

Synthesis and Characterisation of Ag- Cu-Doped Nano TiO₂

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Abstract. TiO₂ nanopowders, single and double doped with Ag and Cu, were prepared using the sol-gel method, with titanium isopropoxide as the precursor. For comparison, an undoped sample was also prepared. The synthesised samples were calcined to a temperature of 300°C and characterised by X-ray diffraction (XRD), Raman and scanning electron microscopy (SEM) techniques. The single-doped powders (as well as the undoped sample) featured only the anatase phase. The co-doped powder was found to be constituted by anatase and brookite phases. The results suggest that multiple doping of titania may favour a two-phase structure at lower temperatures than single doped powders.

1. Introduction

Nanomaterials, in general, are receiving a wide attention because of their unique physical and chemical properties. Nanosized titanium dioxide (Titania, TiO₂), in particular, is of special interest in scientific research and technological applications. Thus, extensive studies of the electric, magnetic, catalytic and electrochemical properties of TiO₂ have been conducted^[1-4]. Its high surface area contributes to its optical properties and is a key factor in its photocatalytic capability^[5].

TiO₂ is known to exist in three major natural crystalline polymorphs or phases namely, rutile (R), anatase (A) and brookite (B), of which anatase and brookite are metastable states – at all temperatures – that transform to rutile upon heat treatment. Brookite is rarely studied as it is difficult to synthesise^[5]. Other phases that are of little significance in research and technological applications have been reported in literature^[6].

In general, the various methods used in synthesising crystalline TiO₂ primarily yield the anatase phase^[7]. The structure of the resulting nanoparticles is closely related to the preparation method. The sol-gel technique, being simple and of low equipment requirement, is often used to synthesise amorphous oxide of titanium which is subsequently transformed into crystalline anatase by heat treatment^[8].

It is of significant interest to understand the conditions that affect the transition from one phase to another; particularly for high-temperature applications, in which phase transformation may affect the properties and performance of devices. The efficiency of nanosized TiO₂ in applications is greatly influenced by electronic modification techniques such as doping^[9]. Several studies have recently investigated the effect of doping TiO₂ with metal impurities by chemical synthesis.^[9] Factors that are influenced by doping include dopant concentration, distribution and the d-electronic configuration, as well as the crystallite size of TiO₂.^[10] It has been noted that the simultaneous introduction of two or more atoms into TiO₂ structures, as well as the mixture of phases, can significantly improve photocatalytic activity and other peculiar characteristics^[11-14] over single element doping.

This study is aimed at examining the effect of metal double-doping on the structural properties of TiO₂ nanopowders, synthesized by the sol-gel method. The structural properties are investigated using x-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) techniques.

2. Experimental

2.1. Synthesis (Sample Preparation)

Three doped TiO₂ samples were prepared, namely Ag-doped, Cu-doped and Ag and Cu co-doped. A fourth sample (Pure-TiO₂) that excluded any doping was also synthesised. The dopant levels were 5% by weight each. Analytical reagent grade chemicals and the sol-gel technique were used in the preparation of samples. Tetraisopropyl Orthotitanate (Titanium (IV) Isopropoxide or Ti{OCH(CH₃)₂}₄) was used as a precursor of TiO₂, Silver Nitrate (AgNO₃) for Ag and Cupric chloride (Copper(II) Chloride or CuCl₂) for Cu. The dopants were prepared by first dissolving the solids in water. 10 ml of ethanol was then added to the required amount of each precursor. For the doped samples the dopant solution was added dropwise to the Titanium Isopropoxide, with vigorous stirring for up to 1 hour. The precipitate (xerogel) was further diluted with 30 ml water, filtered and left to dry at room temperature for 16 hours. Calcination of the samples was done at 300°C for 1 hour before being ground to powders.

2.2. Characterisation

Powder diffractogram (XRD) data were obtained with Xpert-Pro diffractometer using Cu K α radiation (1.5406 Å). Crystallite sizes, $D_{(hkl)}$, were estimated with the Debye-Scherrer equation:

$$D_{(hkl)} = \frac{0.9\lambda}{\beta_{(hkl)} \cos \theta}$$

For quantitative analyses of the samples, the most intense peaks of the individual phases, (101) and (200) for anatase and (110) and (211) for rutile, were considered^[12]. Lattice parameters were calculated from Bragg's law, $2d_{(hkl)} \sin \theta = n\lambda$, and the formula for the crystal system:

$$\frac{1}{d_{(hkl)}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2},$$

in which anatase and rutile systems are tetragonal ($a = b \neq c$) while the brookite is an orthorhombic system ($a \neq b \neq c$).

The phase content (mass fraction f_x) of each sample was determined from the integrated intensities I_A , I_R and I_B of the respective peaks of anatase (101), rutile (110) and brookite (121) as^[15]:

$$f_A = \frac{k_A I_A}{k_A I_A + I_R + k_B I_B}$$

$$f_R = \frac{I_R}{k_A I_A + I_R + k_B I_B}$$

$$f_B = \frac{k_B I_B}{k_A I_A + I_R + k_B I_B},$$

where the coefficients I_R and I_B assume the values 0.886 and 2.721.

Raman spectra from 50 to 1200 cm⁻¹ were recorded by a spectrometer equipped with a He-Ne laser source and a charge-coupled device (CCD) detector. Micrographs of the samples were obtained with a scanning electron microscope (SEM).

3. Results and discussion

3.1. XRD

Figure 1 displays XRD patterns of the four samples – undoped Pure-TiO₂, Ag-doped TiO₂, Cu-doped TiO₂ and Ag/Cu co-doped TiO₂. All samples were heat treated at 300°C for 1 hour. Single-doped samples display the same anatase patterns as the Pure-TiO₂ but with reduced intensities. The Ag-doped sample shows stronger attenuation than the Cu-doped. However, the double-doped powder exhibits the brookite phase, in addition to the anatase. The unit cell parameters (Table 1) suggest that the TiO₂ lattice is not deformed by doping. Further, the crystallite sizes of doped powders are smaller than that of the “Pure” sample.

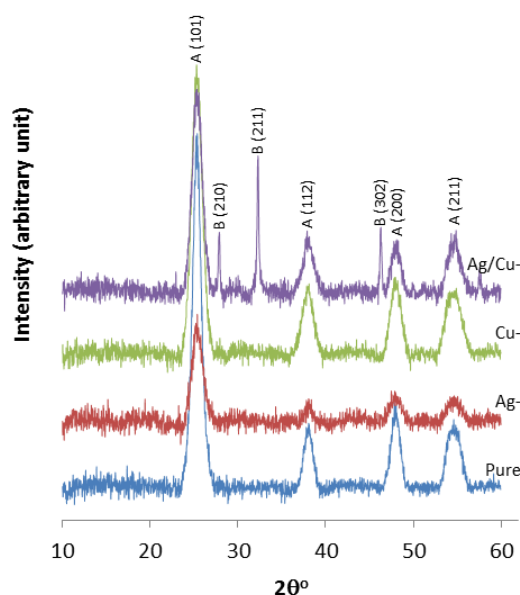


Figure 1. XRD patterns of undoped (Pure), Ag-doped, Cu-doped and Ag/Cu co-doped TiO₂, calcined at 300°C.

Table 1. Crystallite size and lattice parameters of undoped, single-doped and co-doped TiO₂, calcined at 300°C.

Sample	Phase	Crystallite size (nm)	Lattice Parameters (Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
Pure	A	8.39	3.80	3.80	9.10
Ag-doped	A	7.02	3.83	3.83	8.77
Cu-doped	A	6.54	3.79	3.79	9.44
Ag/Cu-doped	A	6.93	3.80	3.80	9.11

3.2. Raman

The Raman shifts for the four powders are shown in Figure 2(a). Characteristic bands for anatase (153, 399, 519 and 639 cm⁻¹ [16]) are presented for all samples. In Figure 2(b), the brookite phase that was revealed by the XRD results for the co-doped sample (Ag/Cu-doped) is confirmed by the Raman peaks (identified with vertical dotted lines).

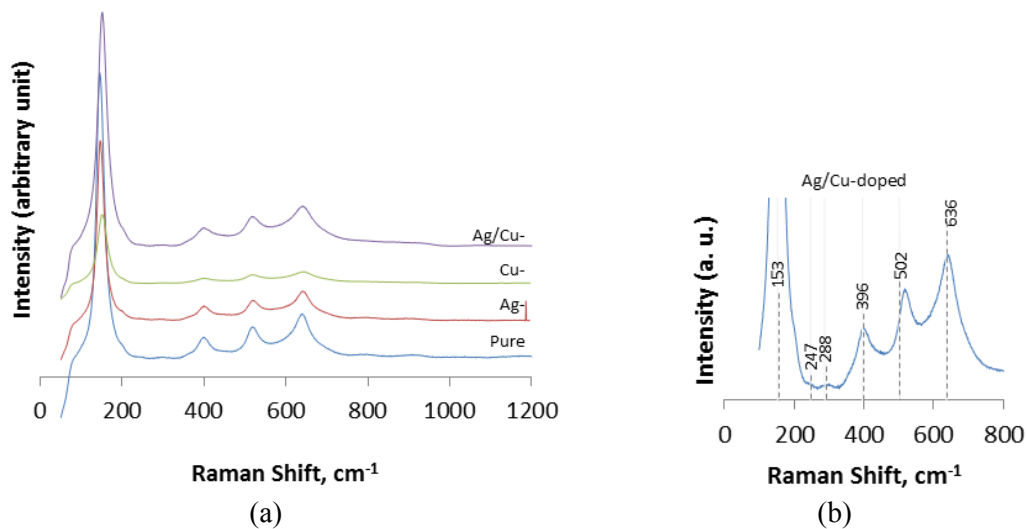


Figure 2. (a) Raman spectra of undoped (Pure), Ag-doped, Cu-doped and Ag/Cu co-doped TiO₂, calcined at 300°C. (b) Brookite peaks in the Raman spectra of the Ag/Cu co-doped TiO₂.

3.3. SEM

The morphology of the samples is displayed in the SEM micrographs of Figure 3. The undoped sample displays spherical shapes, while the images of the doped powders feature irregularly-shaped, aggregated particles. Intra-particle pores are indicated by the pores within the aggregates, while the voids between the aggregates themselves are the inter-particle pores^[17].

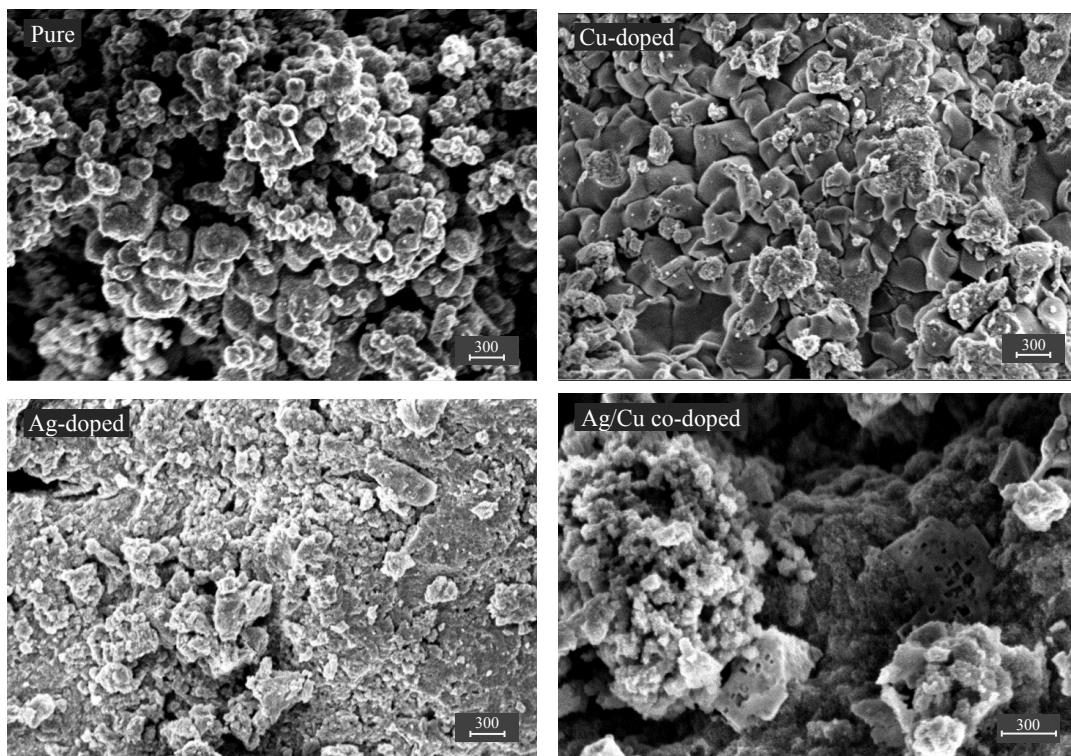


Figure 3. SEM micrographs of undoped, single-doped and co-doped TiO₂ samples. The scales are in nm.

4. Conclusions

The crystallisation of the brookite phase of titania was achieved at low temperatures ($< 300^{\circ}\text{C}$) through the introduction of multiple dopants into the TiO_2 structure. In contrast to single doping, co-doping of TiO_2 favoured a two-phased (anatase and brookite) structure without high temperature heat treatment. Single-doped samples display the same anatase patterns as the Pure- TiO_2 but with reduced intensities which results from the reduced particle sizes. The results suggest that the Ag dopant particles reside on the surface of the TiO_2 nanocrystals while Cu is incorporated into the titania matrix.

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