PHOTOCATALYTIC ACTIVITY OF ZRO2 NANOPARTICLES ON DEGRADATION OF RHODAMINE B

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Abstract

ZrO_2 nanoparticles were synthesized through reactive plasma processing of zirconium hydride. X-ray diffraction (XRD) analysis of the as prepared nanoparticles indicates formation a mixture of nanocrystalline ZrO_2 monoclinic and tetragonal phase structures. Transmission electron microscopy (TEM) images illustrate spherical ZrO_2 nanoparticles with 3–30 nm diameter range. X-ray photoelectron spectroscopy (XPS) analysis confirms formation of ZrO_2 and presence of oxygen vacancies. Photodegradation of Rhodamine B (Rh. B) shows that the prepared sample with lower particle size and higher surface area has higher photocatalytic activity.

Keywords: *nano ZrO_2, photocatalytic activity, plasma processing*

Introduction

ZrO_2 nanoparticles find much interest because of their specific optical and electrical properties and potential applications in transparent and optical devices, sensors, fuel cells, advanced ceramics and photocatalysts [1–5]. Particularly, much attention has been paid towards their photocatalytic properties because of its application in environmental purification and decomposition of toxic and organic compounds. A key requirement for improving the photocatalytic activity is to increase the specific surface area and enhance the crystallinity [4]. These requirements are met by crystalline nanostructured materials. Several methods including hydrothermal [5], sol–gel [6], chemical vapor deposition (CVD) [7] and sputtering [8] have been used to prepare ZrO2 nanoparticles.

In the present work, nano-crystalline ZrO_2 powder was synthesized by oxidizing ZrH_2 powder 'in-flight' in a thermal plasma jet. Reactive plasma processing (RPP) is a novel technique, which takes advantage of the high temperature and high enthalpy of the thermal plasma jet to effect 'in-flight' chemical reactions in the presence of a reactive gas to synthesize nano-sized powders of advanced ceramics, novel coatings and convert minerals and industrial wastes to value-added materials [9]. We have studied the effect of operating parameters on size distribution and the photocatalytic activity of the produced nanoparticles. The major advantages of the RPP technique includes versatility, short processing time, large throughput, adaptability to process thin films and coatings. Also, the process can be customized to synthesize any desired product.

Experimental method

Reactive plasma synthesis of nano-sized ZrO_2 powder

Nano-crystalline powder of ZrO_2 was synthesized by reactive plasma synthesis. ZrH_2 powder, 99.8% pure from CERAC, USA was used as the precursor material. TiH_2 powder (38–53 m size) was injected into the plasma jet using argon as the carrier gas. Oxygen gas was introduced 10mm downstream of the exit of the plasma torch. ZrH_2 dissociates to form Zr particles and hydrogen gas in the plasma jet that are subsequently converted to ZrO_2 and water vapour, which escapes along with the exhaust gas stream. Zirconium oxide formed collects as nano-sized dust on the walls of the reactor, collection chamber rand flanges. The nano-sized powder of ZrO_2 generated by this method is used for photo catalytic experiments. Experimental set up and process details are described elsewhere [10].

Powder Characterization

The zirconia powder samples collected from different locations of the plasma reactor were characterized by X-ray powder diffraction, Raman and FTIR spectra analysis for their phase composition. X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a Bruker D8 advanced X-ray powder diffractometer. Ni- filtered Cu k-α radiation in θ-2θ geometry was used for recording the diffraction patterns. The BET surface area measurement was carried out using a Micromeritics TriStar 3000 at 77 K with N_2 as adsorbate. Particle size and morphology of the samples were carried out using JEOL transmission electron microscope (JEM 2100F, Japan) operated at 200 KV. XPS analysis was taken out by a dual Mg–Al anode X-ray source. A concentric hemispherical analyzer (from Specs company model EA10 plus) was employed to analyze the emitted electrons from the surface. The energy axis was calibrated by adjusting the carbon peaks at 285 eV.

Photocatalytic Characterization

Photocatalytic properties of the zirconia powders were studied by following the degradation of Rh. B dye solution under ultraviolet (UV) radiation. The UV light photocatalytic experiments were carried out in a specially designed photochemical reactor which is equipped with16 numbers of 15W, UV-C, Phillips T-UV lamps, each 41cm long and 2.5 cm diameter. Low-pressure mercury vapor arc lamp was used as the source of ultraviolet radiation. The bulbs are made of special glass that transmits the short-wave ultraviolet radiation emitted from the lamp. The UV lamps were supported in a cylindrical stainless steel cavity with aluminium reflectors, 60 cm long and 32 cm diameter surrounding the lamps. Approximately 95% of the energy radiated from the lamp corresponds to radiation at a wavelength of 253.7nm. The intensity of UV light falling on the quartz cell was 2520 lx, measured by a Luxmeter (LutronLX-105). 25 mg of the synthesized zirconia powder was dispersed in 25 ml Rh. B dye solution of 40 ppm concentration and irradiated with UV light in the photocatalytic reactor while the suspension was kept under stirring. The dye sample was removed at regular intervals of time and then centrifuged to separate ZrO_2 particles for analysis. The degradation of the dye was monitored at different intervals of time using UV–visible spectrophotometer. The UV–visible spectra of the filtered reaction mixture were recorded in the absorption mode using distilled water as reference.

The percentage of residual Rh. B dye solution (R) is given by the relation $R (\%) = C/C_0 \times 100$ where C_0 is the optical density value at irradiation time t = 0, C is the optical density value at various irradiation time t = 20, 40, 80, 100 min, etc. The catalytic activity and characterization studies of the RPP samples (A, B and C) were discussed.

Results and Discussion

XRD analysis

Figure 1 shows the diffraction patterns of samples (synthesized at 16 kW) collected from different locations of the plasma reactor. The diffraction patterns show that the synthesized powder is a mixture of monoclinic and tetragonal phase corresponding to JCPDS files 37-1484 and 79-1771 respectively. The crystallite size is determined using Scherrer's formula and is tabulated (Table 1)

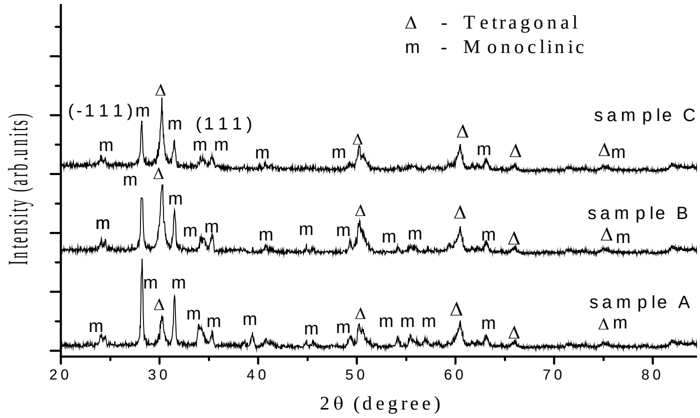

Figure 1 X-ray diffraction patterns of plasma synthesized ZrO_2 powders at 16 KW

The percentage of the tetragonal phase present in the samples was calculated from the following relation [11, 12].

$$X_t = \frac{I_t(111)}{I_t(111) + I_m(111) + I_m(-111)} \times 100 \quad (1a)$$

$$X_m = 100 - X_t \quad (1b)$$

Where X_t and X_m stand for the weight percentage of the tetragonal and monoclinic phases respectively, whereas I_t and I_m are the intensities of their diffraction peaks [11- 15].

Sample	Collection Region	Monoclionic		Tetragonal / Cubic	
		Amount (%)	Size (nm)	Amount (%)	Size (nm)
Sample A	Torch Head	72	34	28	20
Sample B	Reactor	60	30	40	18
Sample C	Flanges of collection chamber	44	25	56	15

Table 1. Phase composition of reactive plasma synthesized nanocrystalline ZrO_2

It is evident from figure 1 that the phase structure of the different samples collected from torch head region (A), the reactor wall (B) and flanges of collection chamber(C) consist of a mixture of the monoclinic phase and the tetragonal phase [13 – 16]. However, the relative amounts of the monoclinic and tetragonal phases were different in the samples as shown in Table 1. It is observed that sample collected from the flanges of the collection chamber has the highest amount of the tetragonal phase. The monoclinic form of ZrO_2 is the major phase in the sample collected from the torch head region (A).

BET Surface Area

The Brunauer–Emmet–Teller (BET) nitrogen adsorption–desorption analysis was undertaken to measure the specific surface area of the samples A, B and C. The samples were out gassed under vacuum at 473 K for 24 h before starting the measurements [16 – 20]. The comparison of the BET surface area obtained for the samples A, B and C are shown Table 2. It is observed from the table that the specific surface area increases from sample A to sample C.

Sample	Region of collection	Monoclinic X_m (%)	Tetragonal X_t (%)	BET surface area (m^2/g)
A	Torch head	80	20	18
B	Reactor	62	38	23
C	Flanges of collection chamber	56	44	34

Table 2 Sample identification, phase composition and BET surface area.

XPS analysis

Figure 2 (a–c) shows the XPS spectrum of sanple C. From XPS spectrum the binding energies of O 1s, Zr 4p, Zr 3d, Zr 3p3/2, Zr 3p½ and Zr 3s for the prepared ZrO_2 nanoparticles are 530.7, 28.5, 181.5, 333, 346.5 and 433.5 eV, respectively. To determine the chemical state we used Auger parameter of Zr (using Zr 3p3/2 peak and Auger peak at 459 eV) which is equal to 2011.2 eV. This value confirms formation of ZrO_2. Also O 1s peak (Fig. 2c) has two parts: main part at 530.7 which reflects ZrO_2 state and another part at 532 eV which is due to C–O bound [17 -20]. The ratio of oxygen to zirconium peaks determines O to Zr ratio about 1.8. The deficiency ratio from 2 is due to oxygen vacancies at the surface of the sample [21 – 25].

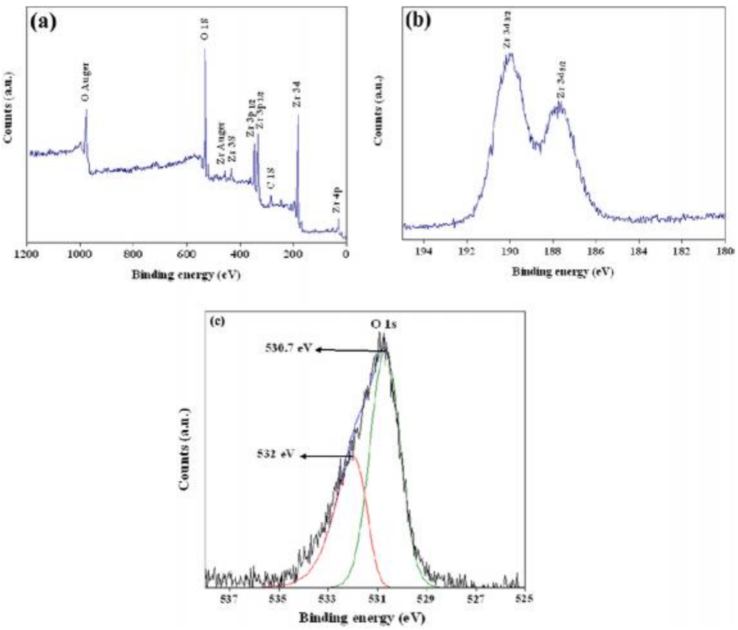

Figure 2. XPS analysis for ZrO_2 nanoparticles at 16 KW (sample C), (a) survey scan, (b) high resolution spectrum of Zr 3d peaks and (c) high resolution spectrum of O 1s peak.

TEM Analysis

Transmission electron microscope (TEM) photographs of reactive plasma synthesized nano ZrO_2 are shown in figure 3(a-c). The corresponding particle size distribution is shown in figure 3 (d-f) as bar charts alongside the TEM micrographs. Individual particles are well resolved and their spherical morphology is evident from the figures. It is seen from particle size distribution more than 90% of the particles are below 25 nm. However, a very small fraction of particles are found to have size below 4 nm and above 30 nm. It was observed that there was significant variation in size distribution of particles collected from different locations [26 – 30]. It is seen from TEM results that powder collected from the torch head zone (A), has maximum number of coarser particles. On the other hand, the powder sample collected from the flanges on the collection chamber (C) has about 75% of the particles in the size below15 nm. It is also observed that the relative amount of the tetragonal phase increases with the amount of finer particles from sample A to sample C.

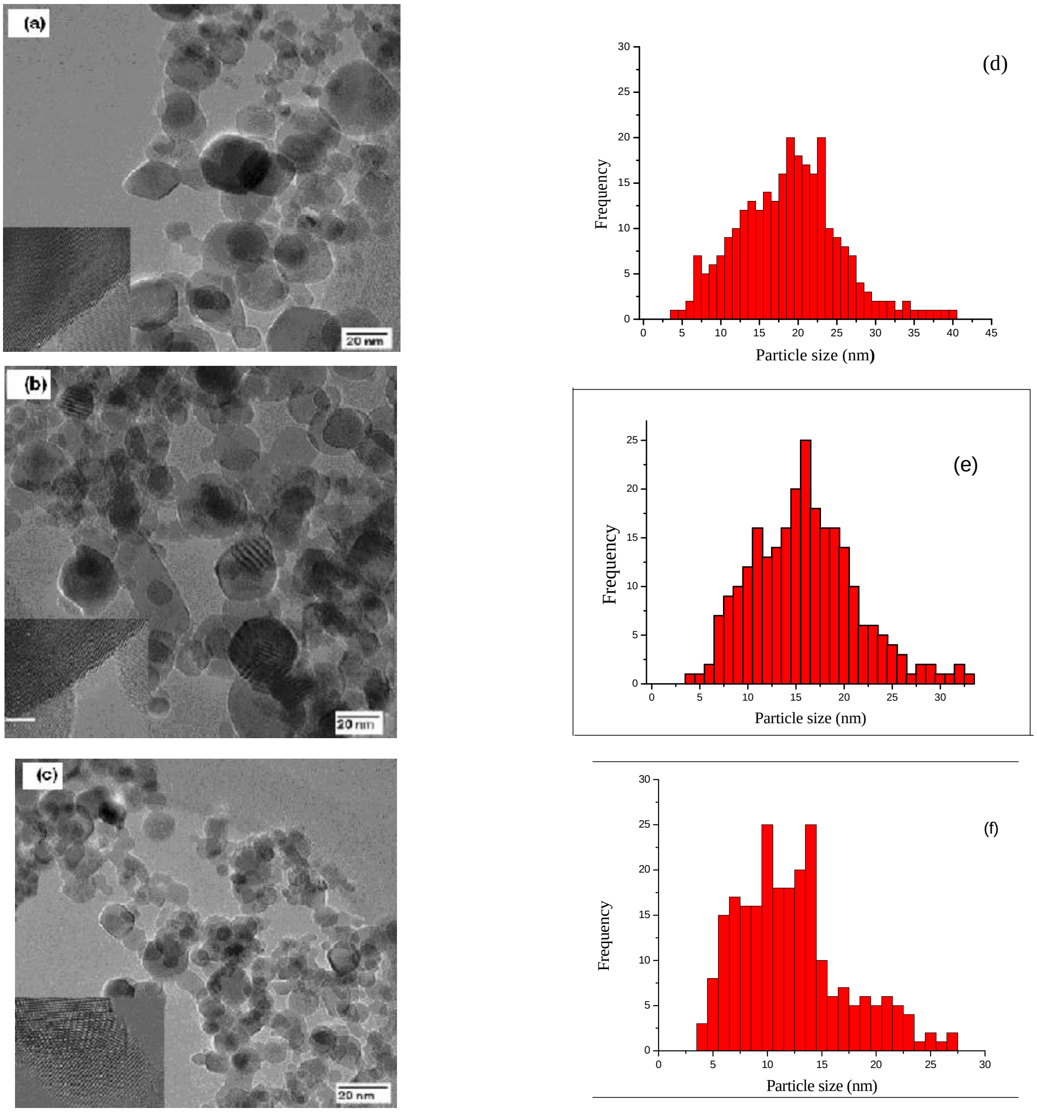

Figure. 3 TEM photographs and particle size distribution of reactive plasma synthesized nanocrystalline ZrO_2: (a) and (d) sample A, (b) and (e) sample B, (c) and (f) sample C

Photocatalytic Activity Measurements

The UV – visible absorption spectrum of 40 PPM Rh. B dye solution with and without ZrO_2 nanoparticles for different UV irradiation times is shown Fig 4. No remarkable changes in the concentration of the Rh. B solution were observed in the absence of ZrO_2 nanoparticles (Fig. 4(a)). For the dye solutions with ZrO_2 nanoparticle the concentration of Rh. B decreases with respect to irradiation time duration. This shows that the decomposition of Rhodamine B only depends on the photo excitation of ZrO_2 nanoparticles [31 – 35]. The kinetics of photocatalytic degradation is found to be fast initially. The concentration vs time curve is linear with a sharp change of slope. Initially, in a short exposure of 20-mintime, the concentration of Rh. B dye solution decreases rapidly and then the rate of degradation is slowed down. This trend was observed in all the cases. The lower rate of decrease in concentration of the dye solution after an initial sharp decrease is possibly due to the fact that the reaction products (CO_2 and water) formed are not removed from the reaction zone. These molecules of CO_2 and H_2O adhere to the surface of the catalyst and slow down the reaction, leading to the observed trend [36 – 40].

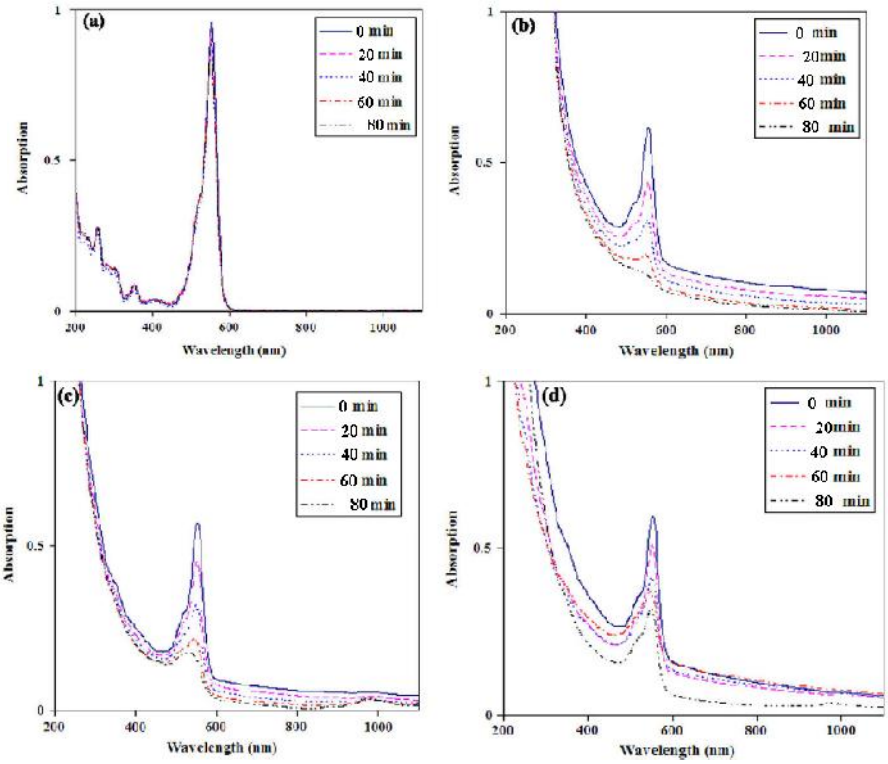

Figure. 4. Photocatalytic activity of ZrO_2 nanoparticles by photodegradation of Rh. B. (a) Rh. B without ZrO2 nanoparticles, (b) sample C, (c) sample B and (d) sample A

Further, the samples are compared with commercial TiO_2 photocatalyst (Degussa P25) in an equal situation. The results showed that our sample C shows near two times more photocatalytic activity than the Degussa P25 [41 – 45].

Conclusion

We have prepared ZrO_2 nanoparticles by reactive plasma processing of ZrH_2 . XRD results showed that the nanocrystalline ZrO_2 is a mixture of monoclinic and tetragonal phase and the particle size varied from 3 – 30 nm. The tetragonal content increased from sample A to C as the fraction of fine particles increased from sample A to C. TEM images revealed spherical morphology of the nanoparticles. Surface chemical composition of the nanoparticles is determined by XPS analysis. Further, the photocatalytic activity of ZrO_2 nanoparticles is demonstrated by UV light irradiation for various irradiation times. The maximum absorption peak and concentration of Rh. B decreases in the presence of ZrO_2 nanoparticles. The sample C showed higher photocatalytic activity due to higher tetragonal content and increased surface to volume ratio.

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