Synthesis and Characterization of TiO$_2$ Nanoreservoirs Supported with Platinum II and Sodium Bicarbonate Solution

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Abstract: In the past 10 years, the nanoreservoirs to based on TiO$_2$ have taken the lead to develop new and better ways to control and possible “removal” of diseases that have bewildered mankind since its existence. In seeking to contribute to these expectations, at this early stage we synthesized nanoreservoirs of TiO$_2$ with sodium bicarbonate solution to 15% (NaHCO$_3$-15/TiO$_2$), with salt of platinum(II) to 0.1% (Pt-0.1/TiO$_2$) and with the NaHCO$_3$ 15% and the platinum(II) 0.1% “in situ” (Pt-0.1-NaHCO$_3$-15/TiO$_2$) by sol-gel. We show that TiO$_2$ and Pt-0.1/TiO$_2$ nanoreservoirs are amorphous. While the NaHCO$_3$-15/TiO$_2$ and the Pt-0.1-NaCO$_3$-15/TiO$_2$ nanoreservoirs are crystalline. The NaHCO$_3$-15/TiO$_2$ and Pt-0.1-NaCO$_3$-15/TiO$_2$ nanoreservoirs are crystalline because to transformation of the sodium bicarbonate (NaHCO$_3$) to trona phase. The trona phase increases the average particle size of the Pt-0.1-NaCO$_3$-15/TiO$_2$ nanoreservoirs of 180 nm to 130 nm (NaHCO$_3$-15/TiO$_2$). The nanoreservoirs doped with platinum decreases the particle size to 50 nm (Pt-0.1/TiO$_2$).

Key words: TiO$_2$, NaHCO$_3$, Pt, nanoreservoirs, sol-gel.

Nomenclature

- **DNA**: Deoxyribonucleic acid
- **nm**: Nanometer, unit of length in the metric system
- **U.S.**: United States
- **UV-VIS**: Ultraviolet–visible spectroscopy
- **IR**: Infrared spectroscopy
- **XRD**: X-ray Diffraction
- **wt%**: Weight percentage
- **a. u.**: Absolute units
- **Eg**: Bandgap energy

Greek letters

- **$\lambda$**: Wavelength
- **$\nu$**: Frequency
- **$2\theta$**: Angle twice that of the theta angle

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1. Introduction

Of the oxides of transition metals internal as the titanium dioxide (TiO$_2$) has been one of the most studied for decades as a nanomaterial. It presents physicochemical properties, optical and structural (texture) that can be applied in various processes of industrial, environmental and health sector [1-20]. The TiO$_2$ has been reported as a semiconductor with excellent photocatalytic properties in the degradation of the highly polluting chemicals as organic solvents [21-26] and volatile organic compounds (VOC’s) [27-32], it used in processes intermediates catalytic as commercially valuable products end [33-35] such as disinfectant [36-39], in the orientation of DNA genes [40-42], in biological probes [43], in the diagnostic assay [44] and recently as nanoreservoirs in the control
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1. Introduction

The quantum effect of TiO\textsubscript{2} has been widely studied for its potential in cancer treatment due to its ability to photogenerate holes and vacancies. These reactions can be used to treat tumor cells due to cell membrane peroxidation [53]. The incorporation of transition metals internal inert as Pt in the TiO\textsubscript{2} matrix can significantly improve the photocatalytic activity of the semiconductor due to charge separation between the metal and the remaining holes are in the photocatalytic surface [54, 57].

We propose that the platinum coordination complexes can act as cytotoxic agents. The cis-diamminedichloroplatinum (II) or better known as cisplatin was the most active of these substances in experimental tumor systems and has proved to be clinically useful. Carboplatin was approved for the treatment in the ovarian cancer in the U.S. in 1989. Cisplatin has broad antitumor activity and is especially useful in the treatment of epithelial cancers. It has become the foundation of curative regimes in testicular cancer and has remarkable activity against ovarian cancers, head and neck, bladder, esophagus and lung [56-64]. Recently, a group of experts led by Dr. Simoncini proposes that the Candida may be the cause of cancer and he eliminate the fungus with sodium bicarbonate (NaHCO\textsubscript{3}) [65]. Therefore, in this first phase, we report the synthesis and using spectroscopic techniques such as UV-VIS, IR and XRD of three nanomaterials of TiO\textsubscript{2} doped with Pt at 1\% by weight (Pt-0.1/TiO\textsubscript{2}), with solution at 15\% NaHCO\textsubscript{3} (NaHCO\textsubscript{3}-15/TiO\textsubscript{2}) and both impurities in the support of TiO\textsubscript{2} (Pt-0.1-NaHCO\textsubscript{3}-15/TiO\textsubscript{2}). In later work, such nanoreservoirs are evaluated in the treatment and control of skin, breast and prostate cancer on rat Wistar.

2. Experiments

Three nanoreservoirs were prepared by sol-gel based on titanium oxide (TiO\textsubscript{2}). To one was added 0.1 wt\% platinum (Pt-0.1/TiO\textsubscript{2}). The platinum precursor was platinum acetylacetonate (C\textsubscript{10}H\textsubscript{14}O\textsubscript{4}Pt, Sigma-Aldrich, 97\%), to another was added 50 mL of a solution of sodium bicarbonate 15\% (NaHCO\textsubscript{3}-15/TiO\textsubscript{2}) using as precursor sodium bicarbonate (NaHCO\textsubscript{3} ACS, 99.7\%) and the third was added "in situ" platinum salt to 0.1 wt\% and 50 mL of sodium bicarbonate solution to 15\% (Pt-0.1-NaHCO\textsubscript{3}-15/TiO\textsubscript{2}). All the nanoreservoirs were prepared from a homogeneous solution containing 150 mL of anhydrous butyl alcohol (Sigma-Aldrich, 99.8\%), 10 mL of deionized water, 0.5 g of polyvinylpyrrolidone (Sigma-Aldrich, PM 100,000). At these solutions was added separately the respective amount of platinum salt and the corresponding volume of 15\% NaHCO\textsubscript{3} solution. When the homogeneous solution presents a temperature to 70 °C of reflux and constant stirring, was added 21.5 mL of titanium n-butoxide (Sigma-Aldrich, 97\%). Each final solution (with gelling properties) was immersed in a vessel containing ice water at 3 °C for 15 min. The solvent (water and alcohol) of each hydrogel synthesized was removed on a rotary evaporator at 60 °C under vacuum. All the nanoreservoirs synthesized, are thermally treated at 110 °C for 4 h.

3. Results and Discussion

3.1 Infrared

In the identification of the functional groups present in the nanoreservoirs synthesized, we utilized a Digilab FTIR Scalibur of VARIAN model, FTIR spectrophotometer. The spectra of the nanoreservoirs are shown in the Fig. 1.

The TiO\textsubscript{2} (black curve) shows an absorption band at 3,239.2 cm\textsuperscript{-1}, assigned to the vibrational elongation mode of the OH species. It correspond the hydroxyl groups (OH\textsuperscript{-}), water (H-OH), solvent (1-butanol, R\textsuperscript{-}OH) and the hydroxylation of gel (Ti-OH). These functional groups are present in the pores of TiO\textsubscript{2}, they
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formed during the first stage of gelation. The stretching vibration mode located at 2,080.6 cm⁻¹, correspond at mode antisymmetric of both ethoxy and methoxy groups of the reactants which reacted not. At 1,644.9 cm⁻¹ shows the absorption bands of the type vibration modes of bending of the hydroxyl groups of water that is present on the surface of TiO₂ nanomaterial. They are mainly associated with the moisture and solvent. It correspond the vibration deformation mode of the water. At 1,294.7 cm⁻¹ are located the vibration modes of oxidation of the material, generally are associated to impurities present during the condensation process the material. The wave numbers present at 1,217.3 cm⁻¹ and to 1,006.5 cm⁻¹ mode correspond to bending of type C-C, and C-O. They are due to the methoxy bridge species as well as the product and products of the synthesis reaction of the material. The absorption band located at 548.4 cm⁻¹ is assigned to the vibration mode of the Ti-O groups. Regarding the Pt-0.1/TiO₂ and NaHCO₃-15/TiO₂ nanoreservoirs, the absorption bands that presented at 2,939.8 cm⁻¹ (for Pt-0.1/TiO₂) are assigned vibration flexion mode of methyl and methylene groups, at 1,525.5 cm⁻¹ (for Pt-0.1/TiO₂) correspond the vibration stretching mode of asymmetric type for carboxyate ion (COO⁻). At 1,440.7 cm⁻¹ (for Pt-0.1/TiO₂) correspond to symmetric stretching vibration for the COO⁻ ions and to deformation vibration of the -CH₃ species.

At 356.0 cm⁻¹ are present the bending vibrations and of scissors of the C-H groups and at 1,084.9 cm⁻¹ (for NaHCO₃-15/TiO₂), are located the vibration band assigned to the vibration modes of elongation of the C-C and the C-O species. It corresponding the methoxy bridge species. The absorption band at 1,079.3 cm⁻¹ (for Pt-0.1/TiO₂ and the NaHCO₃-15/TiO₂) corresponds to vibrations of elongation of the C-C and the CO groups, it corresponding to the vibration to the bridge methoxy species. At 544.8 cm⁻¹ are located the vibration modes of the metal-oxygen interaction assigned to the Ti-O, Na-O and O-Pt species of the nanoreservorios obtained.

3.2 UV-VIS Spectroscopy.

We used a spectrophotometer of Varian Cary 100 with integration sphere coupled of diffuse reflectance. Fig. 2 shows the UV-VIS spectra of the synthesized nanoreservoirs. Regarding to absorption spectral bands of the TiO₂ nanomaterial, the absorption spectral bands of UV-VIS and of Pt-0.1-NaHCO₃-15/TiO₂ and the NaHCO₃-15/TiO₂ nanoreservoirs are displaced toward the near-UV. This trend is due to impurities of platinum particles and to the formation of trona from to sodium bicarbonate present in each TiO₂ matrix. The magnitude of the band gap energy (Eg) of the nanoreservoirs of Pt-0.1/TiO₂, Pt-0.1-NaHCO₃-15/TiO₂ and NaHCO₃-15/TiO₂ is very similar.
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The small fluctuations in the magnitude of the band gap are the order of hundredth. Only for nanoreservoirs with particles having platinum salt (Pt-0.1-NaHCO₃-15/TiO₂ and Pt-0.1/TiO₂) shows absorption electromagnetic to 2.3 eV and 2.4 eV respectively. This is due, by the interaction between the platinum particles and the active centers with different charge density on the surface of TiO₂.

According to the study of X-ray diffraction are not observed spectral bands corresponding to the platinum particles. Table 1, shows the value of band gap of the nanoreservoirs studied. The TiO₂ is present in form to anatase according to recorded value of 3.2 eV. The nanoreservoir of NaHCO₃-15/TiO₂ has the highest value of energy band gap ($E_g = 3.50$ eV) compared to the other nanoreservoirs synthesized (Pt-0.1-NaHCO₃-15/TiO₂, $E_g = 3.44$ eV and Pt-0.1/TiO₂, $E_g = 3.37$ eV). We believe that the sodium bicarbonate (NaHCO₃) is transform in trona phase and it this on the surface of TiO₂, i.e. it covers almost the entire surface of TiO₂, as shown in the studies diffraction ray X. The maximum value of the ultraviolet absorption of NaHCO₃-15/TiO₂ nanoreservoir coincides with the maximum value of ultraviolet radiation of commercial sodium bicarbonate. Do not forget that the sodium bicarbonate is not a semiconductor, such as the nanomaterial NaHCO₃-15/TiO₂, which is supported on the TiO₂.

The nanoreservoirs of NaHCO₃-15/TiO₂ and the TiO₂ have a maximum electromagnetic absorption in the visible region, while the nanoreservoirs of Pt-0.1/TiO₂ and NaHCO₃-15-Pt-0.1/TiO₂, it presented in the near-UV region.

Fig. 3 shows the XRD patterns of the TiO₂, Pt-0.1/TiO₂, Pt-0.1-NaHCO₃-15/TiO₂ and NaHCO₃-15/TiO₂ nanoreservoirs.

The TiO₂ and Pt-0.1/TiO₂ nanomaterials tend to be amorphous. While the NaHCO₃-15/TiO₂ and Pt-0.1-NaHCO₃-15/TiO₂ nanoreservoirs. They are crystalline and exhibit diffraction bands characteristic to the trona phase. The structural formula of the trona phase is $[\text{Na}_3(\text{CO}_3)(\text{HCO}_3)\cdot2\text{H}_2\text{O}]$. These bands of high intensity are located in $2\theta = 9.3, 18.3, 28.3$ and 44.6, it presents the form monoclinic.

No shows diffraction band corresponding to platinum material, which suggests that is dispersed in the TiO₂ matrix, this may be due to the concentration found in the sample of platinum on the mesh of TiO₂, which is to 0.1% by weight. The trona phase formation can be expressed through the Eqs. (1) and (2).

\[
\text{NaHCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Na}^+ + \text{HCO}_3^{2-} \quad (1)
\]

\[
2\text{CO}_3^{2-} + 3\text{Na}^+ + 2\text{OH}^- + \text{H}_3\text{O}^+ \leftrightarrow \text{Na}_3(\text{CO}_3)(\text{HCO}_3)\cdot2\text{H}_2\text{O} \quad (2)
\]

3.4 Scanning Electron Microscopy (SEM)

The textural properties and the average particle size of TiO₂ was made by scanning electron microscopy (SEM), using a computer model JSM-6610LV, JEOL. The nanoreservoirs were placed in the sample holder and they coated with Au for better contrast and image quality. The voltage applied to accelerate electrons was 20 Kv. Fig. 4 shows the TiO₂ nanoreservoir micrographs. They showed an average particle diameter to 70 nm. In the micrographs are observed to form agglomerated particles hemispherical coral type. Micrographs of the NaHCO₃-15/TiO₂ nanoreservoirs show an average particle diameter between 130 nm greater than of TiO₂ nanoreservoirs. Tend to form agglomerated to hemispherical particles.
Table 1  Optical and electrical properties of nanoreservoirs synthesized.

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>$\lambda$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>$\lambda$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>$\nu$ (Hz) ($\times 10^{14}$)</th>
<th>spectral region</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>389</td>
<td>3.20</td>
<td>-</td>
<td>-</td>
<td>7.7</td>
<td>VIS (violet) - UV</td>
</tr>
<tr>
<td>NaHCO$_3$-15 /TiO$_2$</td>
<td>351</td>
<td>3.50</td>
<td>--</td>
<td>-</td>
<td>8.5</td>
<td>VIS (violet) - UV</td>
</tr>
<tr>
<td>NaHCO$_3$-15- Pt-0.1/TiO$_2$</td>
<td>360</td>
<td>3.44</td>
<td>530</td>
<td>2.3</td>
<td>8.3 - 5.7</td>
<td>Near UV</td>
</tr>
<tr>
<td>Pt-0.1/TiO$_2$</td>
<td>368</td>
<td>3.37</td>
<td>517</td>
<td>2.4</td>
<td>8.2 - 5.8</td>
<td>Near UV</td>
</tr>
</tbody>
</table>

Possibly, they are supported on the amorphous trona phase. As shown by the XRD study (Fig. 5).

The average size of the particle diameter of Pt-0.1-NaHCO$_3$-15/TiO$_2$ nanoreservoirs according to the micrographs of Fig. 6 is to 180 nm. Amorphous agglomerated particles are observed. The presence of platinum particles on the TiO$_2$ nanomaterials presented some influence in the morphology of Pt-0.1-NaHCO$_3$-15/TiO$_2$ nanoreservoir, because the plates are not amorphous as in the case of NaHCO$_3$-15/TiO$_2$ nanoreservoirs. We are establishing the forming a platinum complex (caboxyplatinum) on to trona phases and the TiO$_2$ nanomaterials.

We assume that platinum(II) ions have a higher affinity to trona phase and the platinum complex molecules are interacting physically on the surface of
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Fig. 6  SEM images of the Pt-0.1-NaHCO₃-15/TiO₂ nanoreservoirs.

Fig. 7  SEM images of the Pt-0.1/TiO₂ nanoreservoirs.

Scheme 1. The interaction of the trona phase with the surface of TiO₂

Scheme 2. Interaction of trona phase and particles of platinum as a complex on the surface of TiO₂
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TiO₂ and the trona phase. The micrographs of the Pt-0.1/TiO₂ nanoreservoirs are shown in Fig. 7. Agglomerated hemispherical particles are observed with an average particle to 50 nm size.

The Pt-0.1/TiO₂ nanoreservoir morphology is completely different compared to 15-NaHCO₃-15-Pt-0.1/TiO₂ nanoreservoirs. The presence of platinum(II) ions tends to form spherical particles and significantly reduce the average size of mesh particle TiO₂ to 30 nm. Therefore, we propose the interaction of the trona phase with the surface of TiO₂ nanomaterial and simultaneously the interaction of the molecules of the platinum complex on the mesh of TiO₂, as shown in the Scheme 1.

The interaction of the highchair and platinum on the TiO₂ mesh of can be represented by the Scheme 2.

4. Conclusions

The XRD study of the NaHCO₃-15/TiO₂ and of the Pt-0.1-NaHCO₃-15/TiO₂ nanoreservoirs shows that the sodium bicarbonate solution is transformed to trona phase. This crystalline phase is adsorbed in layer form on the TiO₂ nanoreservoir. It is Interacting with the active sites on the surface of TiO₂ (Ti²⁺ and O²⁻). During the synthesis of the Pt-0.1-NaHCO₃-15/TiO₂ nanoreservoirs, platinum molecules interact with the sodium bicarbonate to form complex carboxyplatinum; they interact with active sites on the surface of TiO₂. Later the trona phase encompasses to the Pt/TiO₂ nanomaterials. Therefore, platinum(II) particles are between the surface of the TiO₂ and the trona phase surface. The presence of platinum in form of complexes and the sodium bicarbonate solution increases the average particle size of the Pt-0.1-NaHCO₃-15/TiO₂ and the NaHCO₃-15/TiO₂ nanomaterials to 130 nm and the Pt-0.1/TiO₂ material to 50 nm.

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