

XRD, DRS and SEM studies of the effects of metal dopants (Pt and Au) on the structural and optical properties of TiO₂

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Abstract. Au and Pt doped TiO₂ 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 TiO₂. 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 TiO₂ 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 gas sensing [1] and photovoltaic cells [2]. Generally, TiO₂, 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 incorporated into TiO₂ to study their effects on the structural and optical properties.

2. Experiments

Appropriate amounts of HAuCl₄·3H₂O and PtCl₄ 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 5 wt% dopants.

X-ray powder diffraction patterns of the samples were recorded using a conventional laboratory diffractometer, a Phillips PW1720, using a Cu K_α tube operating at 35 KV and 20 mA. The average

grain size of the samples, L , was determined by the broadening of peaks on the XRPD pattern, using the Scherrer equation.

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

DRS measurements in the spectral range of 200-800 nm 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 incorporated 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.

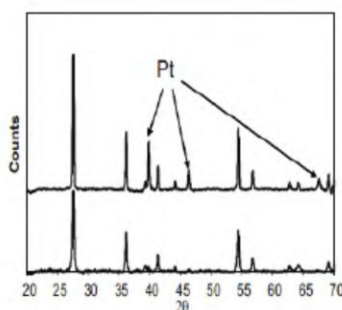


Figure 1. XRPD spectra of 5% Pt-doped TiO_2 annealed at 600 °C (bottom) and 900 °C (top).

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 $2\theta=25^\circ$ and [200] at $2\theta=48^\circ$ for anatase and also [101] at $2\theta=36^\circ$ and [200] at $2\theta=39^\circ$ for rutile.

Table1. Lattice parameters of pure and metal loaded TiO_2

Sample	Calcination temperature	Crystal Phase	Lattice parameters			
			a (Å)	b (Å)	c (Å)	Unit cell Volume (Å ³)
Undoped TiO_2	Untreated	Anatase ^[9]	3.788	3.788	9.53	136.76
		Rutile ^[8]	4.594	4.594	2.959	62.45
TiO_2 (5% Au)	600 °C	Anatase	3.76	3.76	9.535	134.80
TiO_2 (5% Pt)		Rutile	4.62	4.62	2.936	62.66
TiO_2 (5% Au)	900 °C	Rutile	4.60	4.60	2.962	62.67
TiO_2 (5% Pt)		Rutile	4.62	4.62	2.936	62.66

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 TiO₂ (not shown) consists of a single intense absorption below approximately 400 nm and this is usually ascribed to a charge-transfer process from the valence band to the conduction band. Beyond 400 nm 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 TiO₂ both at 600 °C 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 [9]. 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.

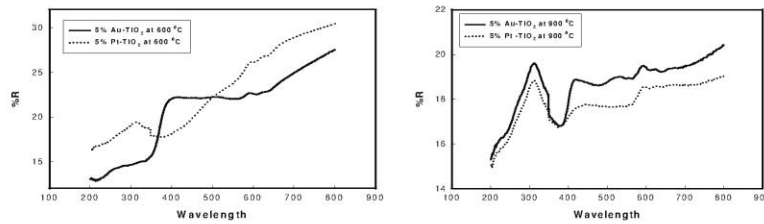


Figure 2. DRS spectra of Au and Pt-TiO₂ both at 600 °C and 900 °C.

The DRS spectra of the metal loaded TiO₂ reveal substantial reduction in reflection (i.e. they show enhanced absorption) from 400 nm 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-TiO₂ samples at 300 °C and 900 °C. The images clearly show that the morphologies of two samples differ significantly.

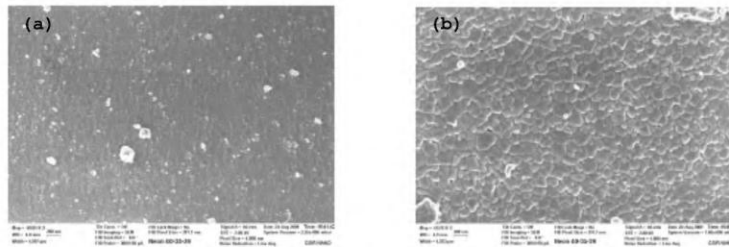


Figure 3. SEM images of Pt-TiO₂ samples at (a) 300 °C and (b) 900 °C.

The lower temperature Pt-TiO₂ composites revealed a relatively compact surface morphology with low porosity. Annealing of the TiO₂ sample at 900 °C produced more homogeneous spherical particles, which aggregated to form bigger particles. Similar results were obtained for Au loaded TiO₂. 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 Au and Pt 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 Au and Pt 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

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6. References

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