



SHORT COMMUNICATION

Characterization of TiO₂-ZrO₂ Nanocomposite Prepared by Co-precipitation Method

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ABSTRACT

TiO₂, ZrO₂ nanoparticles and TiO₂/ZrO₂ nanocomposite were prepared by co-precipitation method. The structure and physicochemical properties of samples were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and UV-vis absorption spectrophotometer. The results show that TiO₂/ZrO₂ nanocomposites are mainly composed of rutile and tetragonal ZrO₂. The photocatalytic reactions confirm that the nanocomposite sample shows better photocatalytic activity than ZrO₂ and TiO₂ samples. The diffuse reflectance UV-vis Spectra of the binary oxides have been shifted to shorter wavelengths with increasing ZrO₂ molar ratio. This study represents example of an attempt to prepare a new potential photoactive mixed oxide system, containing two ions (Ti⁴⁺ and Zr⁴⁺) with good photocatalytic activity in comparison with commercial TiO₂ calcined at 450°C

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1. Introduction

Widely used dyes in industries often create severe environmental pollutions in the form of colored wastewater discharged into environmental water bodies. TiO₂ has been advantageous in photo-degradation of pollutants in both water and air so it has been widely used as an effective photocatalyst for the photo-degradation of organic pollutants in various fields of applications because of its relative high activity, stability, low cost, and no toxicity. However, owing to its wide band-gap energy (3.2 eV for anatase and 3.02 eV for rutile TiO₂), the photocatalytic activation of TiO₂ is restricted to the UV light region; researchers have paid special

attention to discovering a method that can shift the activation of the TiO₂ photocatalyst into the visible light region [1].

The disadvantages of TiO₂ nanoparticles restrict their further applications. TiO₂ with larger surface areas could not be easily obtained at higher temperature because of the phase transformation and crystallite growth. It is well known that the insulator can be the carrier when it composes semiconductor. The composite materials often exhibit enhanced mechanical and thermal properties than the two participating components. After the composition of TiO₂ and some carriers, TiO₂ could maintain the anatase phase and obtain larger pore size [2]. Furthermore, the photocatalytic activity of TiO₂ can be improved. Many researchers have reported that higher photocatalytic activity of TiO₂ composites

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could be found in comparison with pure TiO₂. The ZrO₂/TiO₂ composite has been widely used as a photocatalyst [3, 4]. we investigated the preparation of TiO₂/ZrO₂ by co-precipitation and its photocatalytic activity under the irradiation of UV light. The structural (pore size), optical properties (band gap) and photocatalytic activity of the samples have been studied. The morphological and structural properties of these binary TiO₂/ZrO₂ oxides after calcinations at elevated temperatures were investigated and compared with pure titania and zirconia.

2. Experimental Procedure

Titanium (IV) isopropoxide (TTIP), zirconium oxychloride salt (ZrOCl₂·8H₂O), NH₃OH and Properanol (2M) were purchased from MERCK manufacturer. Ethanol (98%) and distilled water were obtained from local sources.

2.1. Co-precipitation Method

The Zirconia and titania precursor solutions were prepared separately; the TTIP and ZrOCl₂·8H₂O were used as titanium and zirconium precursors of synthesizing TiO₂-ZrO₂ mixed oxide. The zirconium precursor solution was obtained by dissolving ZrOCl₂·H₂O in ethanol afterward a 2M NH₃OH aqueous solution was added to the previous solution; the mixture was stirred for 15min and finally calcined at 450°C for 2 h. The titanium precursor solution was obtained by mixing TTIP, HCl, Properanol (2M) and distilled water together; the mixture was stirred for 2h and calcined at 450°C for 2 h.

In order to obtain TiO₂-ZrO₂ nanocomposite, ZrO₂ produced by previous solution was added in TiO₂ solution in which the ZrO₂ to TiO₂ molar ratio was adjusted to a value of 1:1, finally calcined at 450°C for 2 h in the furnace.

2.2. Characterization

The X-Ray Diffraction (XRD) patterns obtained on an X-ray diffractometer (type D-64295) using Cu K_α radiation were used to characterize the crystalline phase and crystallite size of the TiO₂ powders. The nanoparticle size and morphology of structures were characterized by scanning electron microscopy (SEM; LEO-1450VP).

The absorbance spectra of the photocatalysts were obtained using a UV-visible spectrophotometer (AvaSpec-2048Tec) at room temperature. The absorption onset wavelength (λ_{gs} , nm) is the crossing

point between the line extrapolated from the onset of the rising part of the absorbance spectra and x-axis of the plot. The band gap energy (E_g) of the photocatalysts was then estimated using the following equation [5]:

$$E_g = \frac{1243.1}{\lambda_g} \quad (1)$$

3. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of the TiO₂, ZrO₂ and TiO₂/ZrO₂ powder. In figure 1a all the peaks in the XRD pattern showed there are mixed anatase and rutile in the tested sample.

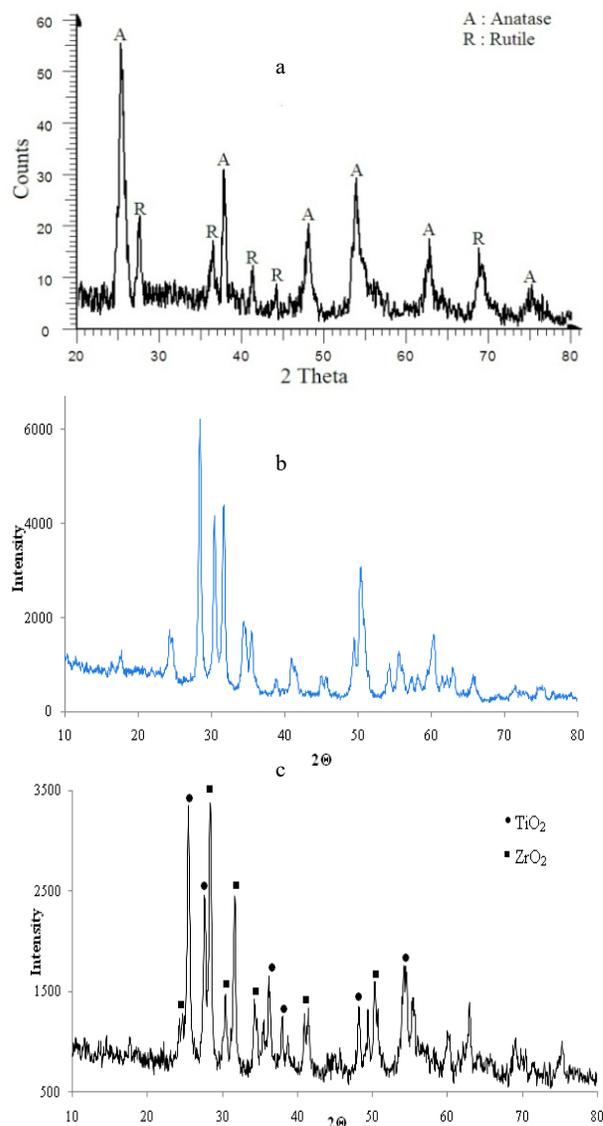


Fig. 1: XRD patterns of, a) TiO₂, b) ZrO₂ and c) TiO₂/ZrO₂.

Using the Scherrer equation, the average crystalline size is estimated to be 19nm and 21nm for anatase and rutile, respectively. The crystalline phase is determined by integrating intensities of the anatase (101) peak ($2\theta=25.4^\circ$) and the rutile (110) peak ($2\theta=27.5^\circ$). The weight fraction of rutile (W_R) is calculated from the following equation [6].

$$W_R = \frac{A_R}{0.88A_A + A_R} \quad (2)$$

Where A_A represents the integrated intensity of the anatase (101) peak and A_R represents the integrated intensity of the rutile (110) peak. From Eq 2, the fraction of the rutile in our samples is 0.32.

Figure 1b shows the XRD pattern of the ZrO_2 . The average crystalline size is estimated to be 19nm. XRD pattern of composite in Figure 1c shows the existence of TiO_2 and ZrO_2 , annealed at $450^\circ C$. Although the ZrO_2 is incorporated up to 50 mol%, the crystalline structure of the mixed oxides is still the anatase TiO_2 . TiO_2 exists in an anatase phase in the binary oxide catalysts. No phases associated with pure zirconia are observed; only tetragonal titania anatase is detected after $450^\circ C$ calcination. It implies that some titanium atoms are substitutes for zirconium in the anatase structure due to increase the transition temperature of anatase to rutile.

Scanning electron microscopy (SEM) images of TiO_2 , ZrO_2 and TiO_2/ZrO_2 powder are shown in Figure 2. Images show spherical morphology of the particles with agglomerate state and the size range of 20-30nm. The results suggest that the ZrO_2 incorporation tends to cause a decrease in particles size. In addition, a further increase in amount of zirconia increases the particles size [4]. The UV-visible absorption spectra of the TiO_2 , ZrO_2 and TiO_2/ZrO_2 powders are shown in Figure 3. as shown, The E_g value can be obtained by extrapolating the linear portion to the photon energy axis. It can be seen that the TiO_2 has an absorption edge around 410 nm corresponding to the band gap of 3.02 eV. It is seen that ZrO_2 has a band gap of 5.17 eV corresponding to 240 nm. The Optical transmittance of TiO_2/ZrO_2 is also shown in Figure 3 (curve-b). Its absorption edge is around 325 nm corresponding to the band gap of 3.81 nm. Therefore, the results show that the band gap energy increases with loading ZrO_2 on TiO_2 ; that is, it increases from 3.02 eV for the pure TiO_2 to 3.81 eV for the TiO_2-ZrO_2 mixed oxide. The

blue shift of onset edge of the absorption band to a lower wavelength in the TiO_2-ZrO_2 mixed oxide agrees well with the well-known quantum size effect for smaller crystallites.

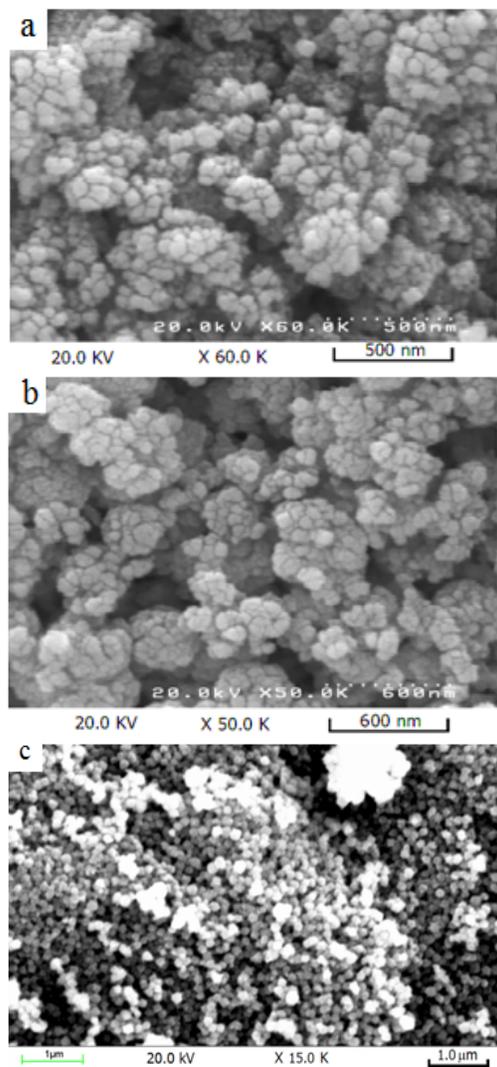


Fig. 2: SEM images of, a) TiO_2 , b) ZrO_2 and c) TiO_2/ZrO_2 .

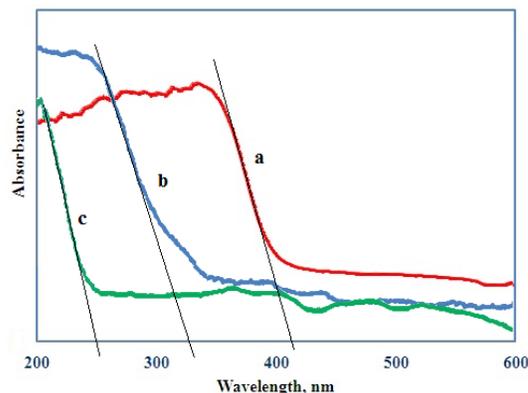


Fig. 3: a) TiO_2 , b) TiO_2/ZrO_2 and c) ZrO_2 .

4. Conclusions

In this study, nanopowder of TiO₂, ZrO₂ and TiO₂/ZrO₂ were produced by precipitation methods. Structures were studied by XRD and SEM. The optical band gap of sample was detected by the UV-vis spectra. Not only, The incorporation of ZrO₂ phase could effectively improve the structure stability of the TiO₂, but also could inhibit its anatase-to-rutile phase transformation during the calcination in 750°C. The presence of ZrO₂ led the values of the band gaps to become slightly larger than those of the pure TiO₂ (a slight blue shift).

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