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Original Research Paper

Shed light on submerged DC arc discharge synthesis of low band gap gray Zn/ZnO nanoparticles: Formation and gradual oxidation mechanism

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ABSTRACT

Synthesis of colloidal metal oxides with controllable size and morphology is burgeoning field of research in nanoscience. Low band gap gray Zn/ZnO colloidal nanoparticles were fabricated by plasma-liquid interaction of DC arc discharge in water. Scanning electron microscopy, X-ray diffraction and UV–vis spectroscopy were employed for morphology, crystal structure and optical characterizations respectively. Optical emission spectroscopy was used to investigate the plasma properties during the synthesis and formation mechanism of nanoparticles. Nanoparticles with different size and shape were fabricated only by adjusting discharge current during synthesis without introducing any chemical agent. Electric discharge current was set to 20, 50, 100 and 150 A during synthesis. Estimated values of plasma excitation energies were 2.41, 2.66, 2.86 and 3.04 eV and diameter size of nanoparticles were 63, 42, 37 and 29 nm for these applied currents respectively. Synthesized nanoparticles were dark gray as prepared and became more transparent gradually getting white color finally. XRD and UV–vis results revealed that the oxidation process was time dependent. The colloidal nanoparticles composed of two metal and metal-oxide phase and white crystalline ZnO was achieved after complete oxidation process. These results provided a flexible and versatile method to synthesize metal oxide nanoparticles with controlled composition.

1. Introduction

ZnO is a n-type semiconductor with direct band gap of 3.37 eV and high electron mobility of 100 $cm^2/V\,s$ [1]. Zinc oxide nanoparticles (NPs) have attracted lots of attentions due to wide range of applications in solar cells [2–4], light emitting diodes [5], piezoelectric devices [6], catalysis [7,8], and UV and microwave absorbers [9]. Furthermore, it has been widely used as a photocatalyst in environmental pollution remediation. It is a non-toxic and biocompatible semiconductor but with the drawback of wide band gap energy that requires UV light absorption. Most researches on metal oxide photocatalysis focus on band gap narrowing to achieve visible light activity of metal oxide semiconductors [10–14].

Several chemical and physical methods have been used for synthesis of zinc oxide NPs including, hydrothermal processing [15], sol-gel [16], spray pyrolysis [17], solvothermal method [18], microemulsion [19], pulsed laser ablation [20] and thermal evaporation [21]. Since Optical and structural properties of ZnO nanostructures strongly depend on the applied fabrication method, choosing the appropriate synthesis approach is of great importance to control final properties. In most of mentioned procedures reducing agents and chemical additives are required, that may cause undesirable by-products [9,22]. Moreover, these methods are usually time consuming and costly [23]. While new approaches based on solution plasma have attracted attentions recently. Solution plasma methods are mass producible, clean, cost–effective, and environment-friendly [20,24,25]. Submerged arc discharge [24,25], microwave plasma [26], DC thermal plasma [27], and laser ablation [28] are often numbered as solution plasma techniques and used to prepare different metal oxide NPs. Different experimental setups of solution plasma synthesis with different liquid medium, applied voltage, electrode material and configuration have been reported [29,30]. Saito et al. produced ZnO nanostructures through submerged arc discharge in K_2CO_3 solution [25]. A Zn wire and a Pt mesh were applied as cathode and anode respectively [31]. Ashkarran et al. have synthesized ZnO nanostructures through arc discharge of zinc electrodes in deionized water [24]. Hattori et al. synthesized Zn and ZnO NPs from zinc electrode using microwave plasma [32]. Burakov et al. studied formation of ZnO

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NPs during arc discharge synthesis in water. Shaikh et al. investigated plasma parameters during laser ablation of Zn and Cd [28]. Many experiments based on solution plasma methods show oxidation of metallic NPs [33–36] but the mechanism is still not clear. ZnO NPs are formed through plasma-liquid interactions due to existence of oxidizing species and high temperature of plasma. However, because of reactions in non-equilibrium plasma in this synthesis oxidation process is different compared with other routes. Synthesis of two phase metal/metal-oxide NPs via arc discharge in water instead of single metal-oxide phase enables achieving a low band gap and composition controlled colloid.

In this research, low band gap Zn/ZnO NPs with controllable size, composition and optical properties were synthesized. In this method NPs prepared in one step without any treatment on ZnO to modify optical properties. Hence, the important parameter is aging effect on optical transmission and phase composition of NPs. In this regard, formation and oxidation mechanism of Zn/ZnO NPs was investigated, completely. Zn/ZnO NPs were synthesized with submerged arc discharge of zinc electrodes in deionized water without use of any stabilizer or capping agent. Arc discharge produce high-pressure and high-temperature zinc plasma in solid-liquid interface. Interaction of zinc clusters with reactive species in water form Zn-ZnO composite NPs. Optical emission spectroscopy (OES) was used to determine the generated plasma elemental composition and parameters. Spectra emitted from species in plasma used to develop the analytical information about the formation and oxidation process. Formation of ZnO NPs during arc discharge in water was tracked by OES and oxidation mechanism was investigated by UV–vis spectroscopy. By investigating the oxidation process we hope to optimize the synthesis procedure to obtain visible-active ZnO NPs. The aim of this research is to understand formation and oxidation process of metallic NPs. We hope our results open the way to prepare stable gray ZnO NPs with visible-light activity.

2. Experimental details

2.1. Materials

Zn rods (99.9%, Sigma-Aldrich) with 3.0 mm in diameter employed for synthesis of zinc oxide nanostructures. Zinc rods were submerged in deionized water (pH = 6.5–7.5 and conductivity = 0.8–0.9 μS) and used as electrodes for DC arc discharge in liquid setup.

2.2. Experimental setup

Fig. 1 shows schematic of the experimental setup used for arc discharge plasma synthesis in water. The anode and cathode electrodes were zinc rods of length 40 mm and diameter of 3 mm. The electrodes positioned opposite each other along the vertical axis. The upper electrode is movable while the downer one is fixed. In this experiment applied current was varied from 20 to 150 A. The dielectric environment was deionized water for all samples and no surfactant and stabilizer were used. All samples were synthesized at room temperature and atmospheric pressure. It takes almost 3 minutes for generation of plasma in water and dispersion of nanoparticles. During synthesis, electric discharge generates plasma in extremely short distance between zinc electrodes. The electric field energy is great enough to vaporize zinc electrodes and form zinc plasma. Light emission with arc discharge was observed during the synthesis in all experiments and characterize in-situ with optical emission spectroscopy. Immediately after synthesis dark smoky stream of zinc particles diffuse in water. In this step the synthesis process is finished but, the oxidation will continue. White zinc oxide powder achieved after complete oxidation

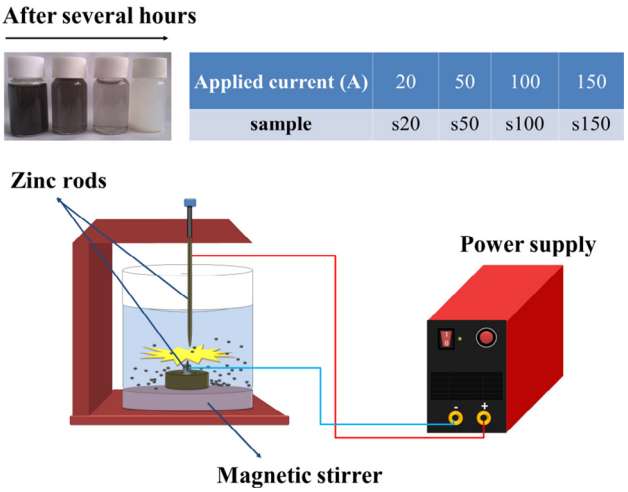

Fig. 1. Schematic representation of arc discharge setup in deionized water, samples s20, s50, s100 and s150 were synthesized with discharge currents of 20, 50, 100 and 150 A respectively.

of zinc in water. The oxidation process and composition of nanostructures monitored with UV–vis and X-ray diffraction spectroscopies in different time after synthesis.

2.3. Characterization and plasma diagnostic

Size and morphology of the samples were determined by field emission scanning electron microscopy (FESEM) (MIRA-TESCAN). Optical transmission spectra were recorded using SPUV-26 spectrophotometer. The crystallographic identifications were done by X-ray diffraction using the Philips X'Pert MPD system with wavelength of Co K_α radiation at $\lambda = 1.78897$ A°. Generated plasma during synthesis was characterized with optical emission spectroscopy by AvaSpec 3648-2 spectrophotometer. At last, transmission electron microscopy (TEM, CM30, Philips at 150 KV) was also used to confirm the spherical morphology of the nanoparticles.

3. Results and discussion

3.1. Shape and size of nanostructures

To prepare a proper coating for morphological studies a drop of synthesized ZnO colloid which was dispersed in ethanol 96% deposited on an aluminum film followed by drying in room temperature for few minutes. Fig. 2 presents SEM images of the samples and the corresponding histograms with Gaussian fit ascribed while this analysis was performed several days after colloid synthesis. Fig. 2a shows sample s20 with spherical shape and average diameter of 63 nm. In Fig. 2b, c and d aggregation of nano-spheres with different morphology are observed. Samples s50, s100 and s150 had average diameter size of 42, 37, 29 nm, and average length size of 114, 117, 120 nm, respectively. It can be seen that as the current increased, shape of the nanoparticles changed from spherical to bead-like aggregates and became smaller in diameter size. Fig. 3a illustrates particle diameter reduction and growth of bead lengths with increase of applied discharge current. Linear aggregation of nanoparticles may occur during synthesis or in oxidation process after synthesis. For further investigation of morphology and bead-like growth, TEM image of a typical sample with linear aggregates prepared. Fig. 3b shows TEM image of the as prepared sample s100; this figure indicate that nanoparticles are spheres while SEM image of this sample, Fig. 2c, demonstrates

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