Characterization of TiO_2-ZrO_2 nanocomposite prepared by co-precipitation method

Hassan Koohestani[a, *], Mona Alinezhad[a], Seyyed Khatiboleslam Sadrnezhaad[a, 1]

[a]Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

[*]hasan.81m@gmail.com, [1]sadrnezh@sharif.edu

Abstract

TiO_2, ZrO_2 nanoparticles and TiO_2/ZrO_2 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), UV-vis absorption Spectroscopy. The results show that TiO_2/ZrO_2 nanocomposites are composed of mainly titania and tetragonal ZrO_2. The photocatalytic reactions confirmed that the nanocomposite sample showed higher photocatalytic activity than ZrO_2 and TiO_2 samples for the degradation aqueous methyl orange (MeO) under UV light.The diffuse reflectance UV-vis Spectra of the binary oxides are shift to the shorter wavelength with increasing ZrO_2 molar ratio. This study represents example of attempt to prepare a new potential photoactive mixed oxide system, containing two ions (Ti^{4+} and Zr^{4+}) with good photcatalytic activity if it is compared with commercial TiO_2 calcined at 450°C.

Keywords: TiO_2, nanocomposite, photochemical, ZrO_2.

Introduction

Dyes widely used in industries often create severe environmental pollutions in the form of colored wastewater discharged into environmental water bodies. TiO_2 has been to be advantageous in photodegradation of pollutants in both water and air so it is widely used as an effective photocatalyst for the photodegradation 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 (3.2eV for anatase and 3.02eV for rutile TiO_2), the photocatalytic activation of TiO_2 is restricted to the UV light region, researchers have focused attention on discovering a method that can shift the activation of the TiO2 photocatalyst to the visible light region [1].

The disadvantages of TiO_2 nanoparticles restrict its further applications TiO_2 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 with semiconductor. The composite materials often exhibit enhanced mechanical and thermal properties than the two participating components. After the composition of TiO_2 and some carriers, TiO_2 could maintain the anatase phase and obtain larger pore size [2]. Furthermore, the photocatalytic activity of TiO_2 can be improved. Many researchers have reported that higher photocatalytic activity of TiO_2 composites could be found in comparison with pure TiO_2. The ZrO_2/TiO_2 composite has been widely used as a photocatalyst [3,4]. On the basis of we investigated the preparation of TiO_2/ZrO_2 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 TiO_2/ZrO_2 oxides after calcinations at elevated temperatures were investigated and compared with the properties of pure titania and zirconia.

Experimental

Titanium (IV) isopropoxide (TTIP), zirconium oxychloride salt ($ZrOCl_2.8H_2O$), ethanol (98%), NH_3OH, Properanol (2M) and distilled water were used as starting chemicals.

*Coprecipitation method.*The Zirconia and titania precursor solutions were prepared separately, the TTIP and $ZrOCl_2.8H_2O$ were used as titanium and zirconium precursor for synthesizing TiO_2-ZrO_2 mixed oxide. The zirconium precursor solution was obtained by dissolving $ZrOCl_2.H_2O$ in ethanol afterward a 2M NH_3OH 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 of 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 TiO_2-ZrO_2 nanocomposite, ZrO_2 produced by previous solution was added in TiO_2 solution in which the ZrO_2 to TiO_2 molar ratio was adjusted to a value of 1:1, finally calcined at 450°C for 2 h in the furnace.

Characterization. The X-ray diffraction (XRD) patterns obtained on an X-ray diffractometer (type D-64295) using Cu K_α radiation used to characterize the crystalline phase and crystallite size of the TiO_2 powders.The nanoparticle size and morphology of structures were characterized by scanning electron microscopy (SEM; LEO-1450VP).

The UV-Vis diffuse reflectance spectroscopy was obtained using a UV-visible spectrophotometer (AvaSpec-2048Tec).

Results and Discussion

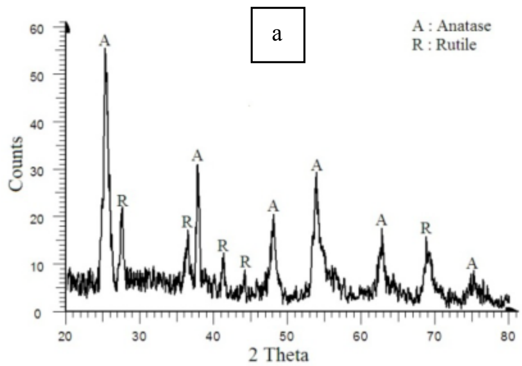
Figure1 shows the X-ray diffraction pattern of the TiO_2, ZrO2 and TiO2/ZrO2 powder. In figure 1a all the peaks in the XRD pattern showed there were mixed anatase and rutile in the tested sample. Using the Scherrer equation, the average crystalline size was estimated to be 21nm and 19nm for anatase and rutile, respectively.

The crystalline phase was determined from integration intensities of the anatase (101) peak (2θ=25.4°) and the rutile (110) peak (2θ=27.5°). the weight fraction of rutile (W_R) can be calculated from the following equation [5].

$$W_R = \frac{A_R}{0.88A_A + A_R} \qquad (1)$$

Where A_A represents the integrated intensity of the anatase (101) peak and A_R represents the integrated intensity of the rutile (110) peak.

Figure 1b shows the XRD pattern of the ZrO_2. The average crystalline size was estimated to be 19nm. XRD pattern of composite in Figure 1c show the existence of TiO_2 and ZrO_2, annealed in 450°C.



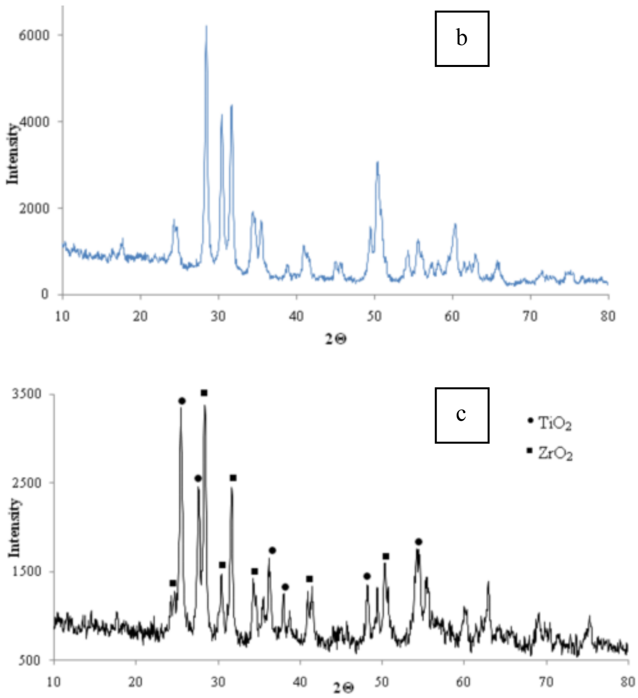


Fig.1: XRD patterns of, a) TiO_2, b) ZrO_2 and c) TiO_2/ZrO_2.

Scanning electron microscopy (SEM) images of TiO_2, ZrO_2 and TiO_2/ZrO_2 powder are shown in Figure 2. Images showed spherical morphology of the particles with agglomerate state and the size range of 20-30nm.

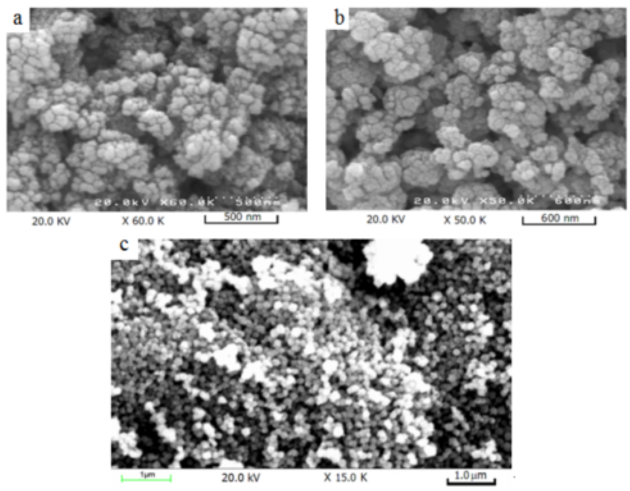


Fig.2: SEM images of, a) TiO_2, b) ZrO_2 and c) TiO_2/ZrO_2.

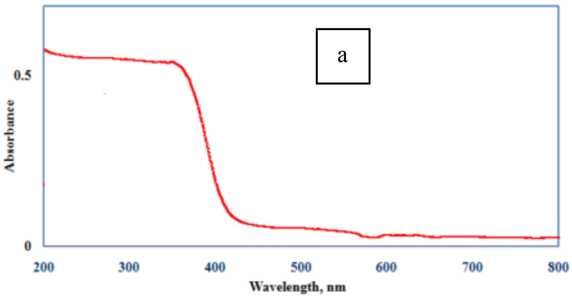
Figure 3a presents the absorbance spectra of the TiO_2, ZrO_2 and TiO_2/ZrO_2 powder. Due to the fundamental absorption in the vicinity of band gap, the transmittance decreases abruptly as the wavelength reaches the UV range. The band gap B_g can be derived from the expression:

$$\alpha h\nu = A(h\nu - B_g)^m \qquad (2)$$

where A is the constant correlating with an ordered crystalline structure in the films, and m=2 for the indirect allowed electronic transition, α is the absorption coefficient obtained by,

$$\alpha = \left[\frac{1}{d}\ln\left(\frac{1}{T}\right)\right] \qquad (3)$$

where d is the film thickness, and T is the transmittance [6]. The B_g value can be obtained by extrapolating the linear portion to the photon energy axis, as shown in Figure 3b.



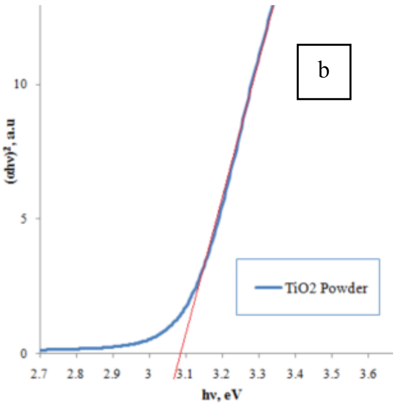


Fig. 3. (a) absorbance spectra and (b) dependence $(\alpha h\nu)^{1/2}$ of on photonenergy for TiO_2.

Conclusions

In this work, nanopowder of TiO_2, ZrO_2 and TiO_2/ZrO_2 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.

References

[1]. M. A. Lazar, S. Varghese, S. S. Nair, " Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates", *Catalysts,* 2 (2012), 572-601.

[2]. J. Y. Kim, C. S. Kim, H. K. Chang, "Synthesis and characterization of N-doped TiO_2/ZrO_2 visible light photocatalysts", *Advanced Powder Technology*, 22 (2011), 443-448.

[3]. J. C. Garcia, L. M. R. Scolfaro, "Structural, electronic, and optical properties of ZrO2 from ab initio calculations", *applied physics*, 100 (2006), 104103.

[4]. A. Burri, N. Jiang, S. E. Park, "High surface area TiO2–ZrO2 prepared by caustic solution treatment, and its catalytic efficiency in the oxidehydrogenation of para-ethyltoluene by CO2", *Catal. Sci. Technol.*,2 (2012), 514-520.

[5]. Y. V. Kolenko, V. D. Maximov, A. V. Garshev, P. E. Meskin, N. N. Oleynikov, "Hydrothermal synthesis of nanocrystalline and mesoporous titania from aqueous complex titanyl oxalate acid solutions", *Chemical Physics Letters*, 388 (2004), 411-415.

[6]. Y. Yang, Q. Zhang, B. Zhang, W. B. Mi, L. Chen, "The influence of metal interlayers on the structural and optical properties of nano-crystalline TiO2 films", *Applied Surface Science*, 258 (2012), 4532-4537.