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Effect of UV light irradiation on the In_2O_3 nanoparticle films synthesis by the sparking method

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ABSTRACT

Sparking method has been demonstrated as a powerful method in nanoparticles synthesis. In this research, we proposed a UV light irradiation strategy to enhance the nanoparticle fabrication technique. The sparking method was performed under UV light irradiation without heat treatment for In_2O_3 nanoparticle films preparation. The results showed that UV light can effect on properties of In_2O_3 nanoparticle films as a function of light intensity. The mechanism was proposed based on photoelectric effect. Under UV light irradiation, the In_2O_3 nanoparticles aggregated and accumulated faster and efficiency of adhesion between particles during their collisions was improved. Additionally, the band gap energy of In_2O_3 decreased with increasing the intensity of UV light irradiation.

1. Introduction

The physical properties of semiconductor nanoparticles are strongly influenced by synthesis methodology, including crystalline structure, electrochemical performance, morphology and size. Recently, we developed a new procedure called sparking method for synthesis different nanoparticles materials. This methodology is simple, rapid and utilizes nontoxic starting materials. However, the sparking method could be further improved. For instance, the direction of nanoparticles prepared in the sparking method cannot controlled, leading to a low deposition rate of nanoparticle film on the substrate. Moreover, the nanoparticle film shows low crystalline quality. Several modifications to the sparking method have been investigated. For examples, applications of external magnetic fields [1] and magnetic/electric fields [2] led to increased uniformity and improved quality of the nanoparticle films. In the past, the use of UV light in assisted process to the synthesized of titania nanoparticles has also been reported. With application of UV light, the aggregation of TiO_2 particles in deionized water was detected, while no aggregation was observed without UV irradiation [3].

Here, we investigated the effect of UV light irradiation during the sparking method on properties of synthesized nanoparticle films. This irradiation-assisted process is a new advancement in sparking process to optimize the synthesis of metal oxide nanoparticles. The influence of UV light on the structure, morphology, and band gap energy of In_2O_3 films were examined and discussed in detail.

2. Experimental

Schematic diagram of the sparking apparatus used to deposit In_2O_3 on glass substrate was shown in Fig. 1(a). The wire tips were placed ~1.0 mm apart and ~8.0 mm above the center of substrates. The UV–visible lamp (40 W) was installed horizontally 15 cm away from the center of substrates. An indium wires (0.5 mm in diameter and purity of 99.999 %) were sparked by supplying a DC high voltage under atmospheric environment with and without UV light irradiation for 1 h. The intensity of UV light was varied into three conditions: no irradiation (No UV), 1 unit of UV intensity (1UV), and 2 units of UV intensity (2UV). The spectroscopic profiles of UV light conditions used in this research were shown in Fig. 1(b).

The structural, morphology, and optical properties of the In_2O_3 films

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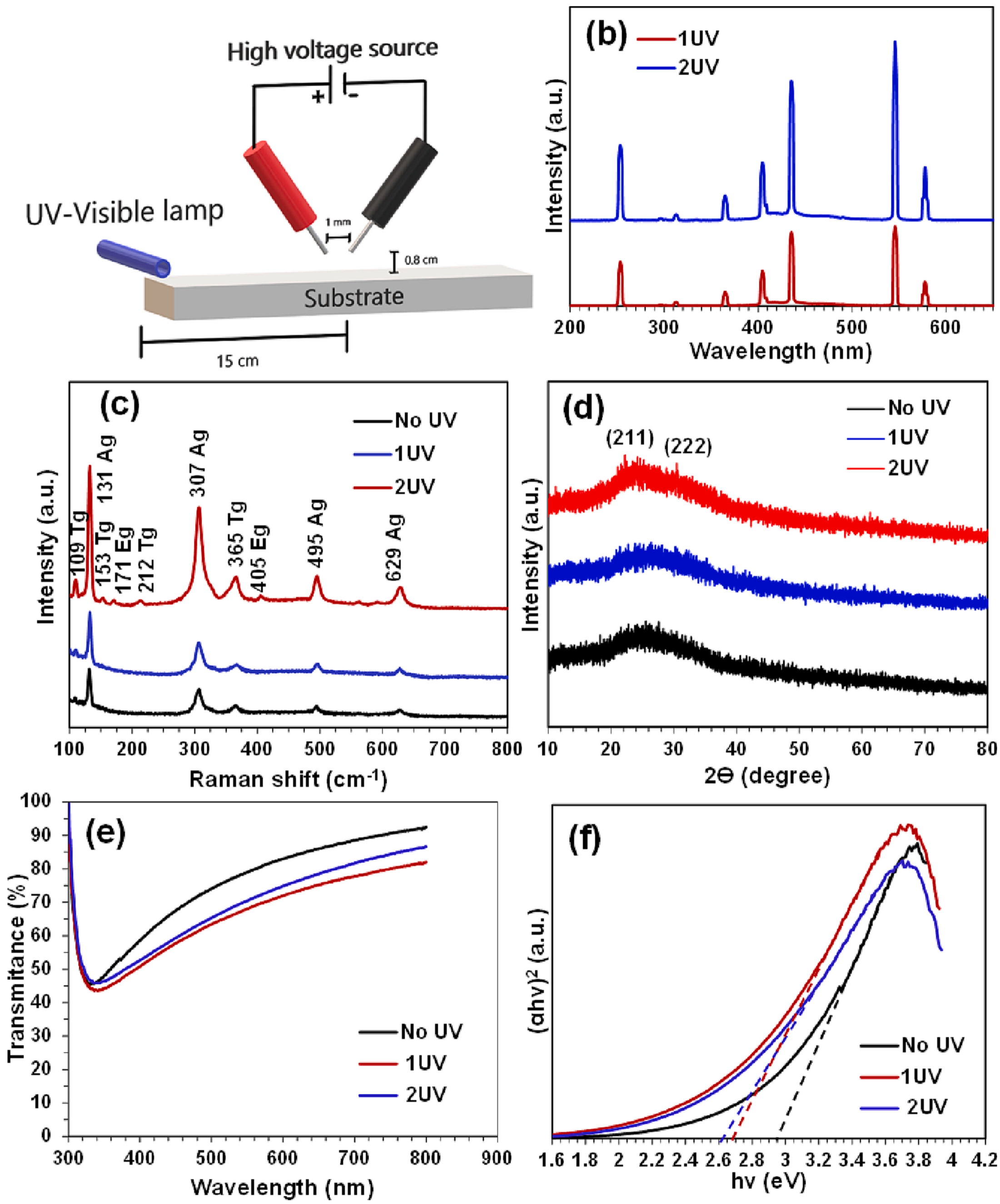

Fig. 1. (a) Schematic diagram of the sparking apparatus with UV irradiation and (b) the spectrum of UV–vis light used in this research. (c) Raman spectra, (d) XRD patterns, (e) UV–vis transmittance spectra of films and (f) the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for estimating band gap of the In_2O_3 films (dashed lines).

were characterized by several analytical techniques including X-ray diffraction (XRD, Rigaku MiniFlex600), Raman spectroscopy (T64000 HORIBA Jobin Yvon), FE-SEM (JEOL JSM 6335F) operating at 15 kV and UV–visible spectrophotometry (Perkin Elmer Lambda 25).

3. Results and discussion

Under different irradiation conditions, the prepared In_2O_3 films were analyzed using Raman spectroscopy to examine the crystal structure and impurity. As shown in Fig. 1(c), we found modes of A_g, E_g and T_g corresponded to the crystal structure of cubic In_2O_3 with space group $\frac{Ia\bar{3}}{T_h^7}$ [4] and observed no notable impurity peaks. Moreover, the increasing intensity of Raman spectra coincides with the intensity of UV light. This result suggested the higher crystallinity and/or the increase deposition rate of In_2O_3 nanoparticle films on the glass substrate. Fig. 1(d) shows XRD patterns of samples. For XRD analysis, peaks of In_2O_3 were observed only in the 2UV sample. As marked in the Fig. 1(d), the trace peaks were observed at 21.5° and 30.5°, in accordance with (211) and (222) plans of cubic In_2O_3, respectively (JCPDS no. 06–0416). This finding agrees with our previous works [5] as we found that metal oxide films synthesized by sparking method were barely measurable in XRD due to the interfering signal from the glass substrate, which is amorphous in nature. The optical transmittance (%) and energy band gap (E_g) were also affected by UV light intensity, shown in Fig. 1(e, f). The E_g of In_2O_3 decreased with increasing intensity of UV light. We estimated the band gap energies as 2.63, 2.70 eV and 2.95 eV for samples prepared under 2UV, 1UV and without UV light irradiation, respectively.

The prepared In_2O_3 nanoparticle films were also characterized with

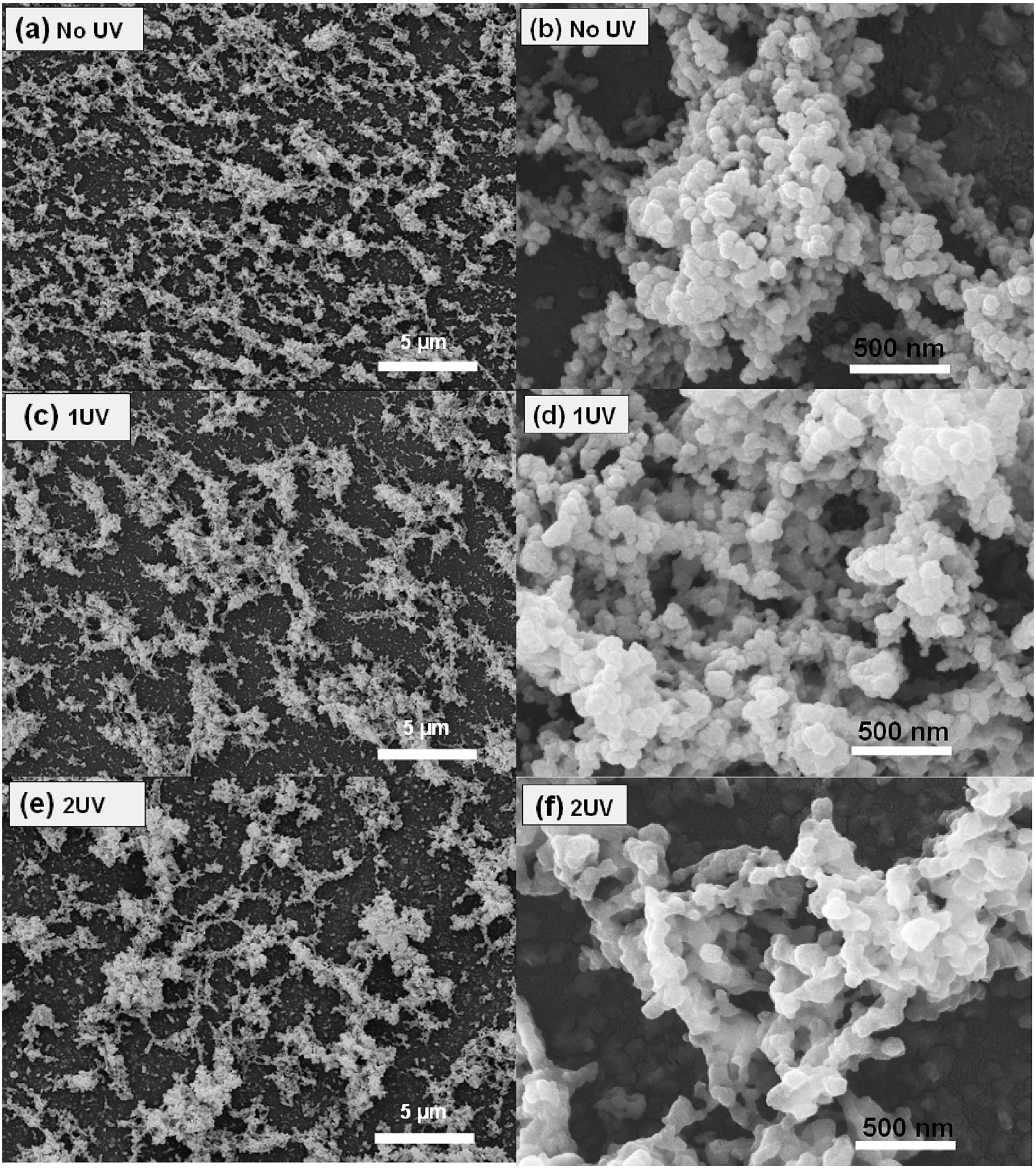

Fig. 2. SEM images of In_2O_3 nanoparticle films prepared by sparking method with different irradiation conditions. (a, b) without UV light, (c, d) with 1UV, and (e, f) 2UV light irradiation.

scanning electron microscopy (SEM), Fig. 2. The SEM images suggested that aggregate nanoparticles of In_2O_3 were agglomerated with a network-like structure. The film prepared without UV irradiation showed the aggregation of irregular particles (Fig. 2(b)). Interestingly, the morphology of In_2O_3 films prepared under UV light irradiation exhibited higher agglomeration and porosity characteristics. Furthermore, the compactness of aggregation also increase as a function of UV light intensity. These results also support that the decrease of E_g which was observed when nanoparticles size increase [6], as a result of UV irradiation.

To understand the effect of the UV light on the formation mechanism of nanoparticles, we have to revisit the phenomena occurred during the parking process. In brief, high voltage across two indium wires causes the spark discharges of high-energy electrons which then generate extremely high temperature. As a result, gas molecules in the sparking gap were ionized while indium wire surface was also melted and then

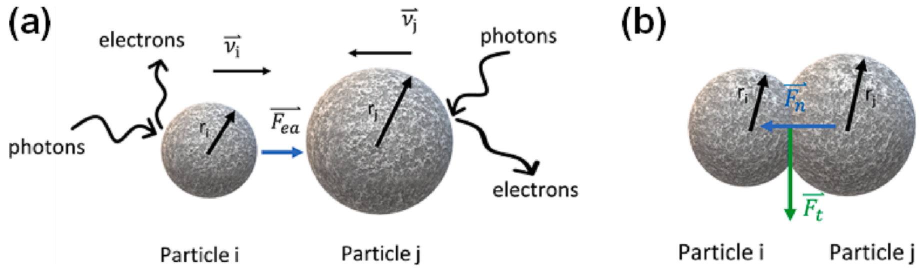

Fig. 3. Mechanisms model for the creation In_2O_3 nanoparticles by sparking process under UV irradiation.

evaporated. The molten indium was bombarded by high-energy ions and electrons in plasma which further nucleated indium nanodroplets with varying sizes and velocities. The oxidized indium nanoparticles in air were created and deposited onto the substrate [7]. In absence of UV light irradiation, the aggregation of nanoparticles should occur via collision at high temperature (Fig. 2(a, b)). On the other hand, the UV irradiation (250 nm) could lead to photoelectric effect on the surface since the energy of photon (4.96 eV) is higher than the work function of In_2O_3 (4.3–4.5 eV) [8]. Generally, the characteristics of particles such as Fermi energy, quantum yield and the photoelectron emission constant were controlled by particle size. Since the photoelectron emission constants of particles increased with the decreasing particle size [9], a smaller particle could emit more photoelectrons (e^-). Thus, a smaller particle became more positively charged than a larger particle leading to electrostatic attractive forces (F_{ea}) between particles which then promote collisions, accelerate the aggregation, and induce more accumulation of nanoparticles (Fig. 3(a)). After particle–particle contact, the action force on particle i ($\vec{F_i}$) with mass m_i in a system of N particles could be determined by a summation of interaction forces between particles ($\vec{F_{ij}}$) and gravity force ($m_i\vec{g}$) [10]:

$$\vec{F_i} = \sum_{i \neq j}^{N-1} \vec{F_{ij}} + m_i\vec{g} \approx \sum_{i \neq j}^{N-1} \vec{F_{ij}} \quad (1)$$

where $m_i\vec{g}$ was neglected for nano-size particle.

$$\vec{F_{ij}} = \vec{F_n} + \vec{F_t} \quad (2)$$

where $\vec{F_n}$ and $\vec{F_t}$ is normal and tangential forces, respectively.

The interactions between particles include sinter bridge force, electrostatic force, repulsive force, adhesive forces, attractive contact force and damping forces [10]. Additionally, when electrons were emitted from particles by absorption energy of photons, the positive charges were also amplified. With contact of a pair particle, the interfacial charge transfer occurred until their Fermi level reached equilibrium. The surface diffusion at high temperature could be accelerated by charge transfer event [11] which enhanced the sintering bridge of nanoparticles lead to neck formation between two particles. Furthermore, the increasing UV light intensity (higher number of photons) could contribute to increasing number of emitted photoelectrons, leading to the greater normal force and surface diffusion. For the above reasons, we propose that UV light effected the morphology of In_2O_3 nanoparticles through photoelectric effect in addition to increased collision rate and sinter bridge from elevated temperature.

4. Conclusions

The cubic In_2O_3 nanoparticle films deposited on glass substrates were successfully synthesized by sparking method with and without UV light irradiation. The results showed that morphologies, crystallinity, and energy band gap of In_2O_3 differed under varying irradiation conditions. The mechanism of aggregated nanoparticles with various size and velocity was proposed to be due to the photoelectric effect. The rate of aggregation and accumulation of In_2O_3 nanoparticles under irradiation increased in comparison with the rate of their spontaneous aggregation without supplied photons. The quality and quantity of In_2O_3 nanoparticle films were improved due to higher efficiency of adhesion between particles during their collisions.

CRediT authorship contribution statement

Rukpat Siriariyachai: Methodology, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Narubet Sirithuwanon:** Methodology, Investigation, Validation. **Ekkapong Kantarak:** Validation, Resources. **Wattikon Sroila:** Validation, Resources. **Tewasin Kumpika:** Validation, Resources. **Cholpisit Kiattisewee:** Writing – original draft, Writing – review & editing. **Apichart Limpichaipanit:** Methodology, Writing – review & editing. **Pisith Singjai:** Methodology, Resources, Supervision. **Orawan Wiranwetchayan:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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