Research Article

TiO$_2$-CdS Nanocomposites: Effect of CdS Oxidation on the Photocatalytic Activity

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Received 20 July 2016; Accepted 28 September 2016

Academic Editor: Domenico Acierno

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Nanocomposites TiO$_2$-CdS with different relative contents of CdS (molar ratios Cd/Ti = 0.02, 0.03, 0.05, 0.1, 0.2, and 0.5) were studied. The structural, photophysical, and chemical properties were investigated using XRD, Raman spectroscopy, XPS, GSDR, and LIL. XRD and Raman results confirmed the presence of TiO$_2$ and CdS with intensities dependent on the ratio Cd/Ti. The presence of CdSO$_4$ was detected by XPS at the surface of all TiO$_2$-CdS composites. The relative amount of sulphate was dependent on the CdS loading. Luminescence time-resolved spectra clearly proved the existence of an excitation transfer process from CdS to TiO$_2$ through the luminescence emission from TiO$_2$ after excitation of CdS at $\lambda_{\text{exc}} = 410$ nm, where no direct excitation of TiO$_2$ occurs. Photodegradation of a series of aromatic carboxylic acids—benzoic, salicylic, 4-bromobenzoic, 3-phenylpropionic, and veratric acids—showed a great enhancement in the photocatalytic efficiency of the TiO$_2$-CdS composites, which is due, mainly, to the effect of the charge carriers’ increased lifetime. In addition, it was shown that the oxidation of CdS to CdSO$_4$ did not result in the deactivation of the photocatalytic properties and even contributed to enhance the degradation efficiency.

1. Introduction

In the past years, great interest has been focused on the research and development of water treatment methodologies due to the increasing presence of harmful pollutants in wastewater effluents [1, 2]. It has been shown recently that the efficiency of pollutants photodegradation is mainly determined by the properties of the photocatalysts [3, 4]. The importance of selecting suitable photocatalysts which have the capacity of absorbing solar visible light and the ability to separate photoexcited electrons from the holes have been emphasized. Among the reported semiconductor photocatalysts, titanium dioxide has attracted worldwide interest due to its strong oxidation activity and stability. In recent years, because of the band gap value (3.2 eV) in the UV light range, the modification of TiO$_2$ photocatalysts for the enhancement of light absorption and photocatalytic activity under visible light irradiation became the main research direction. To reach this goal, several modification techniques that exist mainly involve doping TiO$_2$ with metals or nonmetal elements such as Fe, Cu, C, and S [5–8], sensitization of TiO$_2$ by adsorbed dyes [9, 10], and coupling TiO$_2$ with semiconductors having lower band gaps and more cathodic conduction band (CB) [11, 12].

CdS is a semiconductor with a bandgap of 2.4 eV. Its excitation wavelength is $\leq 518$ nm and it has obvious advantages in absorbing within the solar spectrum. So, not only are the TiO$_2$-CdS composite nanoparticles excited easily by visible light, but also the recombination probabilities of the photoelectron-hole pairs are diminished [13, 14]. Bessekhouad et al. [14] found that under visible illumination the coupled CdS-TiO$_2$ exhibit faster degradation rate than both isolated components of the composite photocatalyst. Serpone et al. [15] reported for the first time the photocatalysed oxidation of
several phenol-based molecules by coupled semiconductors suspension in which the beneficial effect of the charge transfer was clearly demonstrated. They mentioned that in addition to the flat band potential of the components the photocatalytic performance of the coupled semiconductors is also related to the geometry of the particles, the surface contact between particles, and the particle sizes. These parameters strongly depend on the preparation method [15]. However, as widely recognized, there are several disadvantages concerning both the preparation and the utilization of such “coupled” systems. Specially, the oxidation of $S^{2-}$ to $S^{6+}$ in CdS semiconductor in the presence of air has been considered for a long time as an inevitable problem which causes uncertainty in the quality of the product and troublesome for the synthesis. The oxidation usually occurs as follows [16, 17]:

$$\text{CdS} + 2\text{O}_2 \rightarrow \text{Cd}^{2+} + \text{SO}_4^{2-}$$  \hspace{1cm} (1)

Therefore, many research groups considered that it is highly desirable to find new approaches that are capable of overcoming the above problems associated with the preparation of nanosized “coupled” CdS-TiO$_2$ photocatalysts. Some attempts have already been made by Zou and coworkers [18]. They successfully deposited CdS on the surface of TiO$_2$ using SILAR process for the CdS immobilization. Recently, Wang et al. [19] reported a simple and straightforward method for obtaining CdS coupled TiO$_2$ hydroxils with competitive physicochemical and photochemical properties. It was based on a microemulsion-mediated solvothermal hydrolysis of tetrabutyltitanate. However, some other studies reported a beneficial effect of SO$_4^{2-}$ produced upon CdS oxidation. In particular, Colón et al. [20] demonstrated that SO$_4^{2-}$ plays an important role in the photocatalytic oxidation reaction using SO$_4^{2-}$/TiO$_2$ catalyst. Sulphate ions increase the adsorption strength of the pollutant to the surface of catalysts which contributes to the improvement of photocatalytic activity. Moreover, Fu et al. [21] reported that the conversion of CH$_3$Br over sulphated TiO$_2$ was six times higher than that over TiO$_2$.

From the above cited references, associating CdS to TiO$_2$ is expected to improve the photodegradation activity since it permits to avoid unwanted charge recombination and to enlarge the light response of TiO$_2$ to visible light.

In the present study, TiO$_2$-CdS samples have been prepared by suspension mixing followed by annealing at 400°C, in order (i) to exploit the optical absorption properties of CdS in the visible energy range and (ii) to increase the surface contact between CdS and TiO$_2$ nanoparticles. The photodegradation of carboxylic acids in aerated conditions served as reference tests for the evaluation of the photocatalytic activity of the prepared TiO$_2$-CdS nanocomposites. The effect of SO$_4^{2-}$ ions on the photocatalytic activity was also investigated and is an innovative aspect of this study.

2. Materials and Methods

2.1. Materials. Titanium(IV) oxide, anatase nanopowder, <25 nm particle size, 99.7% trace metals basis, CdS powder, 99.995% trace metals basis, ethanol absolute ≥99.8%, benzoic, salicylic, 4-bromobenzoic, 3-phenylpropionic, and veratric acids were all purchased from Aldrich.

2.2. Preparation of CdS-Doped TiO$_2$. TiO$_2$-X CdS nanocomposites with different contents of CdS were prepared and the resulting samples were noted as TiO$_2$-X CdS, where X is the molar ratio Cd/Ti (X = 0.02, 0.03, 0.05, 0.1, 0.2, and 0.5). TiO$_2$ nanoparticles were immersed in a suspension of CdS nanoparticles in ethanol. TiO$_2$-CdS powders were dried at ambient temperature for 24 h, and then annealed at 400°C.

2.3. X-Ray Diffraction Analysis. The X-ray diffraction (XRD) patterns were performed using an X-ray Siemens/D5000 diffractometer with CuK$_\alpha$ radiation. The scanning range (2θ) was from 20° to 75° with a scanning rate of 0.5°/min.

2.4. Ground State Diffuse Reflectance Absorption Spectra (GSDR). Ground state absorption studies were performed using a homemade diffuse reflectance laser flash photolysis setup, with a 250 W Halogen lamp as monitoring lamp and in this way recording the lamp profile for all samples under study and also for two standards, barium sulphate powder and a Spectralon disk. A fixed monochromator coupled to an ICCD with time gate capabilities was used for detecting the reflectance signals. The reflectance, R, from each sample was obtained in the UV-Vis-NIR spectral regions and the remission function, F(R), was calculated using the Kubelka-Munk equation for optically thick samples. The remission function is $F(R) = (1 - R)^2/2R$. Details regarding the data treatment can be found in [22] and references quoted therein.

2.5. Raman Spectroscopy. μ-Raman measurements were carried out in a backscattering microconfiguration, with a homemade apparatus with a Cobolt Samba CW DPSSL, 300 mW, and 532 nm as the excitation source, coupled to a BX-FM microscope from Olympus equipped with 10x, 50x, or 100x Olympus LWD objectives. The laser beam was focused on a diameter of about 25, 5, and 1.5–2 μm, respectively. The Raman probe was coupled to a Shamrock i63 spectograph (Andor, with a 100 μm entrance slit) and a Newton DU 971P-BV camera from Andor was used as detector for the Raman signals, working at ~60°C [23].

2.6. Laser Induced Luminescence, LIF; and LIP. The setup for time-resolved luminescence LIL (laser induced fluorescence, LIF, and laser induced phosphorescence, LIP) is presented in [22]. The light arising from the irradiation of solid samples with the laser pulse is collected by a collimating beam probe coupled to an optical fiber (fused silica) and is detected by a gated intensified charge coupled device Andor, model i-Star 720. The ICCD is coupled to a fixed imaging compact spectrograph (Andor, model Shamrock 263). The system can be used either by capturing all light emitted by the sample or in a time-resolved mode by using the ICCD delay unit. The ICCD has high speed gating electronics (2.3 ns) and intensifier and covers the 250–900 nm wavelength range.

Time-resolved emission spectra were performed in the nanosecond to second time range either with a Nd laser
(excitation wavelength, $\lambda_{\text{exc}} = 337$ nm, PTI model 2000, ca. 600 ps FWHM, about 1 mJ per pulse) or using a dye laser coupled to the N$_2$ ($\lambda_{\text{exc}} = 410$ nm, using the PLD400 from PTI as laser dye). Emission spectra were obtained at 77 K, due to the fact that the room temperature luminescence intensity is negligible for the anatase form of TiO$_2$. In all cases under study only the initial 1$\mu$s part of the decay was analysed.

2.7. X-Ray Photoelectron Spectroscopy. For the chemical characterization, a Kratos XSAM800 XPS spectrometer and non-monochromatic Al K$\alpha$ radiation, without any flood gun for charge correction, were used. Typical operating conditions were 12 kV, 10 mA (120 W), and a pressure in the range of $10^{-7}$ Pa. Charge shifts were corrected taking, as references, the binding energy (BE) of aliphatic carbons centred at 285.0 eV for the CdS sample and the BE of Ti 2p$_{3/2}$ in TiO$_2$, centred at 458.8 eV [24], for the TiO$_2$-X CdS samples. The detailed XPS regions were analysed and fitted using Gaussian and Lorentzian function products. Shirley backgrounds and source satellites were subtracted from spectra. Data treatment was performed with the help of XPS Peak 4.1 software package (freeware). For quantitative purposes, sensitivity factors were C 1s: 0.25; O 1s: 0.66; S 2p: 0.54; Cd 3d$_{5/2}$: 3.48; Ti 2p: 1.76.

2.8. Evaluation of the Photodegradation Processes. The photocatalytic performance of TiO$_2$-X CdS samples with different CdS loadings was evaluated by following the absorption spectra, as a function of time, of organic pollutants solutions. For photodegradation tests, different organic compounds were selected and used as pollutant models ($c = 5 \times 10^{-4}$ M) in the presence of TiO$_2$-X CdS and exposed to visible irradiation. Organic pollutants selected were chosen to be not volatile, they can be analysed by UV absorption spectroscopy, and their solubility is larger than $10^{-4}$ mol/L. The maximum absorbance, corresponding to the remaining concentration of the pollutant in solution, was recorded at constant time intervals of 1h during 6 to 8 h by UV/vis spectroscopy. The UV-visible absorbance spectra were obtained using a Cecil UV-visible spectrophotometer in the range 200–800 cm$^{-1}$.

The UV absorbance of the solutes was measured at their corresponding $\lambda_{\text{max}}$ (which are situated, in this work, between 240 and 290 nm). Calibration curves were previously established for each solute here studied.

Each sample was stored in the dark for 1h (before irradiation) to reach the adsorption equilibrium. The adsorbed amount of solute in the dark was lower than 6% for all the samples. The set of degradation experiences was carried out under irradiation by a light source emitting only visible light. A 42 W Halogen lamp power (230 V) was used as a source of irradiation. The use of a lamp is very important to have constant intensity and overcome fluctuations in solar intensity due to the season or the time of day.

3. Results and Discussion

3.1. XRD Analysis. The crystal structure of the TiO$_2$-X CdS samples was examined by X-ray diffraction analysis. All the spectra are qualitatively similar and Figure 1 shows the XRD pattern for the sample TiO$_2$-0.2CdS. Two distinct reflections attributed to the anatase form of TiO$_2$ are observed at 25.6° and 48°. They can be attributed to (101) and (200) crystal planes [25]. Additionally, the XRD patterns of these samples showed four other reflections at 25.1°, 27.1°, 28.8°, 43.8°, and 52.0° which can be assigned to the CdS hexagonal wurtzite phase (100), (002), (101), (110), and (112) crystal planes, respectively [26]. No other forms of TiO$_2$ or CdS were observed in the studied samples. As a result, the XRD patterns clearly show that TiO$_2$ anatase and CdS wurtzite coexisted.

3.2. Ground State Diffuse Reflectance Absorption Studies (GSDR). In Figure 2, we can see the ground state diffuse reflectance spectra of samples with different relative amounts of dopant. TiO$_2$ nanoparticles and CdS powder spectra are also included for comparison. The first conclusion is that the composite spectra are superpositions of the individual spectra of TiO$_2$ and CdS exhibiting 2 distinct cutoffs corresponding to each one of the semiconductors. Tauc plots of all the curves present in Figure 2 yielded for each of the cutoffs the gap energy values in Table 1. For cutoff 1, corresponding to TiO$_2$, values from 3.18 eV to 3.24 eV are obtained, the variation with the CdS contents being random. For cutoff 2 corresponding to CdS, a constant value of 2.29 ± 0.01 eV is obtained. Since the value for cutoff 1 has a larger associated error due to the superposition of CdS absorption, the values obtained may be also constant (3.21 ± 0.03 eV). This suggests that the composite is mainly made of TiO$_2$ and CdS nanoparticles, restricting the mutual interactions to the interface between them. The energy gap for cutoff 1 is close to the commonly reported value for pristine TiO$_2$ [27]. However, the one obtained for cutoff 2 is somewhat lower than the
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Table 1: Energy band gaps corresponding to cutoffs 1 and 2 for TiO₂, TiO₂-XCdS, and CdS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cutoff 1 (±0.03 eV)</th>
<th>Cutoff 2 (±0.01 eV)</th>
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<tbody>
<tr>
<td>TiO₂</td>
<td>3.18</td>
<td>—</td>
</tr>
<tr>
<td>TiO₂-0.02CdS</td>
<td>3.22</td>
<td>2.29</td>
</tr>
<tr>
<td>TiO₂-0.03CdS</td>
<td>3.20</td>
<td>2.29</td>
</tr>
<tr>
<td>TiO₂-0.1CdS</td>
<td>3.24</td>
<td>2.29</td>
</tr>
<tr>
<td>TiO₂-0.5CdS</td>
<td>3.22</td>
<td>2.29</td>
</tr>
<tr>
<td>CdS</td>
<td>—</td>
<td>2.28</td>
</tr>
</tbody>
</table>

usually accepted value of 2.42 eV for CdS energy gap [28]. The difference is in principle due to the nanoconfinement which, in some systems, has this kind of effect.

3.3. Raman Studies. Well-resolved Raman peaks (Figure 3) were observed for the commercial TiO₂ at 144 cm⁻¹ (E₂g: symmetric stretching vibration of O-Ti-O in TiO₂), 395 cm⁻¹ (B₁g: symmetric bending vibration of O-Ti-O), 517 cm⁻¹ (A₁g: antisymmetric bending vibration of O-Ti-O), and 638 cm⁻¹ (F₂) [29], indicating that only the anatase phase of TiO₂ is observed, which is in agreement with XRD analysis. As the percentage of CdS increases, the Raman spectra show a combination of the two semiconductors characteristic bands. The intensity of the bands assigned to CdS at 300 cm⁻¹ and 604 cm⁻¹ [30] increases proportionally from TiO₂-0.02CdS to TiO₂-0.5CdS. One should also note that the anatase ratio of the E₂g and B₁g (or A₁g) band intensity is roughly constant with CdS content or, in other words, the three weak Raman peaks keep the same intensity ratio to the principal peak. This again suggests that both anatase and CdS crystallinity in the composite are independent of the composition.

3.4. Laser Induced Luminescence Studies. Figure 4 shows the laser induced luminescence spectra, all at 77 K. Figure 4(a) shows the emission of pure TiO₂ excited at 337 nm, Figure 4(b) is the same for the sample TiO₂-0.1CdS excited at 337 nm, and Figure 4(c) refers to the CdS luminescence excited at 337 nm. The TiO₂-0.1CdS sample excited at 410 nm, by the use of the dye laser coupled to the nitrogen laser, is presented in Figure 4(d). Figure 4(e) shows the pure CdS luminescence following excitation at 410 nm, and finally Figure 4(f) exhibits a superposition of the emission spectra obtained immediately after the laser pulse for the TiO₂-0.1CdS sample and for pure CdS, both excited at 410 nm. The emission of CdS peaks at about 686 nm [31] and the observed lifetime at 77 K for the pure CdS were about 575 ns. The laser induced emission spectra of undoped TiO₂, presented in Figure 4(a), exhibit a maximum at ~537 nm with a lifetime decay of approximately 85 ns. The important information that results from Figures 4(d) and 4(f) (from sample TiO₂-0.1CdS) is that luminescence from TiO₂ can be observed after exciting CdS at λexc = 410 nm, where no direct excitation of TiO₂ occurs. This is a very important observation: the occurrence of an excitation transfer process from CdS to TiO₂. Although, at first sight, this seems to be an energetically impossible process to occur, it was recently reported for similar systems, namely, transfer from a plasmonic metal (donor), which is absorbed in the visible, to a semiconductor, which is absorbed in the UV (acceptor) [32,33]. Also, a notorious increase in the lifetime of TiO₂ emission was observed, certainly related to the CdS longer lifetime, allowing a longer time range for the excitation transfer. The fact that it is possible to use visible light to indirectly excite TiO₂ is of utmost importance, since all the visible light up to ~540 nm is, in this way, useful for TiO₂ excitation, therefore increasing the photocatalytic activity. This greatly enhances the visible light photocatalytic activity when compared to the TiO₂ semiconductor alone. The fact that TiO₂ emission occurs following excitation of

![Figure 2: GSDR of all the samples under study in this work.](image)

![Figure 3: Raman spectra of commercial TiO₂ nanoparticles, TiO₂-XCdS composites, and CdS powder.](image)
CdS, while it does not occur in pure TiO$_2$ samples with visible excitation, can be clearly seen in Figure 4(d) where the time-resolved laser induced luminescence spectra clearly show a long lived emission from TiO$_2$ of about 145 ns (much larger than the one obtained with direct excitation).

3.5. X-Ray Photoelectron Spectroscopy. Samples with different CdS/TiO$_2$ ratios were characterized by XPS. The detailed regions corresponding to Cd 3d, S 2p, and Ti 2p are shown in Figure 5.

S 2p presents two different doublets with the main components, S 2p$_{3/2}$, centred at 161.7 ± 0.3 eV and at 168.6 ± 0.2 eV, corresponding, respectively, to sulphur in CdS and in CdSO$_4$. Cd 3d includes one doublet with a spin-orbit split of −6.8 eV. Only the main component, Cd 3d$_{5/2}$, centred at 405.3 ± 0.2 eV and assigned to Cd$^{2+}$ in both CdS and CdSO$_4$ was fitted [34].

XPS (Figures 5 and 6 and Table 2) shows unequivocally that the surfaces of TiO$_2$-CdS samples are composed not only of CdS, but also of oxidized sulphur, as in CdSO$_4$. The as-purchased CdS (from Aldrich) is just slightly oxidized, but in the TiO$_2$-CdS catalysts, the relative amount of SO$_4^{2-}$ is not negligible the ratio $S_{\text{CdSO}_4}/S_{\text{CdS}}$ varying between ~1/3 and 1/1 (Figure 6(a)). This ratio was computed from XPS S 2p peak areas (shown in Figure 5(b)). The degree of oxidation seems to increase for TiO$_2$-CdS formulations with lower overall content of CdS. Probably the degree of oxidation depends mainly on the sample surface ageing. The computed XPS ratios (Cd or S)/Ti follow a clear trend: for TiO$_2$-CdS samples the experimental XPS atomic ratio Cd/Ti deviates to lower values relatively to the nominal ones especially for high nominal ratios indicating that CdS should be aggregating. This "saturation" effect on the relative amount of CdS was also detected in Raman spectra (see, in Figure 3, the ratio between peaks centred at 604 and 638 cm$^{-1}$). The experimental XPS atomic ratio S/Ti follows the same trend as Cd/Ti.

3.6. Photodegradation Studies

3.6.1. Effect of the Content of CdS. Photocatalytic activities of the TiO$_2$-CdS composites were evaluated by measuring the degradation of benzoic acid in aqueous solution under visible light irradiation. The changes in the relative concentration of benzoic acid with time of irradiation were monitored by UV-vis analysis of aliquots at regular time. No detectable benzoic acid photodegradation was evidenced in aqueous solution in the absence of photocatalysts; thus, the pollutant is stable under visible irradiation in the emission range of the lamp.

As shown in Figure 7, the decomposition of benzoic acid increases as the irradiation time increases in presence of

Figure 4: Luminescence time-resolved spectra at 77 K. The initial curve is obtained after laser pulse, and the following curves were obtained with different steps, as indicated: (a) undoped TiO$_2$ excited at 337 nm, step of 20 ns; (b) TiO$_2$-0.1CdS excited at 337 nm, step of 20 ns; (c) pure CdS excited at 337 nm, step of 100 ns; (d) TiO$_2$-0.1CdS excited at 410 nm, step of 100 ns; (e) pure CdS excited at 410 nm, step of 100 ns; (f) superposition of the normalized emission spectra obtained immediately after the laser pulse for the TiO$_2$-0.1CdS sample and pure CdS both excited at 410 nm.
Table 2: Corrected binding energies (eV) and, in brackets, atomic concentration (%). Also, atomic ratios sulphate to sulphide and Cd or S to Ti are shown.

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<th>TiO$_2$-0.5CdS</th>
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<tr>
<td>O 1s</td>
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<td>530.1 [37.7]</td>
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<tr>
<td>Ti 2p$_{1/2}$</td>
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<th>Atomic ratio</th>
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<td></td>
<td>0.06</td>
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<td></td>
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To conclude, the enhanced activity of these oxidized samples can be ascribed to the beneficial effect of Cds which increases the TiO$_2$ lifetime and enlarages the population of charge carriers. In addition, SO$_4^{2-}$ ions resulting from the partial oxidation of S$^{2-}$ to sulphate have been identified at the surface of the catalysts and revealed to have a positive role on the photocatalytic efficiency.
Figure 5: XPS Cd 3d (a), S 2p (b), and Ti 2p (c) regions, from bottom to top, of CdS (Aldrich) and TiO$_2$-X CdS with $X = 0.5$, 0.2, 0.1, and 0.03 CdS.

Figure 8, $C/C_0$ depends strongly on the degraded pollutant. In the presence of TiO$_2$-0.02CdS and after 8 h of visible light irradiation, characteristic times of degradation are 3.8 h, 4.0 h, 5.8 h, 10.5 h, and 12.6 h, which lead to residual relative concentrations, after 8 h of irradiation, equal to 18%, 20%, 30%, 49%, and 58% of benzoic, salicylic, 4-bromobenzoic, 3-phenylpropionic, and veratric acids, respectively. Better performance observed for benzoic acid is probably a consequence of the high adsorption capacity of this pollutant on TiO$_2$-0.02CdS surface, which is the prerequisite step before the occurrence of the degradation process [38, 39].

3.6.3. Reuse of the Photocatalyst. To evaluate the photochemical stability of the catalyst, the repeated experiments for the photocatalytic decomposition of pollutant were performed using TiO$_2$-0.02CdS (freshly prepared) and TiO$_2$-0.02CdS$_{ox}$ (kept in air for three weeks) catalysts, and the results are presented in Figure 9.

As shown in this figure the reused samples show just a slight decrease in the photocatalytic activity. Moreover, photodegradation performance is much better using TiO$_2$-0.02CdS$_{ox}$ sample which emphasizes the excellent photochemical stability for both TiO$_2$-0.02CdS and
Although GSDR does not evidence any significant change in the band gap value, both in the CdS and in the TiO$_2$ phases, the composite that shows the best photocatalytic activity under visible light is the one with a lower relative content of CdS, TiO$_2$-0.02CdS. This sample in both GSDR and Raman has spectra which are composed of the sum of the TiO$_2$ in the form of anatase, and CdS. However, XPS reveals that the surfaces of TiO$_2$-CdS powders with low contents of CdS have a larger relative amount of sulphate species than samples with high CdS loads: the atomic ratios, $SO_4^{2-}/S^{2-}$, computed at the surface of TiO$_2$-0.03CdS and TiO$_2$-0.5CdS, are equal to 1.03 and 0.54, respectively. Moreover, for high doping loads, the XPS results are compatible with an aggregation of CdS, which is also confirmed by Raman, from the relative intensities of peaks centred at 604 cm$^{-1}$ and 638 cm$^{-1}$. This aggregation implies the lowering of the specific interface TiO$_2$/CdS and concomitantly the beneficial effect of CdS on the excitation of TiO$_2$ electrons through the visible light irradiation. The enhanced photocatalytic activity observed for the sample with the largest relative amount of oxidized CdS attests the beneficial role of $SO_4^{2-}$ in the photodegradation process, which is promoted by an increased surface acidity, as shown by Wang et al. [35] and others, due to the formation of a larger number of reactive surface sites enabling the chemisorption of different pollutants.

The effect of the CdS doping on the photophysics of the TiO$_2$-based photocatalysts prepared is clearly shown by the luminescence studies performed at 77 K: the laser induced emission spectra of undoped TiO$_2$ exhibit a maximum at $\sim$537 nm, with a lifetime decay of approximately 85 ns; the emission of pure CdS peaks at about 686 nm and the observed lifetime were around 575 ns; TiO$_2$ is luminescent when the photocatalyst TiO$_2$-0.1CdS is irradiated with an excitation wavelength of 410 nm, where no direct excitation of (undoped) TiO$_2$ occurs. Such emission, which shows an important and increased lifetime of 145 ns, is the result of an excitation transfer process from CdS to TiO$_2$. The fact that it is possible to use visible light to indirectly excite TiO$_2$ is of
Veratric acid
3-Phenylpropionic acid
4-Bromobenzoic acid
Salicylic acid
Benzoic acid

\[
\begin{aligned}
&\text{Veratric acid} \\
&\text{3-Phenylpropionic acid} \\
&\text{4-Bromobenzoic acid} \\
&\text{Salicylic acid} \\
&\text{Benzoic acid}
\end{aligned}
\]

Figure 8: (a) Photodegradation of different carboxylic acids in the presence of TiO\textsubscript{2} -0.02CdS composite under visible light irradiation. Curves correspond to the best nonlinear least square fitting of monoeponential functions to experimental data. Error bars are associated with the fitted curves and do not exceed ±8%; (b) characteristic times (\(\tau\)) that best describe the photodegradation kinetics.

Figure 9: Evolution of the degradation efficiency of benzoic acid after 10h for TiO\textsubscript{2} -0.02CdS and TiO\textsubscript{2} -0.02(CdS)\textsubscript{ox} after different degradation cycles.

The authors declare that they have no competing interests.

Acknowledgments

The authors thank the financial support granted by bilateral cooperation of “Ministère de l’Enseignement Supérieur et de la Recherche Scientifique” (Tunisia) and by FCT Project UID/NAN/50024/2013 (Portugal). A. M. Ferraria, D. P. Ferreira, D. S. Conceição, and A. P. Carapeto acknowledge FCT for the Postdoc and Ph.D. degree fellowships SFRH/BPD/108338/2015, SFRH/BD/95359/2013, SFRH/BD/95358/2013, and SFRH/BD/75734/2011.

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