+) correspond to Si peaks, whereas the (*), to TiO_2 anatase crystalline peaks.

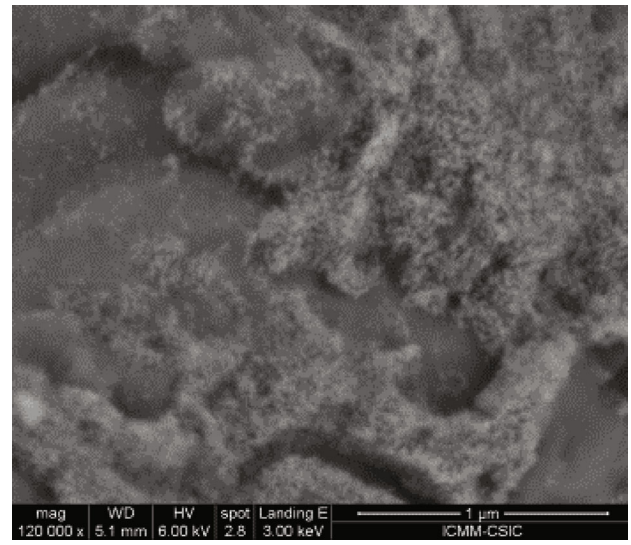

Figure 2: SEM image of 2Cloi/TiCe10 catalyst. The width of the micrograph is 2.43 microns.

The synthesis way employed in this work allows designing catalysts with a varied composition, giving rise to TiO_2/-silicate catalysts with Ce dopant amounts from 0.2 to 10% (w/w). The catalysts thus prepared to describe unstacked layers surrounded by the oxide nanoparticles with a spongy morphology, as shown in the SEM images (Figure 2). There is observed a rough system in which a microstructure is shown. The EDX-mapping micrographs of Ce, Ti, and Si demonstrate a homogeneous distribution of both Ce and Ti over the silicate. Data corresponding to each element is shown in Figure 3(b).

Figure 3 and Table 1 show the main physicochemical properties of the catalysts. In Figure 3(a), the catalysts exhibit surface area values between 180 and 240 m^2/g, with the contribution of both microporous and mesoporous

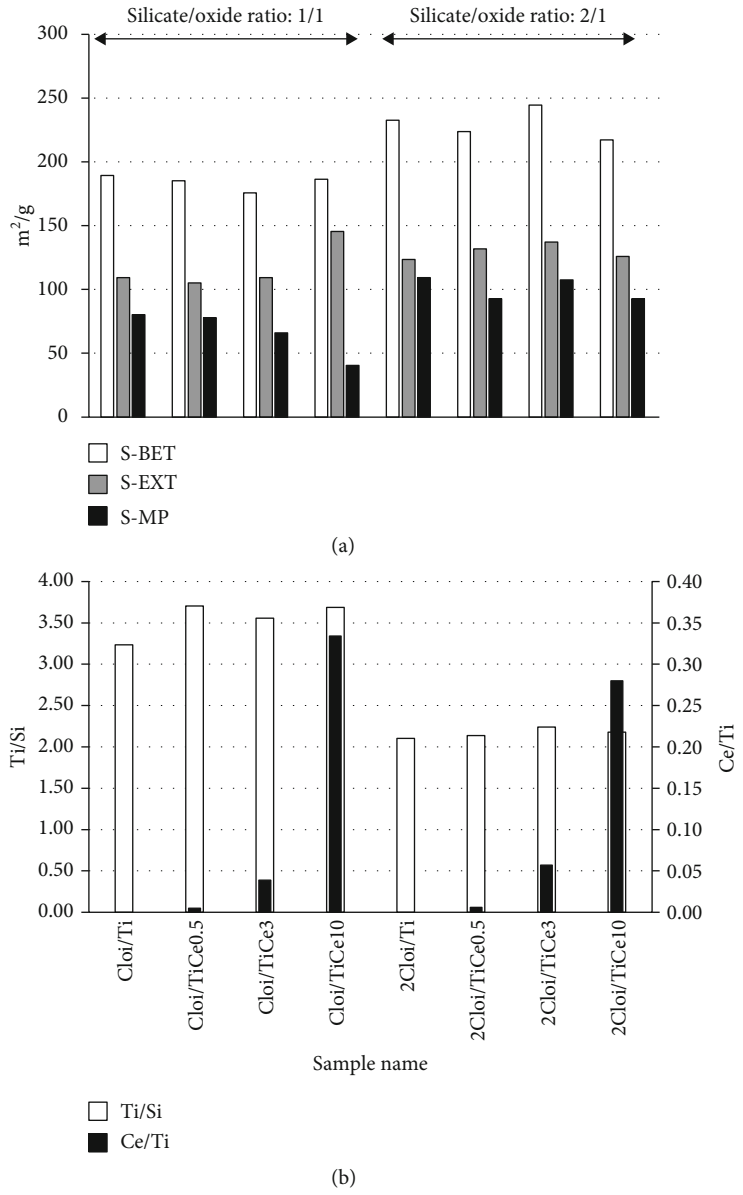

Figure 3: Shows the physicochemical properties: (a) Surface area, S-BET, external surface S-EXT, and internal surface S-MP; (b) Ti/Si and Ce/Ti were obtained by ICP.

Table 1: Physicochemical properties of the catalysts.

Catalyst	Silicate/oxide ratio g/g	S_{BET} m^2/g	S_{EXT}[a] m^2/g	S_{MP}[a] m^2/g	Ti/Si ratio[b]	Ce/Ti ratio[b]
Control UV						
Cloi/Ti	1/1	190	110	80	3.235	0
Cloi/TiCe0.5	1/1	185	106	79	3.705	0.005
Cloi/TiCe3	1/1	176	110	66	3.557	0.039
Cloi/TiCe10	1/1	187	146	41	3.688	0.334
2Cloi/Ti	2/1	233	124	109	2.102	0
2Cloi/TiCe0.5	2/1	224	132	92	2.139	0.006
2Cloi/TiCe3	2/1	245	137	108	2.239	0.057
2Cloi/TiCe10	2/1	218	126	92	2.180	0.280

[a]Calculated by the *t*-plot analysis. [b]Determined by ICP-MS analysis.

Table 2: Bacterial adsorption using different masses of the sample catalyst Cloi/TiCe0.5.

Time min	1 g/l	2.5 g/l	5 g/l
	E. coli, CFU/ml	*E. coli*, CFU/ml	*E. coli*, CFU/ml
0	3×10^9	3×10^9	3×10^9
30	13×10^5	8×10^5	20×10^5
60	45×10^5	7×10^5	21×10^5
90	32×10^5	100×10^5	13×10^5

Table 3: Photocatalytic degradation of *E. coli* using different catalysts. Each value has been obtained twice, and the average value is included. The obtained deviation of each set of the experimental values was about five percent.

		Cloi/TiCe0.5 1 g/l	2Cloi/TiCe0.5 1 g/l	Cloi/TiCe10 1 g/l	2Cloi/TiCe10 1 g/l	Photolysis
	Time min	*E. coli* CFU/ml	*E. coli* CFU/ml	*E. coli* CFU/ml	*E. coli* CFU/ml	*E. coli* CFU/ml
Dark	0	17,000,000	17,000,000	17,000,000	1,7000,000	17,000,000
	30	4,400,000	5,900,000	4,400,000	5,000,000	17,000,000
	60	110,000	870,000	570,000	320,000	8,300,000
Illumination	90	100,000	550,000	620,000	520,000	4,000,000
	120	30,000	29,0000	410,000	250,000	2,500,000

morphologies. The silicate/TiO_2 ratio is an important parameter to enhance the textural properties of the catalysts. Higher silicate/Ti ratio (2/1) yields to higher surface areas (233, 224, 245, and 218 m^2/g) due to the contribution of the silicate layer surface in comparison with the prepared to the 1/1 ratio, giving 190, 185, 176, and 187 m^2/g. Such influence is also observed for the microporous surface, for which the contribution of those to the total active surface is higher.

The absorption capability in the dark was analysed in a series of two repetitions per concentration, using different weights. It is observed in Table 2 that for 1, 2.5, and 5 g of catalyst in the solution, four orders of magnitude of absorbed bacteria were observed after 30 min. However, after this, the concentration reaches a plateau of around 10^5 CFU/ml and keep almost constant, a fluctuation between desorbing and adsorbing the bacteria.

For the photocatalytic disinfecting experiment, we place the sample inside the flask containing *E. coli* ATCC 1.7×10^7 in the dark during 30 min, to ensure bacteria adsorption and then, under UV-A illumination of 40 W/m^2. Results are presented in Table 3.

As a general trend, it is observed in Table 3 a degradation of bacteria in water by the effect of the UV-A irradiation. After 90 min of just photolysis, the degradation of the bacteria population was about one order of magnitude. On the other hand, for the photocatalytic process, in the case of the sample Cloi/TiCe0.5 and for the showed bacteria concentration, two orders of magnitude of decrement were observed after 90 min. This decrement of the bacteria concentration was observed to be higher than the observed for 2Cloi/-TiCe0.5, Cloi/TiCe10, and 2Cloi/TiCe10, respectively. This seems to be in accordance with the observed trend followed by the BET surface (Figure 3 and Table 1), as these samples present higher surface area, then present a higher possibility to adsorb bacteria in the dark and for them; however, as their degradation kinetics is not fast enough, the desorption of the viable bacteria that does not killed by the photocatalyst increases their concentration. In fact, for our Ti-Ce and under the illumination used, sample Cloi/TiCe0.5 presents the optimum active surface area for which all the adsorbed bacteria from the sample is effectively disinfected from the catalyst, avoiding them an increment of the concentration of bacteria during the photocatalytic experiment and obtaining a constant decrement. For all other samples, a fluctuation of bacteria concentration is observed. This fact defines a very interesting phenomenon, having a material that in the dark adsorbs efficiently the bacteria and under illumination degrading it by photocatalysis.

5. Conclusions

In this work, a novel effect has been found using Al Clays-TiO_2-Ce_x to degraded *E. coli* bacteria in water. It has been studied the effect of adsorption followed by the photocatalytic disinfection of *E. coli*; this material has two well-defined characteristic, in the dark, adsorbs *E. coli* for about 4 orders of magnitude for a bacteria concentration of about 10^9 CFU/ml, and under illumination, the photocatalytic disinfection is promoted on the surface of the catalyst degrading the adsorbed bacterial population and avoiding the desorption of the living contaminant, the *E. coli*, to the solution. This fact is particularly important because the bacteria will be adsorbed to a specific place, and then, even with low intensities of solar radiation, these will effectively disinfect.

Data Availability

Data is available from recola project log book.

Conflicts of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Acknowledgments

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