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The Optical Properties of Sub-micrometer WS_2 Preparing Using Electrochemical Fabrication

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Abstract

Photonic band gap tunability is crucial in designing optoelectronic devices. Nanostructure semiconductors with tunable band gaps which depend on the dimensionality, have become the potential candidate for tunable nano optoelectronic devices. However, it has a lot of challenges in their fabrication such as the limited number of homogenous particles and high-cost production. As an alternative, sub-micrometer particles with the order of hundred nanometers are more easily fabricated and exhibit tunable optoelectronic properties. In this study, sub-micrometer WS_2 was fabricated using low-cost electrochemical methods. Two clusters of particles with the average size of 100 nm and 600 nm are observed. The number of sub-micrometer particles increases with the increasing of fabrication time. The photoluminescence spectra show wide peak centered around 800 nm suggesting the possible application in visible light emitting devices. The peak position varies with the time variation showing that the optical properties might be tuned during fabrication. This study points out that simple solution processed fabrication method can produce sub micrometer particles with tunable optical properties.

Keywords: WS_2;Electochemical method; Submicrometer particles; Optical properties; Photoluminescence

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1. Introduction

Particle sizes determine the optical and optoelectronic properties. The smaller the particle size the wider the band gap, which subsequently influences the light absorption and emission. Tremendous efforts have been conducted to modify the particle sizes and to obtain the expected tunable optical and optoelectronic properties. For example, the zero dimension quantum dot semiconductors are known to have superior optical properties in the range of visible and near infrared spectrum and have been attractive for display application [1-3], solar energy harvesting [4-6], biosensors [7-9], and other optoelectronic devices [10-12] The reproducibility of quantum dot fabrication are still quite challenging in order to bring these interesting materials to large scale production.

Transition metal dichalcogenide compounds (TMDCs) are the example of semiconductor material which can be easily engineered into low dimensional material and the band gaps are strongly dependent on the size and thickness. Various fabrication processes have been proposed to obtain single layer TMDCs such as mechanical exfoliation [13,14], liquid phase exfoliation [15,16], chemical vapor deposition [17,18], and electrochemical exfoliation [19,20]. Despite the great success in laboratory scale fabrication, it is still challenging to produce large scale low dimension TMDCs with simple and low-cost method. One of the challenges is the homogeneity of the low dimensional samples.

Previous studies reported the nanoscale TMDCs exhibit unique characteristics such as enhancement of photoluminescence [20,21], high hole mobility [22], and high capacitance [23]. They have been proposed for optoelectronic devices [24-25] and hole transport layer in solar cells [26].Furthermore the sub micrometer TMDCc particles also show interesting features such as high flexibility and conductivity [27,28], high current density [29], and adjustable light emission [30] which open for applications in sub-micrometer thin antennas [27], sub-micrometer channel of field effect transistor [28], supercapacitor electrode [29], and light source [30].

The WS_2 is one of TMDCs member with interesting properties such as high photoresponsivity [15], high intensity polarized photoluminescence [31], and easily blended to form heterostructure material [20]. Possing interlayer van der Waal interaction, the WS_2 is easily exfoliated along *c* direction. Regardless of the interesting properties, the large scale fabrication of sub-micrometer WS_2 is still challenging. The liquid phase exfoliation (LPE) is known as a simple method. However, it requires strong sonicator and is quite time consuming. In this study we expect to verify the ability electrochemical method (EM) to produce sub-micrometer WS_2. In contrary to LPE, the EM requires simpler as well as lower cost equipment and produces a comparable results. We applied 4 V external voltage and varying time up to 30 hours, we found that the optical properties of sub-micrometer WS_2 are varied. This preliminary work has shown that EM can be a potential technique for producing sub-micrometer TMDCs with interesting optical properties. Further investigation is required in order to find the more controllable fabrication process and larger scale production.

2. Research Method

In this research, sub-micrometer WS_2 was fabricated using the 0.2 gram WS_2 powder from Sigma Aldrich with particle diameter of 2 μm. The electrochemical process was conducted using carbon electrodes connected to 3 and 4 V external voltage. The electrolyte was 100 mL, 0.09M Phosphate Buffer Saline (PBS). The electrolysis process varied from 6 to 30 hours. The sample was checked every 6 hours.

The particle size was characterized using Horiba SZ-100 nano particle analyzer. The SU3500-SEM/EDX was used to characterize the morphology of WS_2 particle deposited on ITO/PET substrate. The absorbance spectra were measured using Evolution 220 UV-VIS spectrometer while the photoluminescence spectra were captured using Avantes Starline spectrometer.

3. Result and Discussion

The pictures of WS_2 solution as a function of fabrication times and two external voltages are shown Fig. 1. In the beginning, the solution is transparent. After 12 hours of electrochemical process the color starts changing into brown. The color becomes darker brown with the time increasing until 24 hours. There is no color change after 24 hours. The higher is the external voltage, the darker is the color suggesting more sub-micrometer particles are formed.

The particle size distribution after 18 and 30 hours modifications using 4 V external voltage are presented in Fig. 2. There are two clusters of particles with average sizes around 100 nm and 600 nm. With the increasing time of modification, the size of particles becomes smaller, and the number of sub-micrometer particles increases.

The optical properties of the sub-microparticles were studied by measuring the UV - VIS spectra and photoluminescence. The results are shown in Fig, 3 and 4. There are two main absorption peaks observed at 210 nm and 290 nm (Fig. 3). These peaks have been assigned as transition from low level of valence bands to higher level of conduction band [32]. The increasing electrochemical time did not change the absorption spectra significantly. It is only increase the number of particles as evidenced by the increasing of PSA frequency in Fig. 2. The typical morphology of WS_2 particles after 30 hours electrochemical process is shown by SEM image in Fig. 3. The particles tends to form micrometer flakes

The photoluminescence spectra at Fig. 4 (a) show two peaks at 530 nm and 630 nm associated with direct transition from valence to conduction band and exciton transition , respectively [32] . Fig. 4 (b) shows the relaxation dynamics of photoluminescence. There are relaxation time fitted to the experimental data, suggesting the possible existence of metastable states. The excited electrons experience a fast decay into the metastable states within 2 ns and subsequently decays to the ground state in a time of 5 ns.

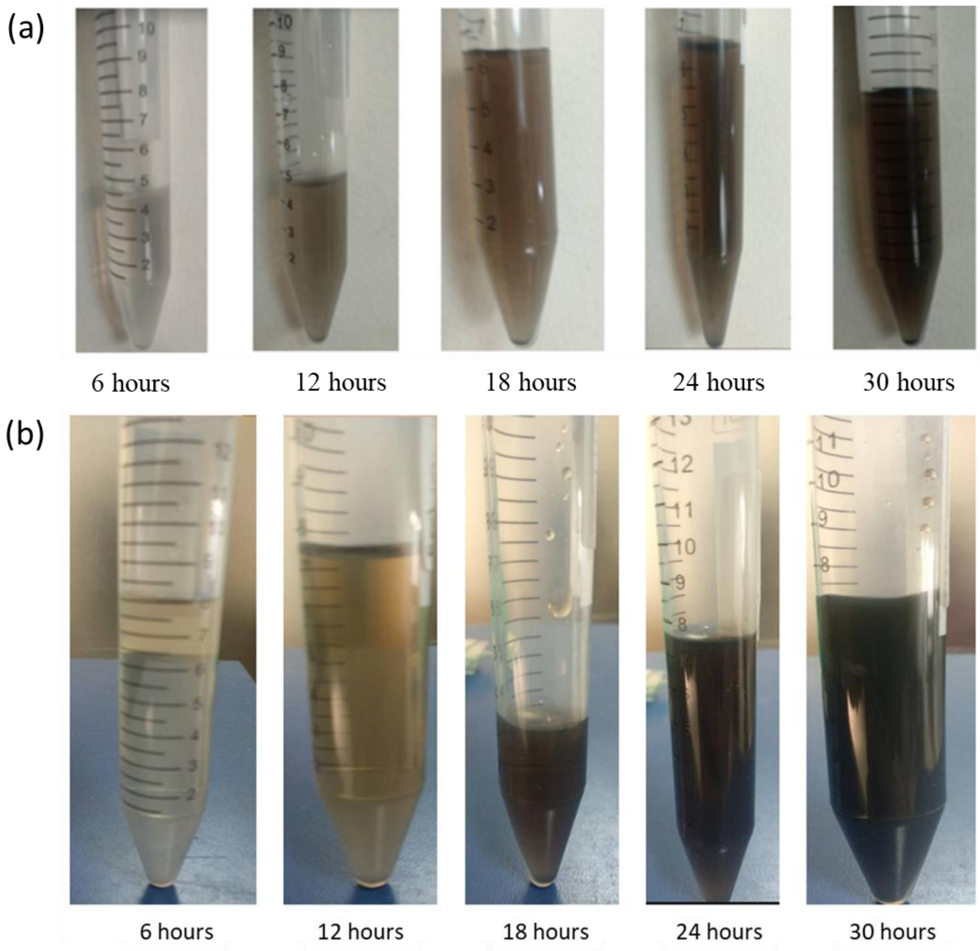

Fig. 1. The WS_2 solution as a function of fabrication time. The external voltage were (a) 3 V and (b) 4 V.

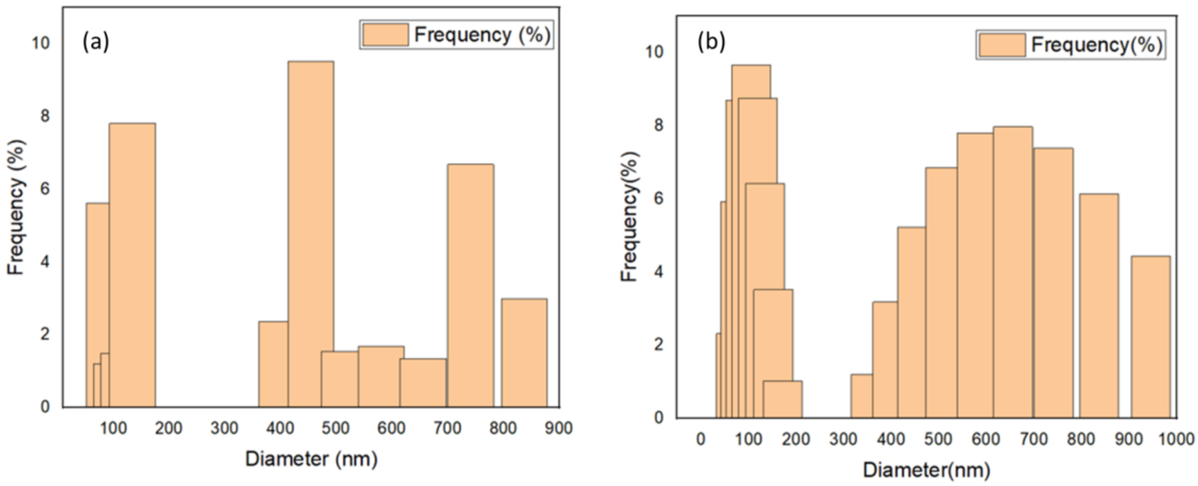

Fig. 2. The particle size distribution of WS_2 solution after (A). 18 and (B) 30 hours electrochemical process.

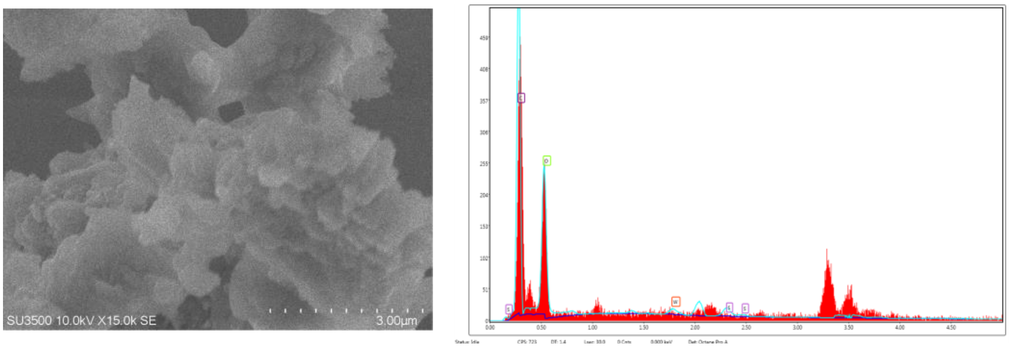

Fig. 3. The typical morphology of WS_2 deposited on ITO/PET

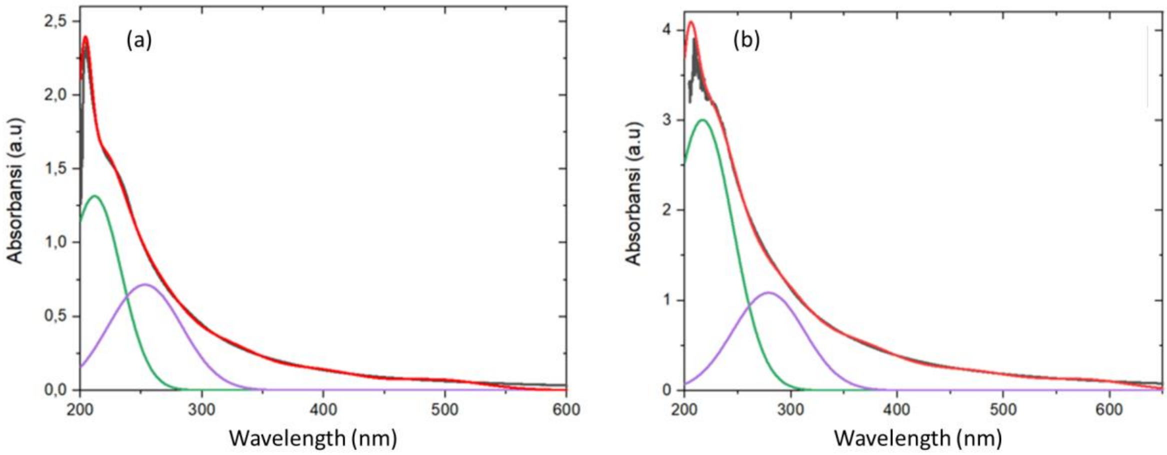

Fig. 3. The UV-VIS spectra of WS_2 solution after (a) 18 and (b) 30 hours electrochemical process. The laser excitation wavelength is 205 nm. Color lines are fitted with Gaussian function to show that the whole spectra consist of multiple peaks centered in various wavelengths.

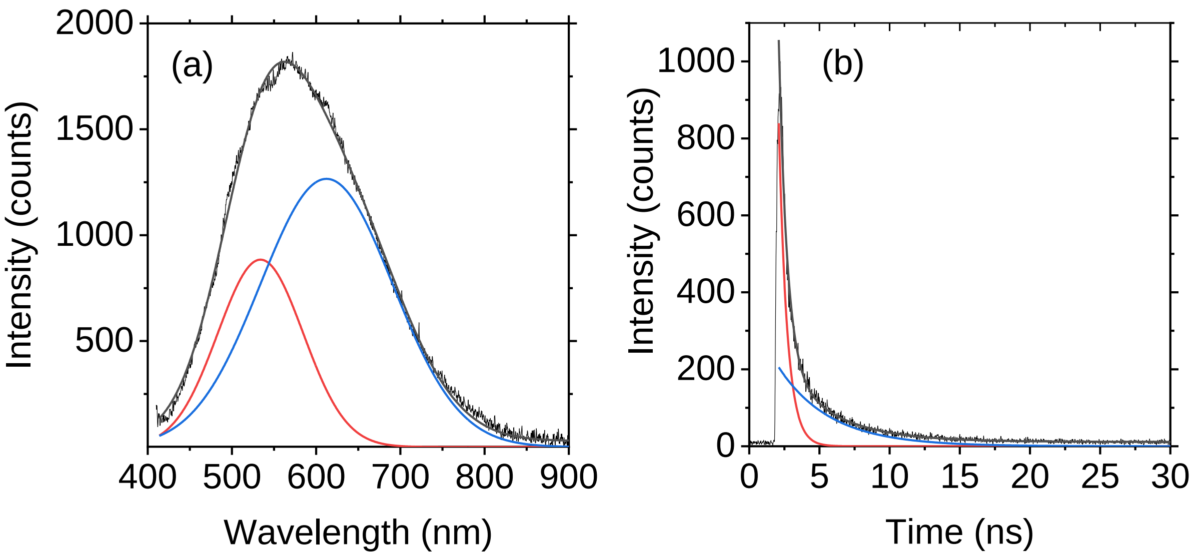

Fig. 4 (a) The photoluminescence and (b) the time resolved photoluminescence spectra of sub-micrometer WS_2. The red and blue lines at (a) to show the Gaussian fits while the ones at (b) to show the exponential fits.

4. Conclusions

In this study, the sub-micrometer WS_2 particles have been fabricated using low-cost electrochemical method. The higher is the external voltage, the more particles are produced. The concentration of submicro meter particles also increase with the increasing electrochemical time. However, there is no increase in the concentration after 30 hours of electrochemical processes. There are two clusters of submicro particles created in this study. Their average sizes are around 100 nm and 600 nm. The optical properties characterization observe two absorption peaks at 210 nm and 290 nm assigned as transition from low level of valence band to high level of conduction band. There are also two photoluminescence peaks at 510 and 630 nm associated with direct transition from valence to conduction band and exciton transition, respectively. The photoluminescence spectra exhibit two decay times suggesting the existence of metastable state in the material.

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