Synthesis, Structural and Optical Characterization of Titanium Dioxide Doped by (Ce, Yb) Dedicated to Photonic Conversion

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Abstract: The synthesis of TiO2 co-doped by (Ce, Yb) rare earth couple has been realized. This couple of rare earth can convert a high-energy photon into two low energy photons to enhance the energy efficiency of silicon solar cells. The undoped, 2% Ce doped- and (2% Ce, 4% Yb) Codoped- Titanium oxide were prepared by the co-precipitation method. The Infrared spectroscopy FTIR-ATR analysis indicates a continuous visible absorption in the 750–400 cm–1 region, confirming the formation of a titanium-oxygen bond. The X-Ray Diffractometer characterization showed the dominance of the rutile crystalline phase with the presence of anatase one and the calculated crystallite size is between 7 to 13 nm. The X-Ray Fluorescence confirms the insertion of the dopants while the Inductively Coupled Plasma Mass Spectrometry ICP-MS showed the ratio 2 between Ce and Yb concentration. The thermogravimetric analysis indicated that Ce/Yb doped titanium was thermally stable. The absorption in the UV-visible (200 and 1000 nm) has been improved proportionally with the dopants.

Keywords: titanium dioxide; co-precipitation; rutile; anatase; photonic conversion

INTRODUCTION

Photovoltaic energy is one of the most important renewable energies, but this energy source has an efficiency limitation problem due to silicon used as a material for photon-electricity conversion. Recently, the Quantum Cutting process through which one high energy photon is converted into two near infrared ones attracted considerable attention. It can be adopted to minimize the energy loss by the thermalization of the charge carries caused by the absorption of high-energy photons. Until here, some work has been done by combining Ytterbium (Yb) with other rare earth elements. In this paper, the preparation of Titanium dioxide, known as Titania, TiO2, doped with the couple (Ce, Yb) was presented. It belongs to transparent semiconducting oxides (TCOs) class materials, which are simultaneously optically transparent and electrically conductive. Titanium dioxide has great potential for a lot of applications such as photocatalytic treatment in wastewater, transparent devices in electronics and probes or light detectors and telecommunication transmitter devices [1-5].

There are different methods for the TiO2 nanopowders preparation like thermal (ethanol thermal, hydrothermal and solvothermal) [6-12], dip coating [13], spin coating [14], electrochemical [15-17], chemical solvent [18], RF sputtering [19] and sol-gel [20-25]. The sol-gel process is one of the most successful techniques for preparing nanocrystalline TiO2 due to its flexibility in fabrication, low cost, and low processing temperature. Due to the low absorption efficiency of commercial Silica-based cells, which are around 15%, titanium was used to improve the performance of these cells [26].
Fig 1. Schematic energy-level diagram of Ce/Yb cooperative energy transfer process from Ce$^{3+}$ to Yb$^{3+}$

The synthesis of undoped and doped TiO$_2$ with Cerium and Ytterbium has been done by the co-precipitation method. This couple known for their exceptional optical properties attributed to down conversion [27-32], one ultraviolet/visible photon converted into two near infrared photons, which get absorbed by Si solar cells [33]. Indeed, the charge transfer (CT) follows the UV excitation of Ce$^{3+}$, from Ce$^{3+}$:5d$^1$ to Yb$^{3+}$:2F$^5/2$ [34-37]. The NIR emission (976 nm and 1028 nm) occurs through the transition Yb$^{3+}$:2F$^5/2$ to Yb$^{3+}$:2F$^7/2$ [38].

EXPERIMENTAL SECTION

Materials

The undoped and doped titanium dioxide, TiO$_2$, was prepared using titanium trichloride solution 15% TiCl$_3$ (purity ≥ 99.95%), CeCl$_3$·7H$_2$O (99.9%) and YbCl$_3$·6H$_2$O (99.9%) precursors from Sigma-Aldrich. Fourier Transformed Infrared by Attenuated Total Reflection (ATR-FTIR) spectra was recorded in the 400 – 4000 cm$^{-1}$ range on Perkin-Elmer spectrometer UATR two. Powder X-Ray diffraction (XRD) data was carried out with a D2-Phaser Diffractometer from Bruker. S2 Picofox–Bruker based on total reflection X-Ray Fluorescence (TXRF) used to provide a qualitative composition analysis when the Inductively Coupled Plasma Mass Spectrometry ICP-MS exploited for quantitative one. For the thermogravimetric analysis, LABSYS EVO TGA was used in order to measure the amount of change in material as a function of increasing temperature.

Procedure

Undoped and doped TiO$_2$ preparation

For the preparation of undoped TiO$_2$, 10 mL of titanium chloride was added in Erlenmeyer flask to 40 mL of distilled water. For the second sample TiO$_2$ (2% Ce) and the third TiO$_2$ (2% Ce, 4% Yb), 20 mg of CeCl$_3$ and (20 mg of CeCl$_3$ + 125 mg of YbCl$_3$) were added with TiCl$_3$, respectively. The mixtures were prepared in an ice bath because the reaction was exothermic. The solutions were heated on a hot plate at 90 °C. The precipitates obtained dried at 110 °C in an oven for 24 h.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis (XRD)

The XRD diffraction spectrum for synthesis materials is illustrated in Fig. 2. The exhibited diffraction peaks for undoped titanium dioxide at 20 values 25.05°, 47.5°, and 62.43° are attributed to anatase phase corresponding to crystal plans (101), (200), (204). Rutile peaks are found at 26.81°, 35.67°, 40.65°, 43.53°, 53.7°, and 56° corresponding to crystal plans (110), (101), (200), (210) and (022). For the Cerium doped titanium, Fig. 2 showed the anatase peaks at 2θ value 24.92°, 47.44°, and 62.43°. The rutile peaks appeared at 2θ = 26.9°, 35.6°, 40.69°, 43.44°, 53.69°, and 56°. For the third sample, the spectrum showed anatase peaks at 2θ = 25.23°, 47.77°, and 62.49°, while the peaks at 26.96°, 35.65°, 40.93°, 43.5°, 53.87°, and 56° are attributed to rutile phase [39-40]. The additional intense peak at 31.2° in all samples is assigned to the reflection on (121) for the Brookite phase [36]. Average particle size D was estimated by using the Scherrer equation (Eq. (1)) [41], the results are presented in Table 1. The lattice parameters a, c and V for the undoped and doped titanium dioxide were calculated from the position (110) peak using the formulas in (Eq. (2)) [42]. Table 2 summarize all the calculated parameters. The introduction of Cerium and
Zobair El Afia et al.

Fig 2. XRD of undoped and doped TiO$_2$: (a) total spectrum and (b) restricted spectrum

Table 1. Size crystallite D for the undoped TiO$_2$

<table>
<thead>
<tr>
<th>Hkl</th>
<th>2θ  (°)</th>
<th>Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(101)</td>
<td>25.05</td>
<td>77.19</td>
</tr>
<tr>
<td>(103)</td>
<td>35.50</td>
<td>123.34</td>
</tr>
<tr>
<td>(121)</td>
<td>31.20</td>
<td>131.61</td>
</tr>
</tbody>
</table>

Table 2. Lattice parameters a, c, and V for different samples in plan (110)

<table>
<thead>
<tr>
<th>Sample</th>
<th>D (Å)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>88.39</td>
<td>3.85</td>
<td>6.68</td>
<td>1.73</td>
<td>86.10</td>
</tr>
<tr>
<td>TiO$_2$:2% Ce</td>
<td>76.75</td>
<td>3.84</td>
<td>6.65</td>
<td>1.73</td>
<td>85.26</td>
</tr>
<tr>
<td>TiO$_2$:2% Ce;4% Yb</td>
<td>79.22</td>
<td>3.83</td>
<td>6.64</td>
<td>1.73</td>
<td>84.70</td>
</tr>
</tbody>
</table>

Ytterbium atoms into TiO$_2$ shifted the position of the peak of TiO$_2$ (Fig. 2), reduced the grains size, and slightly decreased the lattice parameters Table 2.

\[
D = \frac{K \lambda}{\beta \cos \theta} \quad (1)
\]

\[
a = \frac{\lambda}{\sqrt{3} \sin \theta} \quad \text{and} \quad c = \frac{\lambda}{\sin \theta} \quad (2)
\]

where $\lambda$ is the wavelength incident X-ray (= 1.549 Å); K: shape factor (= 0.9); $\beta$: Full-width at half maximum (FWHM) of the peak in the XRD patterns; $\theta$: diffraction angle.

X-Ray Fluorescence Spectroscopy (XRF)

To study the elemental composition of TiO$_2$, qualitative analysis was performed by X-Ray Fluorescence (XRF) Spectroscopy analysis. The spectrum obtained is shown in Fig. 3. XRF pattern shows peaks at 4.51 keV and 4.93 keV corresponding to Ti, which is the major element present in the powder. The spectra corresponding to the doped TiO$_2$ shows Cerium at (4.80 keV; 5.26 keV; 5.61 keV; 6 keV and 6.30 keV) and Ytterbium at (7.18 keV and 8.40 keV) suggesting that

Fig 3. X-Ray fluorescence spectra of: undoped TiO$_2$; TiO$_2$ (2% Ce); TiO$_2$ (2% Ce, 4% Yb)
they were incorporated into the TiO$_2$ lattice. However, along with these elements, some impurities traces in the form of chlorine was observed.

**Fourier Transform Infrared Spectroscopy (ATR-FTIR)**

Fourier transform infrared spectroscopy was usually employed as an analytical technique to identify organic (in some cases inorganic) material. Fig. 4 shows the FTIR spectra for doped and undoped TiO$_2$. Water and alcohol content is marked as a broad peak in the region 3100–3500 cm$^{-1}$ and the narrow peak at 1620–1640 cm$^{-1}$.

The continuous absorption visible in all the samples in the region 750–400 cm$^{-1}$ are caused by the strong stretching vibrations of Ti-O and Ti-O-Ti bonds [43-44].

**Inductively Coupled Plasma Mass spectroscopy (ICP-MS)**

The concentrations obtained for sample (TiO$_2$: 2% Ce, 4% Yb) by ICP-MS technique are $39.89 \pm 0.23$ mg/g of $^{47}$Ti, $4.20 \pm 0.06$ mg/g of $^{140}$Ce and $8.74 \pm 0.21$ mg/g of $^{172}$Yb. These data show a ratio of 2 between the concentrations of Ce and Yb and coincide with the quantity of the used precursors.

**Thermogravimetric Analysis**

The as-synthesized powder was measured for its thermal properties from room temperature to 900 °C. The TG analysis in Fig. 5 presents a weight loss of 8.5% between 25 to 198 °C, 4.5% in the range 198–600 °C and non-appreciable loss is observed beyond 600 °C for (Ce, Yb) doped TiO$_2$ and an essentially constant mass (87% sample) has been found indicating the thermal stability of the sample. The mass loss until 198 °C attributed to complete dehydration of the powders. The DSC curve showed a broad peak around 799 °C which can be assigned anatase to rutile transformation [45].

**UV-Vis Absorption**

Fig. 6 shows the absorbance of the TiO$_2$ recorded between 200 and 1000 nm at room temperature. This absorbance is improved proportionally with the insertion of the dopants used; therefore, even small proportions of...
the rare earth cerium and ytterbium enhance the optical properties of the TiO$_2$ remarkably.

**CONCLUSION**

The nano-powder titanium dioxide was synthesized by a simple co-precipitation method with an average crystalline size of 77 to 131 Å. The structure deduced from the XRD analysis shows that the nanoparticles are crystallized in the structures of rutile, which is the most dominant phase, also the presence of anatase and brookite phases. However, the introduction of the dopants decreases the size and lattice parameters of TiO$_2$ slightly. The elemental analysis by RFX shows the incorporation of Cerium and Ytterbium ions into the matrix, while the thermogravimetric analysis shows the transformation of the anatase structure into a rutile structure happened at high temperature between 700 and 800 °C and proved the thermal stability of the materials. Finally, the optical study by the UV-visible showed that the doping with the Ce and Yb rare earth increases the absorption of TiO$_2$ slightly, which allows it to be used for down-conversion in photovoltaic cells.

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