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Tailoring bismuth oxide flower-, bowtie- and brushwood-like structures through microfluidic synthesis

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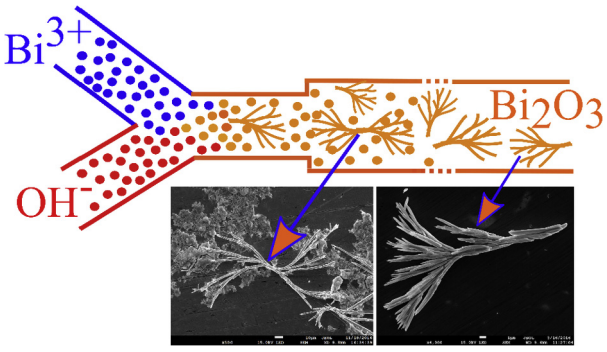
HIGHLIGHTS

- Bi_2O_3 particles resembling flowers, bowties and brushwood are created in microfluidic network.
- The surfactant PEG shapes the particles, while laminar flow keeps the structures undamaged.
- The fluid dynamics calculations reveal the critical residence time along micro-channels.
- Flower-like particles are superior oxidizers than brushwood-like structures in Al-Bi_2O_3 nano-energetic formulation.

GRAPHICAL ABSTRACT



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ABSTRACT

Bismuth oxide structures resembling flowers, bowties and brushwood-like assemblies were successfully produced utilizing microfluidic synthesis approach. The molecular length of surfactant polyethylene glycol (PEG) was critical in shaping the particle morphology, while the laminar flow in micro-channels assured the complete structures without breakage. The PEG with 200 Molecular Weight (MW) assists to produce 1–2 μm flower-like structures, while the PEG with 8000 MW yields to the highly crystalline bowtie and brushwood-like structures with up to 60 μm size. The particle morphology examination along microfluidic network coupled with fluid dynamics calculations showed that the complex structures are completed at the end of micro-channel tubes, at the residence time less than 13 s. The as-received bismuth oxide particles were tested for oxidizing activity in nano-energetic material Al-Bi_2O_3. The formulation containing flower-shaped structures was superior to brushwood-like oxidizer, and produced the maximum pressure discharge value of about 4.9 kPa m^3 g^{-1}, which is comparable to highest reported values in literature.

1. Introduction

Bismuth oxide Bi_2O_3 is an important component of ferroelectric [1] and electrochemical supercapacitors [2]. Bi_2O_3 is used in the field of optical materials [3,4], gas sensors, photocatalysts, solid oxide fuel cells, etc [5–7]. It was shown that spectroscopic properties of bismuth oxide based glasses are strongly influenced by preparation conditions such as melting temperature and composition [8]. Glasses containing bismuth oxide exhibit suitable radiation shielding ability [9]. The bismuth oxide-platinum sensors show the largest positive response among other oxide based carbon

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monoxide sensors [10]. The photocatalytic activity of bismuth oxide can be further enhanced by introducing carbon quantum dots [11]. Pure bismuth and amorphous bismuth oxide nanospherical particles can be used for removal of atmospheric nitrogen oxides NO_x [12]. Being a strong oxidizer, Bi_2O_3 is also used in nanoenergetic materials called Nanoenergetic Gas-Generators (NGG), which are alternatives to traditional energetic materials including pyrotechnics, propellants, primers and solid fuels [13]. It was shown that bismuth oxide is one of the best oxidizers in the field of NGGs [14]. The synthesis of bismuth oxide particles with various shapes and size has focused significant attention. There were several attempts to synthesize flower-like bismuth oxide hierarchical structures [15–18], but the formation mechanism was not well understood. It is important to receive the particles with complete structure, as the three-dimensional bismuth oxide flower-like microspheres have attracted great attention due to their particular optical, electrical, and ion-conducting properties [19–21]. It is known that introduction of templates can lead to microstructures of bismuth oxide with desired shape [22–26].

Moreover, production of particles with various morphology, using an easily controllable method to tune the size and shape of bismuth oxide particles, is desired.

In this work, the effect of surfactant polyethylene glycol PEG with 200 and 8000 molecular weight, are evaluated for the preparation of bismuth oxide particles with various morphology and size, using microfluidic synthesis approach. The microfluidic synthesis is preferred, because performing the synthesis with magnetic stirring produces broken structures [27]. During the violent mixing with magnetic stirrer, the formed particles tend to break into 1–10 μm irregular shaped segments.

Thus, the microfluidic preparation is critical for preserving the complete structures of bismuth oxide particles. The flow dynamics along the microfluidic network is examined to quantitatively describe the complex structure formation for bismuth oxide particles. Furthermore, the impact of the particle shape on oxidizing activity of bismuth oxide in nanoenergetic formulation Al-Bi_2O_3 was studied.

2. Experimental methods and procedures

The $Bi(NO_3)_3$*$5H_2O$ (98%) and NaOH (98%) were purchased from Sigma Aldrich. HNO_3 concentrate (70%, Sigma Aldrich) was diluted to receive 1.5 M concentration. Microfluidic pump (ISMATEC Reglo Digital, Peristaltic, MS-4/8) was used to synthesize bismuth oxide particles. The Y connector inner diameter was 0.5 mm connected to output channel with 0.76 mm diameter. As a bismuth source reagent, 0.7 g $Bi(NO_3)_3$*$5H_2O$ was added to 30 ml 1.5 M HNO_3, and sonicated for 30 min to completely dissolve the $Bi(NO_3)_3$, then 15 g PEG (200 or 8000, Sigma Aldrich) was added and sonicated for another 30 min. As a neutralizing reagent supplying hydroxide ions, a 4.5 g NaOH was dissolved in 45 ml H_2O by 1 h sonication.

Both reagents were placed near microfluidic pump, and were sent through separate tubes to Y-connector with 60 rpm pumping drive speed, and the product was collected from output microfluidic channel. The reaction between $Bi(NO_3)_3$ and NaOH took place in the presence of PEG macromolecules acting as a surfactant. The PEG-s with various molecular weight resulted in various shapes of end product Bi_2O_3. The product vial contained sodium nitrate, PEG, and bismuth oxide particles. The end product pH value was between 13 and 13.5 in all cases. The $NaNO_3$ and PEG were removed from the end product by washing it with water and centrifuging 3 times. The product was dried under 65 °C for 12 h. Flowchart illustrating the synthesis of the bismuth oxide with various particle size and shapes is presented in Fig. 1.

The particle morphology was analyzed with JEOL 7800F Field Emission Scanning Electron Microscope. The XRD analysis was performed by Bruker D-2 Phaser with Cu Kα anode, in 2θ range 20–60°, where the main peaks of bismuth oxide are distributed. The scans were taken with θ precision 0.02° and sample was rotated with 15 rpm to statistically increase the number of particles contributing to XRD signal intensity. The thermo-gravimetric analysis (TGA) was performed using Differential Scanning Calorimeter (DSC) with the sensitivity 0.1 μg (Q-600, TA Instruments). The measurements were made in air with 100 ml/min air flow rate. A Nicolet iS5 FTIR spectrometer (Thermo Scientific) with an ID-5 accessory was used to perform Fourier Transform Infrared (FTIR) spectroscopy on a small quantity (~5 mg) of powder that was pressed to receive a flat surface. The measurement was performed in the wavenumber range of 4000–400 cm^{-1}.

For the NGG preparation, the Al: Bi_2O_3 weight ratio was 2:8. For the preparation of 0.25 g mixture, 0.2 g Bi_2O_3 was added into 20 ml isopropanol (IROH, 99.5%, Sigma Aldrich), and 0.05 g Al in 20 ml IROH, and both vials were sonicated in sonic bath for 30 min 80 μl 0.1% Poly-4-vinyl-pyridine (Sigma Aldrich) was added into Al-IROH solution for self-assembly, and both vials were sonicated for another 30 min. The water was changed in sonic bath to avoid heating of the liquids in vials. Al-IROH was added into Bi_2O_3-IROH solution and the mixture was sonicated for another 30 min. The suspension was transferred into glass container and placed in drier set to 65 °C, and was dried 12 h. The dry powder with 0.2 g charge mass was tested in modified Pharr reactor with 0.342 L volume, and equipped with pressure transducer and Omega data acquisition board with 1 MHz data acquisition speed. The voltage was converted into normalized pressure (MPa/g) and pressure discharge peaks were compared for bismuth oxide with various shapes.

3. Results and discussion

The bismuth oxide particles prepared using PEG-200 surfactant were light yellow in color. The drying condition of reaction products is an important parameter for particle morphology. The SEM images reported in Fig. 2(a–c) show that the particles dried at room temperature, are composed of layers of petals with thickness of 20–30 nm (Fig. 2a inset), that are forming flower bud-shaped conformation with diameter up to 2 μm. In case of drying the particles at 65 °C for 12 h, some crystallization of nanoparticles takes place (Fig. 2d and e), which can self-assemble into flower-like structures (Fig. 2 f).

The particles prepared with PEG-8000 surfactant are presented in Fig. 3. In some structures, spherical formations remain on the endpoints of rods, resembling flower bouquets (Fig. 3 a, b). However, drying these particles at 65 °C for 12 h removes all spheres. Presumably, the spherical formations merge into rods. The well-dried particles have brushwood-like and bowtie-like structures (Fig. 3c–f). We note that the rods are growing from common stalk, where the individual rods are further branched, much like in a brushwood (Fig. 3d and e). The EDS mapping of bismuth atoms for a typical brushwood-like structure is presented in Fig. 3d inset, which shows the distribution of Bi atoms in the particle. Many of these structures are connected through common stalk from opposite directions, forming bowtie-like conformations (Fig. 3 f). It is possible, that the separate brushwood-like structures were connected to each other like bowties, but during movement through microfluidic channel, or during product washing they broke from stalk, leaving two brushwood-like structures. The absence of individual rods broken from brushwood-like structures is the result of highly lamellar, calm flow of the product through Y-connector and tubes of microfluidic pump.

The XRD analysis of product powder received with PEG-200 surfactant showed that the particles were amorphous, and