XRD, DRS and SEM studies of the effects of metal dopants (Pt and Au) on the structural and optical properties of TiO$_2$

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Abstract. Au and Pt doped TiO$_2$ nanocrystals were prepared using the sol gel method. Diffuse Reflectance Spectroscopy (DRS) was used to study the characteristics of these precious metals and X-ray diffraction (XRD) with calculated lattice parameters was used to study the location of these precious metal dopants in nanocrystalline TiO$_2$. The effects of these dopants on the phase transformation and grain growth were observed. Electron Microscopy was used to study the morphology. The results of the lattice parameter calculations from the XRD patterns of metal loaded TiO$_2$ are almost the same as for the undoped.

1. Introduction

Titania is a cheap and nontoxic polymorphic material of current interest for a variety of technological applications like in gas sensing[1] and photovoltaic cells[2]. Generally, TiO$_2$, with a band gap of 3.2 eV, can only be excited by a small UV fraction of solar light, which accounts for only 3-5% of the solar energy. Various strategies have been pursued including doping with metallic elements (e.g. Fe) [3] or nonmetallic elements (e.g. N) [4] with the aim of shifting the absorption into the visible range. Their potential applications depend strongly on their crystalline structure, morphology and particle size [5]. The main polymorphs of titania are rutile and anatase. It is now well established that anatase phase transforms into rutile at high temperatures [6]. Although many attempts have been made to control the process of phase transformation in titania, the transformation occurs over a range of temperatures due to the complexity of the crystal growth during the sample calcining process. In the present contribution, Pt and Au were loaded in TiO$_2$ to study their effects on the structural and optical properties.

2. Experiments

Appropriate amounts of HAuCl$_4$.3H$_2$O and PtCl$_4$ solutions were added to titanium iso-propoxide solution and stirred for 60 minutes on the magnetic stirrer. Then, appropriate amount of water was added, the precipitates filtered and dried overnight at room temperature. The solid was then dried at 80 °C, ground and portions calcined at 300 °C, 600 °C and 900 °C. Samples were prepared to give 5wt% dopants.

X-ray powder diffraction patterns of the samples were recorded using a conventional laboratory diffractometer, a Phillips PW1720, using a Cu K$_\alpha$ tube operating at 35 KV and 20mA. The average
grain size of the samples, L, was determined by the broadening of peaks on the XRPD pattern, using the scherrer equation.

The SEM measurements were captured from the JEOL-JSM 7500F Field Emission Scanning Electron Microscope.

DRS measurement in the spectral range of 200-800nm were recorded at room temperature using a Varian Cary 300 spectrometer equipped with a standard diffuse reflector unit.

3. Results and Discussions

3.1. XRD

The structure of all the metal loaded TiO$_2$ samples that were synthesized by standard sol-gel methods appeared to be of anatase phase. Post-synthesis calcination at various temperatures resulted in the sharpness of peaks which clearly indicates the improvement in the degree of crystallinity corresponding to the formation of larger particles. The anatase to rutile (A –R) transformation of pure TiO$_2$ normally occur around 700 °C [6]. In the case of samples doped with some metals, the phase transformation temperature is altered. In figure 1 we show XRD patterns for Pt-TiO$_2$. It is clearly seen that the A-R phase transformation reduces significantly since at 600 °C, the phase transformation had already completely occurred. Au-TiO$_2$ behaves in a similar manner as the undoped sample.

![Figure 1. XRPD spectra of 5% Pt-doped TiO$_2$ annealed at 600 °C (bottom) and 900 °C.](image)

Obvious diffraction peaks associated with metal ion dopants were observed indicating that they have not been fully integrated into the basic structure of TiO$_2$. The lattice parameters of metal loaded TiO$_2$ tabulated in table 1 were determined using the X-ray diffraction peaks of crystal planes [101] at 2θ=25° and [200] at 2θ=48° for anatase and also [101] at 2θ=36° and [200] at 2θ=39° for rutile.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination temperature</th>
<th>Crystal Phase</th>
<th>Lattice parameters (Å)</th>
<th>Unit cell Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (5% Au)</td>
<td>600°C</td>
<td>Anatase [5]</td>
<td>a = 3.76, b = 3.76, c = 9.535</td>
<td>134.80</td>
</tr>
<tr>
<td>TiO$_2$ (5% Au)</td>
<td>900°C</td>
<td>Rutile [5]</td>
<td>a = 4.60, b = 4.60, c = 2.962</td>
<td>62.67</td>
</tr>
</tbody>
</table>

The lattice parameters of pure and doped TiO$_2$ are almost the same indicating that the metal dopants are merely placed on the surface of the TiO$_2$. 
3.2. DRS
The spectrum of undoped TiO$_2$ (not shown) consists of a single intense absorption below approximately 400nm and this is usually ascribed to a charge-transfer process from the valence band to the conduction band. Beyond 400nm it is almost totally reflective indicating that it cannot absorb the visible region of the spectrum. To shift the absorption capability, it is normally doped with some metallic dopants[3,4]. In the present work Pt and Au were used as dopants. In figure 2, we show DRS spectra of Au and Pt doped TiO$_2$ both at 600 and 900 °C. The spectrum of Au doped sample at 600 °C is typical of an anatase structure whereas the one at 900 °C is associated with the rutile phase. For Pt doped sample, both spectra (i.e. at 600 and 900 °C) follow a similar trend and are associated with the rutile structure. The results are consistent with the XRD.

![Figure 2. DRS spectra of Au and Pt-TiO$_2$ both at 600 °C and 900 °C.](image)

The DRS spectra of the metal loaded TiO$_2$ reveal substantial reduction in reflection (i.e. they show enhanced absorption) from 400nm to the entire visible region. The observed enhanced absorption in metal doped systems could be due to the generation of new energy levels resulting from the injection of impurities (i.e. metal clusters) within the band gap and or the generation of oxygen vacancies.

3.3. SEM
In figs. 3(a) and (b) we show the typical SEM images of Pt-TiO$_2$ samples at 300 °C and 900 °C. The images clearly show that the morphologies of two samples differ significantly.

![Figure 3. SEM images of Pt-TiO$_2$ samples at (a) 300 °C and (b) 900 °C.](image)

The lower temperature Pt–TiO$_2$ composites revealed a relatively compact surface morphology with low porosity. Annealing of the TiO$_2$ sample at 900 °C produced more homogeneous spherical particles, which aggregated to form bigger particles. Similar results were obtained for Au loaded TiO$_2$. In general, the characteristic particle sizes become larger at higher calcination temperatures with a corresponding decrease in surface area. The elemental composition of the metal loaded samples was estimated by EDS. The EDS spectra (not shown) showed signals associated with metals.
4. Conclusions
From the XRD results, we calculated the lattice parameters of the metal loaded samples and found that they are almost similar to the undoped sample. The EDS spectra also showed signals associated with metals. We can therefore conclude that the metals have not entered into the lattice but are merely placed on the surface of the crystal. Platinum significantly affects the anatase to rutile transformation temperature whereas the presence of gold does not affect the phase transformation temperature and the results are corroborated by DRS.

5. Acknowledgements
RJM would like to acknowledge the financial support of NRF and Tom Malwela of CSIR Centre for Nanostructured Materials for helping with the SEM measurements.

6. References