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Photocatalytic activity of ZrO_2 nanoparticles prepared by electrical arc discharge method in water

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ABSTRACT

ZrO_2 nanoparticles were synthesized through arc discharge of zirconium electrodes in deionized (DI) water. 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 7–30 nm diameter range, which were formed during the discharge process with 10 A arc current. The average particle size was found to increase with the increasing arc current. X-ray photoelectron spectroscopy (XPS) analysis confirms formation of ZrO_2 at the surface of the nanoparticles. Surface area of the sample prepared at 10 A arc current, measured by BET analysis, was 44 m^2/g. Photodegradation of Rhodamine B (Rh. B) shows that the prepared samples at lower currents have a higher photocatalytic activity due to larger surface area and smaller particle size.

1. Introduction

ZrO_2 nanoparticles have attracted much interest due to their specific optical and electrical properties and potential applications in transparent and optical devices, sensors, fuel cells, advanced ceramics and photocatalysts [1–4]. Specifically, much attention has been drawn 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 [5]. These requirements are met by crystalline nanostructured materials. Several methods including hydrothermal [6], sol–gel [7], chemical vapor deposition (CVD) [8] and sputtering [9] have been used to prepare ZrO_2 nanoparticles. For efficient photocatalytic activity, nanomaterials need to be crystalline, that is, should be grown at high temperatures or at very slow rates. In general, synthesis of ZrO_2 usually results in amorphous structures but, electrical arc discharge in water has the advantage in this regard as it produces self-crystallized nanoparticles due to high temperature caused by joule heating. Moreover, compared with other techniques, electrical arc discharge in water is an attractive method because of simplicity of experimental set up, lack of need for complicated equipments, low impurity, less production steps leading to a high-throughput and cost-effective procedure to generate a high yield of nanoparticles. Also the simplicity of this method allows scaling up for mass production.

The early works by arc discharge method in liquids were based on production of carbonaceous nanostructures such as MWCNTs [10–13], SWCNTs, SW-CNHs [11] and nano-onions [13]. In past few years, few papers have been published regarding synthesis of metal and metal oxide nanostructures such as MoS_2 [14], CuO and Cu_2O [15], Ag [16,17], Au [18,19], WO_3 [20] and ZnO [21] by arc discharge in liquids.

In the present study, we report a simple, inexpensive and one-step synthesis route of ZrO_2 nanoparticles by arc discharge method in DI water. We have studied the effect of arc current on size distribution and the photocatalytic activity of the produced nanoparticles. The main advantage of the present method is the direct formation of ZrO_2 nanoparticles from discharge of zirconium electrodes within water. To the author's knowledge, to date there has been no published report on synthesis of ZrO_2 nanoparticles based on arc discharge using zirconium electrodes in DI water.

2. Experimental

2.1. Synthesis of ZrO_2 nanoparticles

The experimental set up consists of two main parts: a high current DC power supply and a reactor including anode, cathode and a micrometer which moves the anode towards the cathode. In this work, a 10–20 A current was applied between two zirconium metallic electrodes. The voltage was dropped to about 2–3.5 V during the arc formation while the current was fixed to a desired amount. Both the anode and cathode were wire shaped, 1 mm in diameter and had 99.2% purity (from Goodfellow). Initially, we bring the two electrodes into touch leading to a small contact cross

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section and thus to a high current density. Then we separate them from each other and as a result zirconium is ablated from the anode and then condensed in water and forms different nanoparticles.

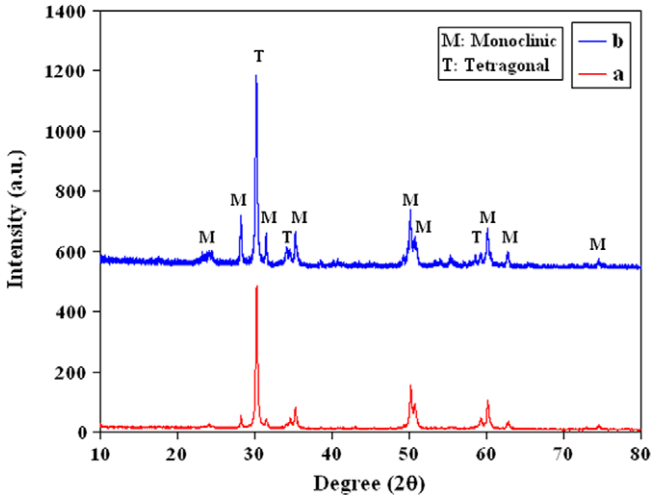

Fig. 1. XRD pattern of ZrO_2 nanoparticles was made at 10 A arc current (a) as prepared and (b) annealed at 500 °C.

2.2. Characterization

Analysis of the crystalline structures was performed by XRD diffractometer (X'pert Philips) with wavelength of Cu Kα radiation in 2θ range from 10° to 80° by 0.005° s^{-1} steps. UV–Vis spectroscopy of the samples was taken out by a Lambda 950 spectrophotometer (Perkin–Elmer) from 200 nm to 1100 nm wavelengths. TEM analysis was performed by a LEO 912 AB instrument at 200 keV accelerating energy by deposition of ZrO_2 nanoparticles onto the copper grid at room temperature. 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. Surface area of the nanoparticles was determined by Belsorp adsorption–desorption (BEL Japan Inc.) instrument. Photocatalytic activity of the nanoparticles was measured by photodegradation of Rh. B with the initial concentration and volume of 10^{-5} M and 30 mL respectively at the presence of 30 mL ZrO_2 solution. First the mixed Rh. B and ZrO_2 solution was stirred in dark for 30 min to equilibrate the

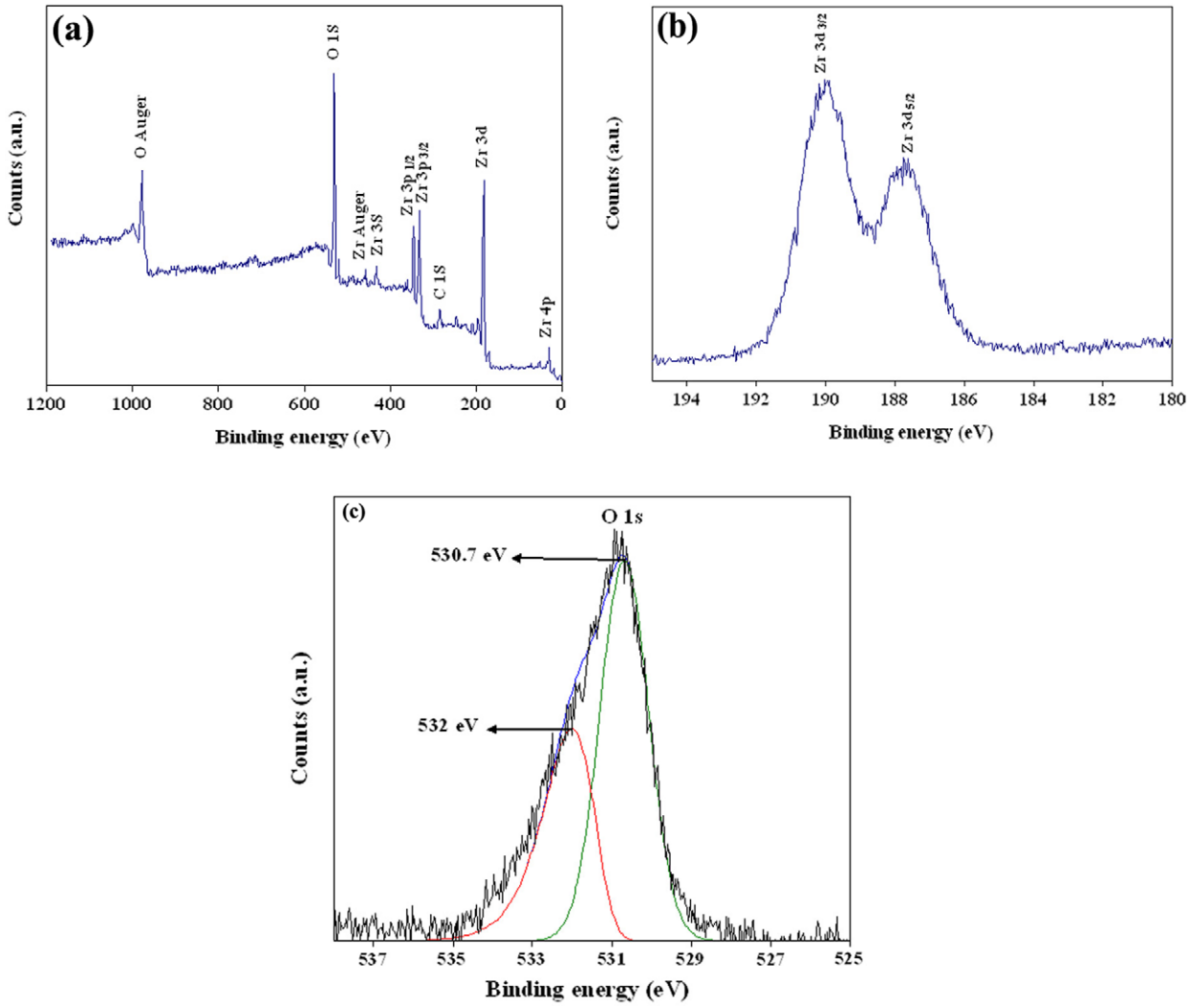

Fig. 2. XPS analysis for ZrO_2 nanoparticles formed at 10 A arc current, (a) wide range of energy survey, (b) energy range related to Zr peaks and (c) energy range related to O 1s peak.