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Research Paper

Impact of plasma treatment on quantum size effect

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Keywords

Plasma, quantum size, treatment

ABSTRACT

Nowadays, cold plasma technology is recognized as a prominent green synthesis and treatment method of nanomaterials which is chemical-free and cost-effective. Based on treating materials, cold plasma technology is operated by gas excitation via an applied energy source, leading to plasma generation with reactive chemical species, charged positive and negative particles, radicals, and heat energy. Considering the plasma characteristics in materials synthesis and treatment, the effect of exerting cold radio frequency low-pressure plasma on the quantum size effect of tungsten trioxide nanoparticles synthesized by cold direct current atmospheric plasma interaction with water was investigated. Nitrogen and argon radio frequency plasmas decreased the nanoparticles size, while oxygen radio frequency plasma increased the nanoparticles size. In oxygen plasma, the energy level approached the quasi-continuous band structure in bulk solid, and the band gap energy was reduced. In nitrogen and argon plasmas, the energy level approached quasi-discrete band structure, and the band gap energy increased.

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مقاله پژوهشی

تأثیر عملیات پلاسما بر اثر اندازه کوانتومی

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کلیدواژه‌ها

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چکیده

Nowadays, cold plasma technology is recognized as a prominent green synthesis and treatment method of nanomaterials which is chemical-free and cost-effective. Based on treating materials, cold plasma technology is operated by gas excitation via an applied energy source, leading to plasma generation with reactive chemical species, charged positive and negative particles, radicals, and heat energy. Considering the plasma characteristics in materials synthesis and treatment, the effect of exerting cold radio frequency low-pressure plasma on the quantum size effect of tungsten trioxide nanoparticles synthesized by cold direct current atmospheric plasma interaction with water was investigated. Nitrogen and argon radio frequency plasmas decreased the nanoparticles size, while oxygen radio frequency plasma increased the nanoparticles size. In oxygen plasma, the energy level approached the quasi-continuous band structure in bulk solid, and the band gap energy was reduced. In nitrogen and argon plasmas, the energy level approached quasi-discrete band structure, and the band gap energy increased.

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I. INTRODUCTION

The properties of materials at 1-100 nm sizes, such as melting point, electrical conductivity, chemical reactivity, and magnetic permeability, change greatly compared to large scales [1]. When the particle size is reduced to a certain value, the electron energy level near the Fermi surface changes from quasi-continuous to quasi-discrete. In other words, the energy level splits or the energy gap increases, which is referred to as the quantum size effect [2-3].

Nowadays, plasma technology has attracted much attention as a prominent green synthesis and treatment method of nanomaterials due to its distinctive properties compared with solid, liquid, and gas phase synthesis approaches. Plasma synthesis offers the possibility of high efficiency, short nanostructure growth time, low cost, and optimized material properties [4]. Synthesis by cold plasma, including plasma species such as ions, electrons, and atoms at different temperatures, promises non-thermal synthesis for a wide range of nanomaterials with high and low melting temperatures. Controlling the generation and transport of plasma species during the nucleation and growth of nanoparticles and nanostructures can lead to the controllable synthesis of nanomaterials with desired structures and properties [4-5].

Change and improvement are achieved in dispersion, mechanical properties, photocatalytic properties, hydrophobicity and hydrophilicity, corrosion and abrasion resistance, refractive index, wettability, and electrical conductivity of nanoparticles and their compatibility with other materials through various chemical and physical methods, such as plasma [6]. The plasma surface treatment includes all possible changes to a certain surface that plasma can create. Surface treatment relies on highly energetic electrons and ions hitting the surface of materials and creating changes on the surface, leading to oxidation, activation, functionalization, plasma polymerization, sterilization, or surface coating.

Considering the plasma potential in the synthesis and treatment of nanomaterials, the effect of exerting cold radiofrequency (RF) plasma was investigated on the quantum size effect of tungsten trioxide (WO_3) nanoparticles synthesized by the cold direct current (DC) atmospheric plasma-water interaction method.

II. MATERIALS AND METHODS

Figure 1 shows the practical setup for synthesis and treatment tungsten trioxide nanoparticles. As shown in Figure 1(a), tungsten trioxide nanoparticles were synthesized by the interaction of atmospheric pressure DC plasma of air with the water surface at 10 kV. The synthesis was started approximately 5 min after discharge and continued for 10 min. The Pyrex reactor chamber was filled with distilled water. Two tungsten rods were used as anode and cathode electrodes. During the experiment, the anode electrode was placed inside the water, and the cathode electrode was placed outside the liquid, on the water surface. Plasma was generated by applying a high potential difference between the cathode electrode tip and the water surface by a DC power supply. The atmospheric electrical discharge process for air was carried out for 10 min. After the discharge was completed, the synthesized nanopowder was collected on the inner wall of the reactor chamber. WO_3 nanoparticles were placed into an induction RF plasma reactor for treatment, in oxygen, nitrogen, and argon, as shown in Figure 1(b).

The resulting samples were examined through field emission scanning electron microscopy (MIRA3 FEG-SEM) and diffuse reflectance spectroscopy (DRS, UVS-2500) analyses.

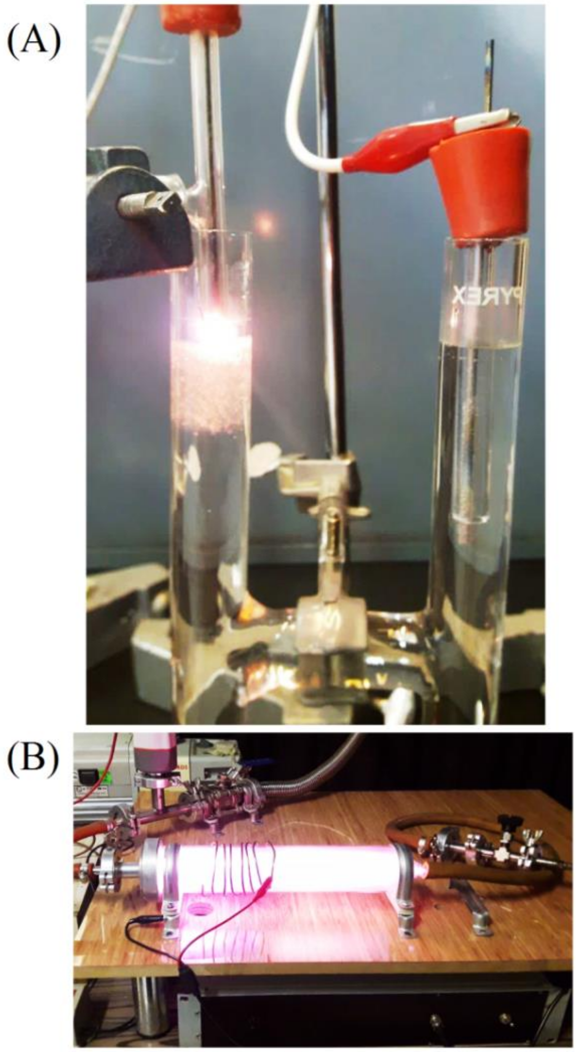
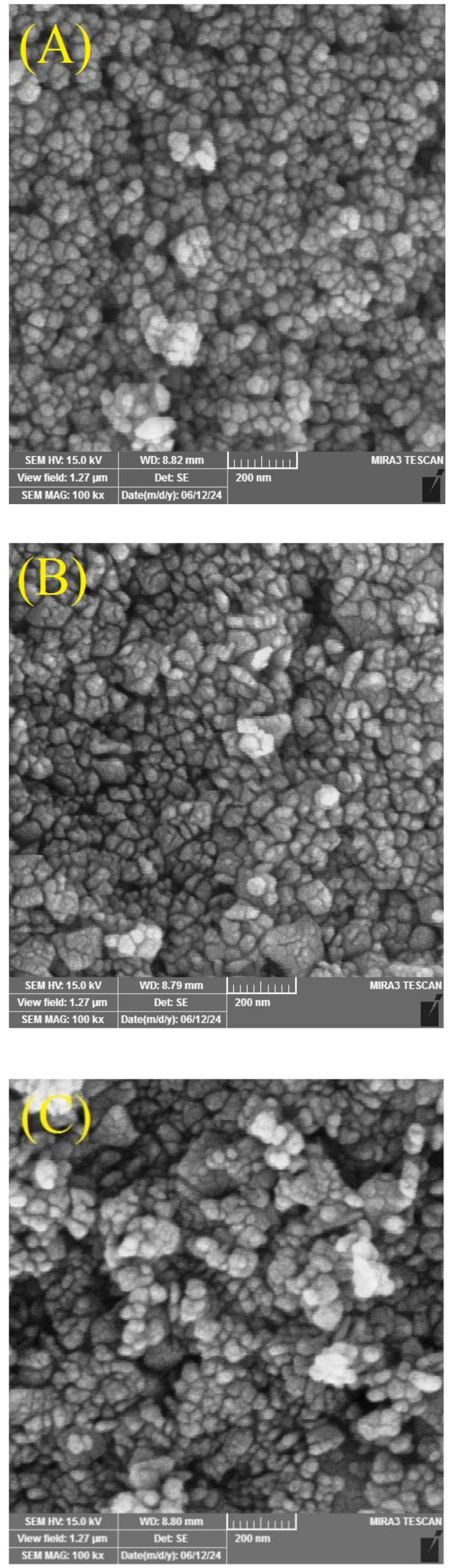


Figure 1. (a) Interaction of DC plasma with water surface synthesizing WO_3 nanoparticles and (b) RF plasma treating WO_3 nanoparticles.

III. Discussion

Figure 2 shows SEM images of WO3 nanoparticles before and after treatment. SEM images show that the nanoparticles are almost spherical and well separated and quite small in size, although large chunks of nanoparticles are occasionally observed.



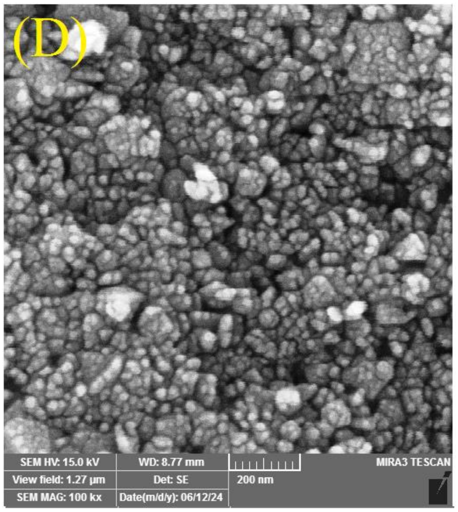
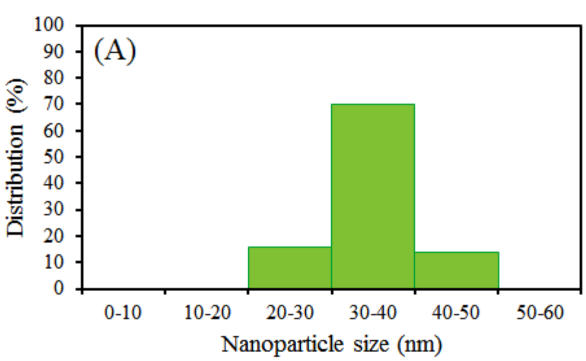
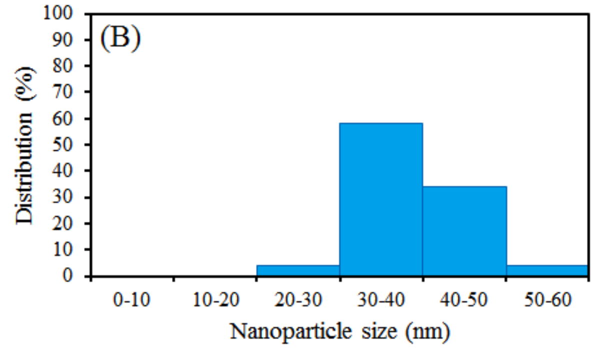
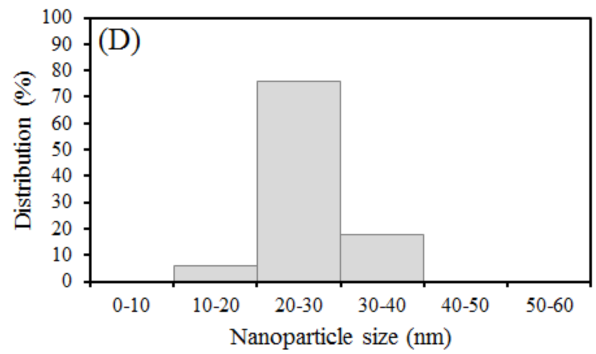


Figure 2. SEM images of WO_3 nanoparticles (a) before RF plasma, and after RF plasmas of (b) oxygen, (c) nitrogen, and (d) argon.

Figure 3 shows the particle size distribution histogram of synthesized and treated nanoparticles for 100 numbers in each case. According to SEM images and nanoparticle size distribution results, the size of WO_3 nanoparticles became larger after oxygen RF plasma treatment and smaller after nitrogen and argon RF plasma treatment. According to Figure 3, the highest distribution is at 30-40 nm before and after oxygen plasma treatment. It is at 20-30 nm after nitrogen and argon plasma treatment. In addition, the size of nanoparticles was observed to be more than 20 nm when synthesized and treated by oxygen RF plasma, and less than 20 nm when treated by nitrogen and argon RF plasmas, too.







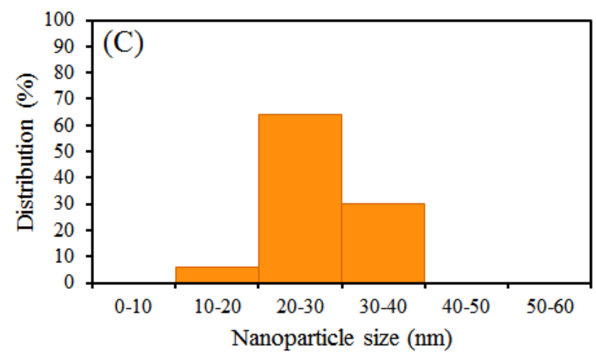


Figure 3. Particle size distribution histogram of WO_3 nanoparticles (a) before RF plasma, and after RF plasmas of (b) oxygen, (c) nitrogen, and (d) argon.

Figure 4 shows (a) the absorption spectrum and (b) the band gap energy plots of synthesized and treated nanoparticles. The band gap energy can be calculated from the absorption spectrum using the Tauc plot method, which involves plotting $(\alpha h\nu)^n$ versus $h\nu$, where α is the absorption coefficient, $h\nu$ is the photon energy, and n is a parameter that depends on the nature of the electronic transfer [7].

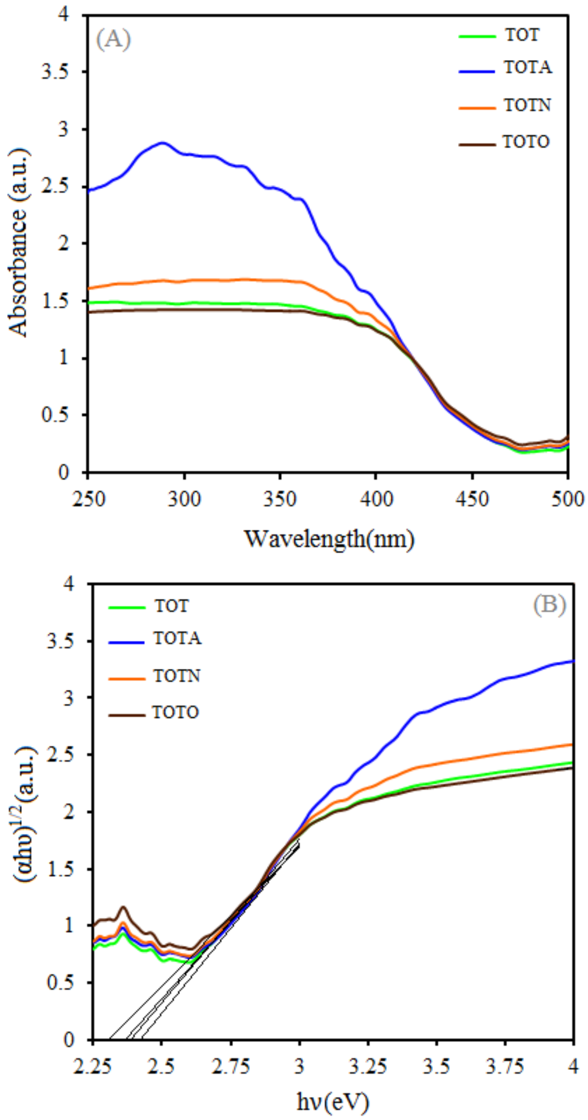


Figure 4. (a) Ultraviolet-visible absorption spectra and (b) band gap energy before and after oxygen, nitrogen, and argon RF plasmas of nanoparticles.

According to Figure 4(b), the band gap energy before RF plasmas was 2.77 eV. It increased after nitrogen and argon RF plasmas treatment to 2.81 eV and 2.86 eV, respectively, while it slightly decreased after oxygen RF plasma to 2.75 eV. Oxidation of cold plasma led to a change in the ratio of tungsten and oxygen atoms in the nanoparticles, which changed their crystal structure and decreased the band gap energy. The decrease in the band gap energy was caused by new energy levels in the electronic bands due to structural defects or new electronic states created by interactions with oxygen. The interaction between nitrogen or argon species in cold plasma and WO_3 nanoparticles changed the electronic structure, including hybridization and bonding type. The introduction of nitrogen or argon led to the formation of new energy levels within the band gap or the treatment of existing levels, and these changes increased the band gap energy.

IV. Conclusions

The results of SEM analyses, particle size distribution, and band gap energy calculations showed that, depending on the gas used to produce the plasma, a quantum size effect can be created in tungsten trioxide nanoparticles. Oxygen plasma treatment led to the energy level approaching a quasi-continuous band structure and reducing the band gap energy. On the other hand, nitrogen and argon plasmas treatment led to the energy level approaching a quasi-discrete band structure, and increasing the band gap energy. In other words, the particle size increased in oxygen plasma, the electron energy level near the Fermi surface moved away from the quasi-discrete energy level and approached the quasi-continuous energy level in the bulk solid. In nitrogen and argon plasmas, the particle size decreased, the electron energy level near the Fermi surface moved away from the quasi-continuous energy level and approached the quasi-discrete energy level. This phenomenon refers to the quantum size effect that created by plasma.

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