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Formation mechanisms, structural and optical properties of Bi/Bi_2O_3 One dimensional nanostructures prepared via oriented aggregation of bismuth based nanoparticles synthesized by DC arc discharge in water

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ABSTRACT

Bismuth based rod-like nanostructures were prepared via oriented attachment of colloidal bismuth based nanoparticles synthesized by direct current (DC) arc discharge in liquid. For the synthesis of bismuth based nanoparticles 5 A and 20 A DC electrical currents were applied between two pure bismuth electrodes in water. Bismuth based nanoparticles extracted from the water after 30 days then dispersed in ethanol. Bismuth based rod-like nanostructures formed via the oriented attachment mechanism in ethanol during 30 days. According to X-ray diffraction (XRD) patterns of as-prepared samples, the main parts of the particles were bismuth phase while after 30 days bismuth oxide and bismuth hydroxide phases were dominant. To investigate the species that formed in plasma during the electrical discharge in water, optical emission spectroscopy (OES) was used. The OES spectra demonstrate the creation of Bi-I, Bi-II, O-I, O-II and H ions and H_2-I molecules for both currents. UV–visible spectroscopy and field emission scanning electron microscopy (FE-SEM) were used for the study of optical properties, morphology and size distribution of the nanostructures respectively. Optical transmission spectra of synthesized nanostructures in water indicated the optical characteristic of both bismuth and bismuth oxide. FE-SEM images illustrate that bismuth based nanoparticles are rather spherical as-prepared and formed rod-like nanostructures by passing the time in the presence of ethanol. Also, the size of nanoparticles and subsequently diameter of rod-like nanostructures for samples that prepared by 5 A arc current is more than samples that prepared by 20 A. The results provide a simple and flexible method for synthesis of bismuth based rod-like nanostructures.

1. Introduction

Trivalent bismuth oxide with Bi_2O_3 chemical formula can consider as a most industrially significant compound of bismuth. Bi_2O_3 is a p-type semiconductor that has five crystallographic polymorphs including, α-Bi_2O_3 with the monoclinic crystal structure, tetragonal β-phase, body-centered cubic, γ-phase, cubic δ-phase and a ε-phase [1–3]. Bismuth oxide has desirable physical properties such as high dielectric permittivity and refractive index, remarkable band gap about 2.85–2.58 eV, excellent photoconductivity and high photoluminescence [4–8]. In addition, Bi_2O_3 has alternative chemical properties such as nontoxic nature, catalytic activities and ionic conductivity [9–12]. These properties make bismuth oxide as an appropriate choice for various applications. In this regard, bismuth oxide hierarchical nanostructures have been employed in photocatalysis application, gas sensing based on bismuth oxides nanowires, bismuth oxides thin films in electrochemical supercapacitors, catalytic application of Bi_2O_3 nanorods, α-Bi_2O_3 nanorods as an efficient sunlight active photocatalyst and fabrication of immunosensors based on bismuth oxides nanorods for mycotoxin detection [2,3,13–16]. There are various synthetic methods to produce bismuth oxide nanostructure. Namely, pulsed laser deposition for the synthesis of cauliflower-like Bi_2O_3 nanostructures, microwave-assisted method to produce β and α-Bi_2O_3 nanoparticles and synthesis of δ-Bi_2O_3 thin films with reactive sputtering method [17–19]. One dimensional nanostructures have gained much attention due to their unique properties such as high dielectric constants, large band gap, appropriate electrical and optical properties and superconductivity [20–23]. These properties make them appropriate for the variety of applications such as biosensors, gas sensors, light-emitting diodes, supercapacitors, electronic, optoelectronic, field emission devices and in vivo applications [24–30]. The oriented attachment mechanism is one of the crystalline one dimensional nanostructures

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growth mechanism that is probable for nanoparticles in colloidal solution. This mechanism is based on the creation of almost isotropic spherical nanocrystals by spontaneous self-ensemble of them along a particular set of crystallographic facets [31,32]. Many physical and chemical techniques are developed to control the growth mechanisms, crystallographic structure, shape, morphology, size distribution and defects of the one dimensional nanostructures [33–35]. Some of the employed methods to synthesis of one dimensional bismuth oxide nanostructures are the synthesis of α-Bi_2O_3 nanowires with vapor transport, hydrothermal synthesis of Bi_2O_3 nanowires, surfactant- free sonochemical route of α-Bi_2O_3 nanorods at ambient conditions and produce of monoclinic bismuth oxide nanorods by a one-step hydrothermal method [12,36–38]. In accordance with one dimensional bismuth oxide nanostructures importance, finding a successful synthesis method that brings new features is necessary. In compared with other synthetic methods, electrical arc discharge in liquid has several advantages. Prominently arc discharge in liquid is a low-cost green process with a high preparation rate of nanomaterials, does not need to vacuum system and cooling equipment or reactive gas [39–41]. Electrical arc discharge in liquid creates high energy plasma between two electrodes that can vaporize the surface of both electrodes and the surrounding liquid. The vaporized metals condense in liquid medium that has much lower temperature than hot plasma and the nanoparticles produce [42]. Plasma of electrical arc discharge in liquid can be generated by various current and voltage regimes such as AC and DC (pulsed, non-pulsed) between the electrodes by different configurations [43]. Chemical nature of liquid environment, the kind of electrodes material and diameter of electrodes are the other parameters that affected the arc discharge and nanoparticles formation [42]. For instance, η-Al_2O_3 based nanoparticles prepared via DC arc discharge in different carrier media [42]. Moreover, it is possible to synthesize aligned carbon nanotubes by electrically heating of substrate in organic liquids [44].

In this research, bismuth based nanoparticles were synthesized via DC arc discharge in water. Two appropriate arc currents selected to the generation of the plasma between bismuth electrodes in water in order to the formation of bismuth based nanoparticles. Bismuth oxide rod-like nanostructures obtained by ordering of spherical bismuth based nanoparticles by oriented attachment growth mechanism. The growth occurred in the presence of ethanol about 30 days. This method is commonly used for the preparation of various oxides and not yet reported for the synthesis of bismuth based nanorods [41,45–47]. In compared with other chemical media, water is a base liquid that simplified the metal and metal oxide nanoparticles synthesis [48]. The results provide a simple and flexible method for synthesis of bismuth based rod-like one dimensional nanostructures.

2. Experimental

A schematic diagram of the DC arc discharge experimental setup is shown in Fig. 1. According to the setup, there is a heat-resistant glass container that filed with deionized water as synthesis medium. Two electrodes are located in front of each other in vertical mode created from bulk bismuth with 99.8% purity and have diameters about 5 mm and length of 30 mm. The anode was held fixed within the container while the cathode held with a movable handle to adjust the cathode near to anode. The distance between the anode and cathode should not be more than 2–3 mm. Bismuth based nanoparticles were synthesized by two different arc currents. A 5 A electric current that exerted by dual output DC power supply (MICRO PW-6053R) and the 20 A electric current that applied by ARC-200 DC power supply. According to regimes of the classical DC electrical discharge diagram, 5 A and 20 A current are in the glow-to-arc transition zone. In this arc regime by increasing the current, voltage decreases significantly that influence the nanoparticles creation and subsequent growth of nanorods [49]. At the beginning of the process electrodes brought into contact together and then the arc discharge slowly separated the cathode from the anode. Each discharge lasted 3–5 s and every discharge emitted very shiny blue lights. For investigation the species that created during the arc discharge the light that emitted from the arc process collected by an optical fiber for OES measurements. For mounting spectrophotometer in a good way, the optical fiber aligned near the arc discharge zone. The OES system was AvaSpec-3646-2-USB2 spectrophotometer that measured the emission spectra from 190 to 950 nm. Bismuth species evaporated from the cathode in each electric discharge and dispersed in water that its temperature is so less than arc hot zone then condensed in arc discharge media and created nanoparticles [45]. To investigate the optical properties of the synthesized nanoparticles the transmission spectra of the colloidal solutions were obtained in the range of 190–1100 nm at different times. The UV–visible absorption spectra were measured by SPUV-26 spectrophotometer. The morphology and size distribution of the samples studied by field emission scanning electron microscopy (FE-SEM) images. These images obtained by a MIRA TESCA field emission scanning electron microscope at room temperature. The samples coated with a thin layer of gold because the bismuth oxide nanoparticles cannot conduct the electrons. The X-ray diffraction pattern (XRD) of the samples earned to identify the crystallographic structure of the prepared colloidal particles by an X'Pert MPD system with Co-K_α radiation with $\lambda = 1.78897$ Å wavelength. To extract the dispersed nanoparticles the solution was centrifuged for 10 min at 1000 rpm.

3. Results and discussion

Bismuth based nanoparticles synthesized by DC arc discharge in water by 5 and 20 A currents. The crystallography characterizations of samples obtained at two different times, immediately after synthesis and after 30 days. Fig. 2 demonstrates the XRD patterns of the samples. Fig. 2a–b related to nanostructures that synthesis by 5 A DC current. According to XRD pattern of as-prepared nanoparticles all of the peaks are based on bismuth phase with rhombohedral crystal system and 01-085-1329 reference code that have reflection from (120), (104), (110), (024), (116) and (122) planes with $a = b = 4.5460$ Å, $c = 11.8620$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ crystallographic parameters [50]. The XRD pattern of this sample after 30 days indicated the maximum diffraction peaks related to specific crystalline planes of different phases, including bismuth, bismuth oxide, and bismuth hydroxide. Here the crystal system of bismuth phase is rhombohedral with 00-001-0688 reference code and $a = b = 4.5500$ Å, $c = 11.8500$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ crystallographic parameters [50]. Bismuth oxide phase are based on monoclinic crystal system with $a = 5.8480$, $b = 8.1660$ Å, $c = 7.5100$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 113^\circ$ system parameters [51]. The bismuth hydroxide peaks indicated a hexagonal crystal system with 00-001-0898 reference code [50]. For this pattern, the calculation based on quantitative analysis of multiphase systems indicates that the sample consists of about 51% bismuth oxide, 35% bismuth hydroxide, and 14% bismuth. The oxidation of nanostructures by passing the time can be explained by reaction of dissolved oxygen in water with bismuth nanostructures. Fig. 2c–d demonstrates the XRD patterns of samples that synthesized by 20 A DC current. As can be seen in the XRD pattern of as-prepared sample, bismuth oxide phase is also created during synthesis. In this pattern, the peaks that indicate bismuth phase crystallized in rhombohedral system with 00-005-0519 reference code and $a = b = 4.5460$ Å, $c = 11.8600$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ parameters that have reflections from (120), (104), (110), (024), (116) and (122) planes [52]. Bismuth oxide peaks related to monoclinic cell with $a = 5.8300$, $b = 8.1400$, $c = 7.4800$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 67.0700^\circ$ crystallographic parameters based on 01-071-0465 reference code that have reflection from (-121), (012), (-202), (221), (-104), (-322), (-233) and (-241) planes [53]. According to this pattern 44% of nanostructures oxidized during the synthesis, however, the whole part of nanoparticles that synthesized by 5 A DC current is bismuth phase. The created