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Dielectric barrier discharge plasma-mediated synthesis of several oxide nanomaterials and its characterization

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ABSTRACT

This study deals with the preparation of SiO_2, CuO and RuO_2 nanomaterials and RuO_2 based nanocomposites using dielectric barrier discharge (DBD) plasma. On account of an increasing attention toward the preparation of one dimensional nanostructure in recent days, the possibility to tune the morphology of the above materials by using plasma was investigated. The prepared nanomaterials were characterized by using Fourier transform infrared spectroscopy, field emission scanning electron microscopy, X-ray diffraction spectroscopy and particle size analysis. Spherical, cylindrical and nanorod structures were observed for SiO_2, CuO and RuO_2, respectively. The morphology and the chemical composition of the RuO_2/SiO_2 and RuO_2/CuO nanocomposites were analyzed using high resolution transmission electron microscopy and energy dispersive X-ray spectroscopy. It was noted that interaction of plasma species with each material differs from one another, and thus the materials exhibit different surface morphology. The reason might be the material's physico-chemical properties and in particular, depending on whether they belong to insulator or semiconductor.

1. Introduction

Preparation of one dimensional structure and shape-specific nanomaterials is gaining momentum in recent times since the performance of the material in various applications is closely related to its dimension. Even though a variety of methods available for synthesizing nanomaterials, plasma-mediated methods [1–8], especially the use of dielectric barrier discharge (DBD) plasma becomes more attractive fields of interest nowadays due to its capability to readily control the morphology. The interaction between plasma constituents (for example, electrons, ions and neutrals) and the nanomaterials plays important roles to determine the chemical composition [9]. Depending on the feed gas, the formation of plasma species varies; for example, an inert feed gas such as Ar and He generates more electrons and the energy loss mechanism is mainly via heat dissipation by collisions [10]. At the same time, using reactive gases such as $Ar + O_2$ enhances the formation of reactive oxygen species, which results in the stoichiometric oxide formation in the nanomaterials. Further, our recent investigation on ruthenium (IV) oxide (RuO_2) nanomaterials suggested that nanorod morphology could be easily obtained when using Ar feed gas [11].

It will be very much beneficial if the morphology of nanomaterials having different physicochemical properties can be tailored using DBD plasma. Therefore, an extension of the plasma-mediated nanomaterial preparation to other materials such as silica (SiO_2), copper (II) oxide (CuO), and composites like RuO_2/SiO_2 and RuO_2/CuO was made in this work and the growth mechanism has also been proposed. It is well known that SiO_2 nanomaterials are widely used from biological to electronics industry [12]. The RuO_2 and CuO are mainly used in catalysis and energy-related applications [13,14] and especially the RuO_2 based nanocomposite is promising both in terms of activity and stability [15].

2. Experimental

2.1. DBD plasma reactor setup

The schematic and the photograph of the home-made DBD plasma reactor used in this study are represented in Fig. 1. Two stainless steel sheets (15 cm long and 4 cm wide) were used as high voltage and ground electrodes. In addition, two glass plates serving as dielectric barrier were also inserted between the electrodes. The gap between the electrodes was 15 mm. The reactor was enclosed in an acrylic chamber with gas inlet and outlet. Throughout this work, the input power was fixed at 38.2 W (operating frequency: 400 Hz). (It is to be noted that the operating frequency does not have much influence on the material synthesis. The power may be provided by choosing either low energy at high frequency or high energy at low frequency modes. Most important is to generate and sustain the plasma for the entire reaction). Depending upon the extent of drying of the solution, the voltage varied between 16 and 20 kV (peak value).

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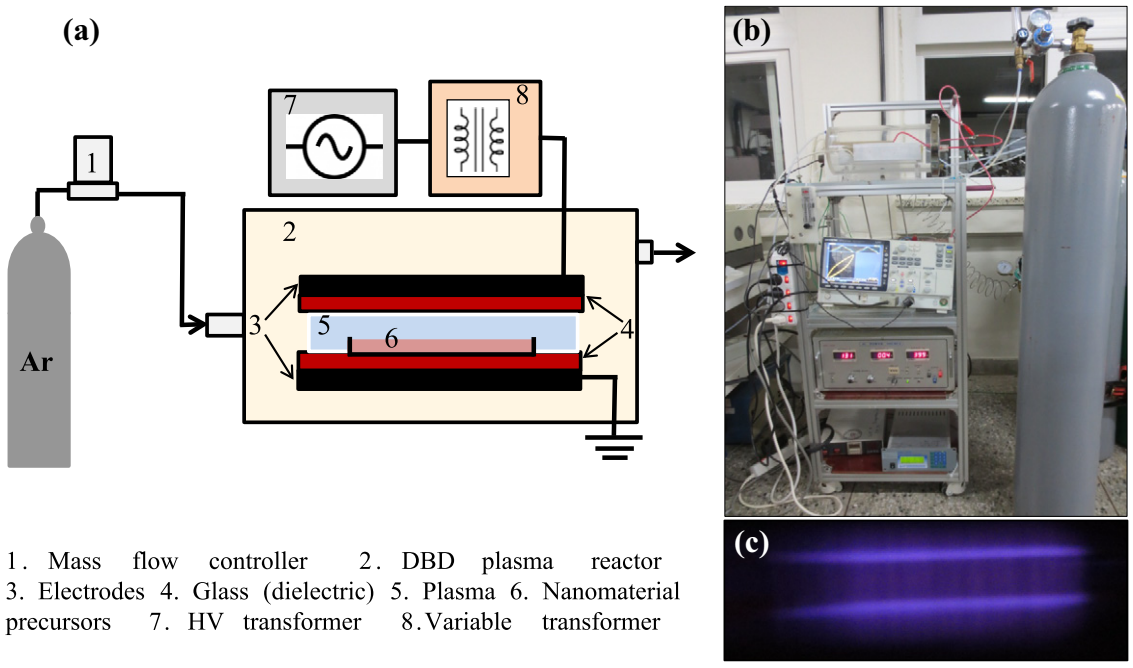

Fig. 1. (a) Schematic and (b) photograph of the DBD plasma reactor. (c) shows the photograph of the plasma during nanomaterial synthesis.

2.2. Materials and methods

Tetraethyl orthosilicate (TEOS), $CuCl_2$ and $RuCl_3 \cdot nH_2O$ were used as precursors for silica, copper oxide and ruthenium dioxide nanomaterials, respectively. TEOS and $RuCl_3.nH_2O$ were purchased from Sigma-Aldrich. The $CuCl_2$ (Hayashi Pure Chemical) and NH_3 (Junsei Chemical Co.) were used as received. About 0.1 M of the above precursors was separately prepared and 500 μL each was kept on a glass plate or in a petri dish. Then, 500 μL NH_3OH (1 M) precipitating agent was added, stirred using a glass rod and kept in between electrodes of the DBD reactor. For silica nanoparticles, ethanol (2.5 mL) was additionally added. In order to prepare the RuO_2/SiO_2 and RuO_2/CuO composites, the corresponding precursors (500 μL each) and NH_3OH (1 mL) were mixed together and placed on the glass plate. Then, Ar plasma was generated and the nanomaterial solution was exposed to the plasma for 3 h. At the end of the plasma reaction, the product was collected, washed and annealed at 350 °C.

2.3. Material characterization

The physical and chemical characterization of the synthesized nanomaterials and composites was performed using Fourier transform infrared spectroscopy (FTIR, model: IFS 66/S, Bruker), X-ray diffraction spectroscopy (XRD, model: D/Max ultima III, Rigaku corporation, Japan), field emission scanning electron microscopy (FESEM, model: JEM 1200 EX II, JEOL Ltd.), high resolution transmission electron microscopy (HR-TEM, model: TECNAI F20, Philips Corp.), energy dispersive X-ray spectroscopy (EDX, model: R-TEM, CM-200 (UT)) and particle size analysis (ELS8000, Otsuka, Japan).

3. Results

3.1. Functional group analysis and crystallinity studies

The FTIR spectra of the synthesized SiO_2, CuO and RuO_2 nanomaterials are given in Fig. 2 (a)–(c), respectively, with its characteristic functional groups. The bands observed at 803, 950 and 1100 cm^{-1} represents Si–O (bending), Si–OH (stretching) and Si–O–Si (stretching) vibration modes of silica nanoparticles [16], respectively. The copper oxide sample exhibited main bands at 530 and 607 cm^{-1} which are attributed to Cu_2O and CuO stretching [17]. The metal–oxygen vibrations corresponding to Cu–O and Ru–O were observed at 445–910 cm^{-1} and 650–800 cm^{-1} [Fig. 2(c)], respectively [18]. Peaks around 1645 cm^{-1} and beyond 3400 cm^{-1} in all samples refer to the O–H stretching of adventitious water molecules.

The XRD diffraction patterns observed for SiO_2, CuO and RuO_2 are given in Fig. 2 (d)–(f), respectively. During the plasma reaction, TEOS liquid was converted into solid silica powder by gradual evaporation of the solvents (condensation reaction involving the loss of water and ethanol). The prepared silica nanoparticles exhibited an amorphous state ($2\theta = 21.86°$) and thus no prominent peak was noticed. This kind of dispersion peak corresponding to amorphous silica has been reported previously [19–21] when following different synthesis procedures. The diffraction patterns observed for copper oxide consisted mainly of CuO and a small diffraction peak at 48.7° corresponds to metallic copper [22]. The XRD peaks shown by rutile type RuO_2 contain major peaks around 28°, 35°, and 54° corresponding to (110), (101) and (211) sets of lattice planes of vibration. Moreover, (101) plane intensity is higher than any other peaks, which showed the growth of one dimensional structures such as nanorods [11].

3.2. Morphological studies

The FESEM morphological images of the plasma-synthesized SiO_2, CuO and RuO_2 nanomaterials are given in Fig. 3 (a)–(c), respectively. The silica nanomaterials exhibited uniform-sized spherical particles of around 300 nm, whereas CuO showed a cylindrical shape with small dips on the surface. The RuO_2 nanomaterials displayed rod structures with length and width > 1 μm and 100 nm, respectively. For direct comparison, the FESEM images of the SiO_2, CuO and RuO_2 nanomaterials synthesized using wet chemical technique are given in Fig. 3 (d)–(f), respectively. It can be easily seen from the images that the plasma mediated process influenced the morphology, which is very different from the materials prepared from conventional synthesis. Basically, in wet chemical routes, aggregation is a major problem which can be prevented by using stabilizing polymers or surfactants [18]. Since