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Synthesis of Zinc Oxide Colloidal Spheres by Sol-gel Method

Sheen-Jeff Teh*, Yew-Keong Sin, Kah-Yoong Chan, Tai-Wenn Law

Centre for Photonic and Electronics Device (CPED), Faculty of Engineering, Multimedia University, Persiaran Multimedia, 63100 Cyberjaya, Selangor, Malaysia

*Corresponding author: tsjeff_89@yahoo.com

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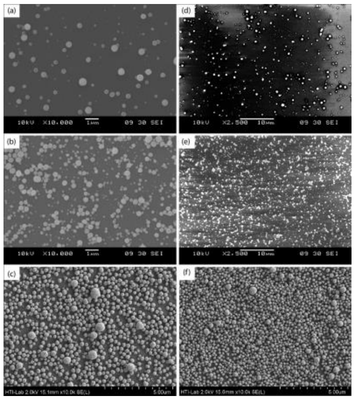
Graphical abstract



Abstract

In this paper, zinc oxide (ZnO) colloidal spheres structures were prepared by sol-gel method which is simple, effective and less costly. The scanning electron microscopy (SEM) images illustrated the ZnO colloidal spheres structures with diameter size ranging between 200–700 nm. The particle size distribution of colloidal spheres was determined by the added amount of supernatant in dehydration process. 3 mL and 6 mL of added supernatant were resulted particle size distribution dominant in the range of 250–400 nm and 150–250 nm, respectively. Transmission spectra demonstrated the photonic band gap (PBG) of colloidal spheres prepared with different amounts of colloidal suspension coating sample were near ultraviolet and violet region. The thermal annealing process was introduced to narrow the PBG width of colloidal spheres based on Bragg's law. Current-voltage measurement of ZnO colloidal spheres based thin film with particles size in the range of 150–250 nm showed that the resistivity of the thin film is 4.5 x 10^6 Ωcm.

Keywords: Zinc oxide; colloidal spheres; colloidal suspension; supernatant; photonic band gap; thin film

Abstrak

Dalam kertas ini, struktur koloid sfera zink oxida (ZnO) telah dihasilkan dengan teknik sol-gel. Teknik ini merupakan satu kaedah yang mudah, effektif dan kos rendah. Koloid sfera ZnO yang dihasilkan seterusnya dianalisis dengan mikroskop imbasan elektron (SEM), dan saiz koloid sfera didapati dalam julat 200–700 nm. Julat saiz partikel bagi koloid sfera dipengaruhi oleh kuantiti supernatant yang ditambahkan dalam proses dehidrasi. 3 mL dan 6 mL supernatant masing-masing telah ditambahkan untuk menyedia partikel yang berjulat saiz antara 250–400 nm dan 150–250 nm. Transmisi spektrum bagi koloid sfera ZnO yang disediakan dengan kuantiti supernatant yang berbeza menunjukkan jurang jalur fotonik adalah dalam jarak gelombang ultraungu dan ungu. Berdasarkan Hukum Bragg, proses penyepuhlindapan terma dapat digunakan untuk mengurangkan lebar jurang jalur yang disebabkan oleh struktur koloid sfera. Pengukuran arus-voltan koloid sfera filem nipis dengan saiz parikel dalam julat 150 –250 nm menunjukkan rintagan filem nipis tersebut adalah 4.5 x 10^6 Ωcm.

Kata kunci: Zink oxida; koloid sfera; koloid suspensi; supernatant; jurang jalur fotonik; filem nipis

■1.0 INTRODUCTION

Photonic crystals (PCs) have attracted great attention due to their periodicity lattice structure in dielectric, which enables them to control and manipulate the photon in the similar way as the electron governed by the semiconductor.[1-3] In ordered PCs nanostructures, light propagation are forbidden in certain frequency range known as photonic band gap (PBG). This phenomenon is based on the Bragg diffraction mechanism along different crystallographic directions and polarizations.[4-6] However, there are difficulties in synthesizing the micro and nano-periodical structures in three dimensions. One of the challenges is the disorder arrangement of the periodic structure of PCs. The disorder of crystal is due to the size dispersions of lattice displacement, building blocks and other imperfections that occur during the synthesizing process.[7] These impurities and defects lead to the propagating modes to lay within the PBG in the photonic density of states, causing difficulties for implementation of PC in various applications.[1,8,9] Up to date, colloidal self-assembly is one of the best methods to fabricate PCs with monodisperse colloidal spheres and minimum crystal disorder.[10]

Colloidal self-assembly is an inexpensive, relatively ease of processing and less time consuming method compared to the stepwise manner of fabrication techniques.[11] Various methods were used to study the self-assembling mechanism, for instances electrophoretic deposition,[12] gravitational sedimentation of colloids,[13] vertical deposition via evaporation,[14] ice crystallization,[15] fluidic cell method,[16] colloidal assembly at air-water interface [17] or on liquid metal surface[18] and sol-gel with spin coating.[19,20] Zinc oxide (ZnO) is an attractive material for broad range of piezoelectric, electronic and optical applications due to its excellent thermal, chemical and structural properties.[21] ZnO is a wide bandgap semiconductor material with relatively high refractive index (2.1-2.2) compared to the typical Silicon dioxide (1.4-1.5), and it has a large exciton binding energy of 60meV.[22] These properties make ZnO an alternative material to be fabricated as optically active colloidal spheres for PCs structure. Sol-gel method was chosen to be used in our study as it is relatively easier method to produce ZnO nanoparticles. There is also report shown that narrow size distribution and excellent crystallization ZnO colloids produced with sol-gel method.[20] In this paper, preparation of ZnO colloidal spheres by sol-gel method with varying amount of supernatant is investigated and the resulting structural and optical properties are discussed.

■2.0 EXPERIMENTAL

2.1 Sol Gel Synthesis of ZnO Colloidal Spheres

The synthesis of ZnO colloidal spheres involves 2 steps, hydrolysis and dehydration processes. The secondary reaction is to initiate a confine disparity of ZnO colloidal particles in the resulting suspension.[10] In the first step, 0.02 mol zinc acetate dehydrate (ZnAc) was added into 150 mL of diethylene glycol (DEG). This reaction solution was heated up to 180^0C. After reaching the working temperature, white precipitation of ZnO spheres occurred. The intermediate product was aged for 30 mins and centrifuged for 30 mins at 1400 rpm. The polydisperse powder was discarded and the remaining mixture (DEG, dissolved reaction products, and unreacted ZnAc and water) was known as the supernatant. The supernatant was used in subsequent dehydration processing.

In dehydration process, similar procedure and reaction as described in first step was performed where the solution mixture of 0.02 mol ZnAc and 150 mL DEG was heated up. Prior reaching to the working temperature, typically at 170^0C, different volumes of supernatant (3 mL and 6 mL) were added into the reaction solution. The temperature of the reaction solution dropped upon the addition, and the precipitation would typically occur at a lower temperature than without such an addition. After reaching the working temperature, the heat source was removed and the solution was stirred continuously for one hour. The ZnO colloidal spheres suspension was prepared as the reaction solution cooled down to room temperature. The size of the colloidal spheres varied dependently with the amount of supernatant added.[10,23]

2.2 Spin Coating Process of ZnO Colloidal Spheres into Thin Film

The ZnO colloidal suspension was dropped onto glass substrate and spun at 3000 rpm for 30 s. After spin coating process, a colloidal spheres film was deposited on the substrate surface. The film was then dried at 300^0C for 5 mins. This process evaporated the solvent and removed the organic residuals contained in the film. Multiple coating were deposited onto substrate by repeating spin coating and drying process on each coating. Then, the resulting films were inserted into furnace and annealed at 450^0C for 1 hour.

2.3 Aluminum Contact

Aluminum contacts with 500nm thickness were deposited on top of the ZnO colloidal spheres based thin film structure via sputtering method. These contacts were created to serve as current injection contact during the electrical characteristic. Current-voltage measurements of ZnO colloidal spheres based thin film with particles size in the range of 150–250 nm was performed by Keithley 238 Digital Multimeter.

■3.0 RESULTS AND DISCUSSION

3.1 Structural Properties of ZnO Colloidal Spheres

Figure 1 shows the scanning electron microscopy (SEM) images of colloidal spheres structures. Observation from Figure 1(a) to 1(f), the particles size distributions were analyzed and demonstrated. The size of colloidal spheres particle are analyzed and measured from the SEM images obtained in our results. By comparing Figure 1 from (a) to (b) to (c) and from (d) to (e) to (f), it is clearly illustrated that the concentrations of colloidal spheres structure increase with the amount of ZnO colloidal suspension coated on the sample. These are due to the self-assembly phenomena which occurs during the coating process. 0.7 mL, 3.5 mL and 6 mL of colloidal suspension were coated onto glass substrate via spin coating technique, as the colloidal spheres were coated onto the substrate, the colloidal spheres assemble spontaneously into specific ordered lattice structure.[24] From the results obtained, a more compact and closely pack colloidal spheres structure was obtained with greater amount of ZnO colloidal suspension used in the sample coating.

The colloidal spheres obtained in our experiment were neither completely closely packed nor perfectly well-ordered. These might be due to the temperature set for drying process is insufficient to evaporate the solvent, henceforth disrupting the self-assembly of the periodic arrays mechanism on the colloidal spheres.[10] In our experiment, 3 mL and 6 mL of supernatant from primary reaction were added into the dehydration stage (second step in synthesis) to form monodisperse colloidal spheres. However, the resulting colloidal spheres obtained in our samples have been yet to achieve the monodisperse colloidal spheres as expected. It should be noted that, the centrifugation and decantation process during preparation of supernatant are crucial to ensure maximal polydisperse ZnO spheres from primary solution are removed. Supernatant consisting of polydisperse spheres shall fail to produce monodisperse ZnO colloidal spheres[10].

The particles size difference was affected by the amount of supernatant added in second step of experiment. The size of the colloidal spheres varies inversely and monotonically with the amount of supernatant added. Similar trend of results were obtained by Seelig, *et al*.[10] Hence, it can be stated that, supernatant had the capability to initiate the release of smaller colloidal particles. These are shown in the particle size distribution in Figure 2 where a greater amount of supernatant added had produced smaller colloidal spheres size dominant samples. Figure 2(a) and 2(b) show the particles size distribution of colloidal spheres produced by 3 mL and 6 mL of supernatant. The particles diameter size is shown in Table 1 for comparison.

By comparing the 2 particle size distributions prepared by different amounts of supernatant, it can be observed that the sample prepared by 6 mL supernatant had a relatively narrower particle size distribution. This showed a better stability of particle size control with greater amount of supernatant used. These enable us to take control over the resulting size of colloidal spheres in the process. Therefore, it is possible to produce larger and smaller colloidal spheres size simply by manipulating the amount of supernatant added during the dehydration process in second step of sol-gel synthesis.

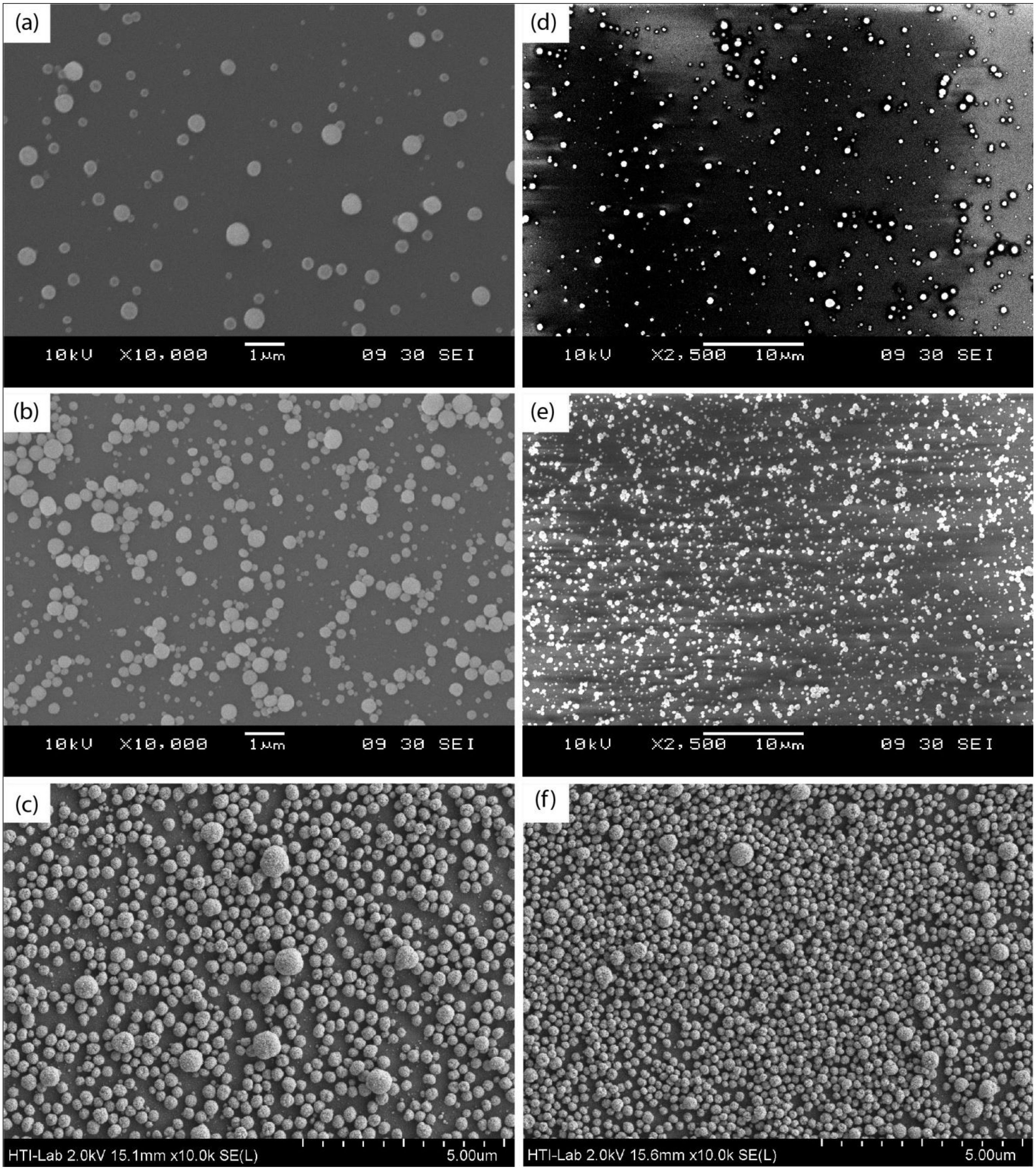
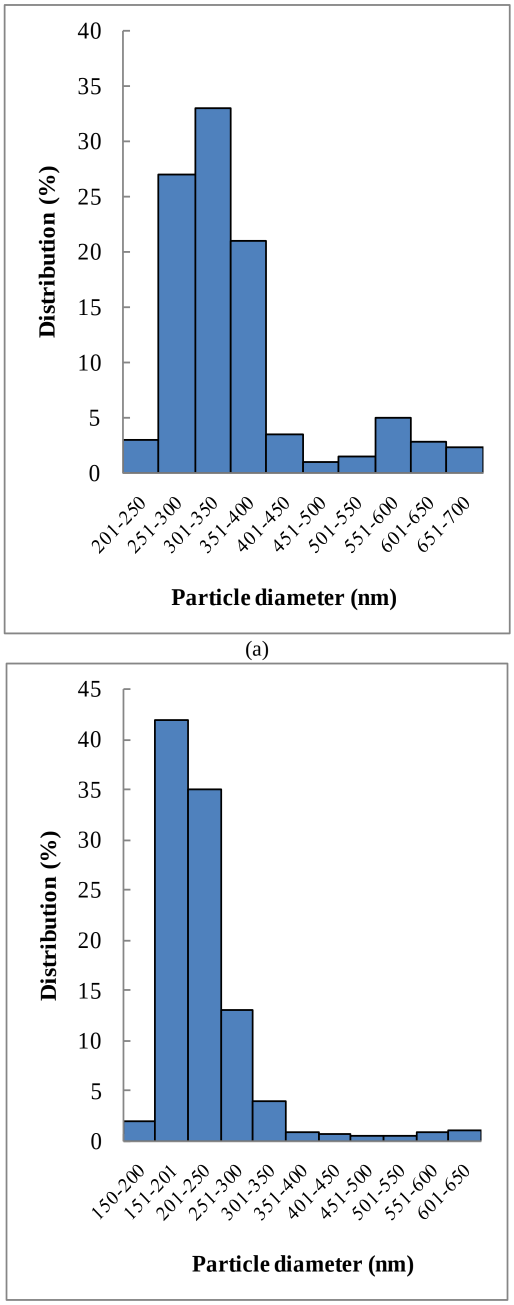


Figure 1 SEM images at 10 kx and 2.5 kx magnification of ZnO colloidal spheres prepared by 3 mL supernatant added (a) 0.7 mL ZnO colloidal suspension coated sample (b) 3.5 mL ZnO colloidal suspension coated sample (c) 6.0 mL ZnO colloidal suspension coated sample; and 6 mL supernatant added (d) 0.7 mL ZnO colloidal suspension coated sample (e) 3.5 mL ZnO colloidal suspension coated sample (f) 6.0 mL ZnO colloidal suspension coated sample



(a)

(b)

Figure 2 Particles size distribution of colloidal spheres with (a) 3 mL supernatant added (b) 6 mL supernatant added

Table 1 Particles diameter size of colloidal spheres prepared with different amount of supernatant

Amount of supernatant (mL)	Particles diameter size (nm)
3	250 – 400
6	150 – 250

3.2 Optical Properties of Colloidal Crystals

Transmission measurement is an effective technique to detect the presence and location of PBG. However, it might be difficult to quantify the width of the exhibited band gap as the measured area may include various periodic photonic domains, disorder and nil-gap exhibited area.[10] Hence, the trends of plots were confirmed by transmission measurements in different locations of the same sample. The transmission spectra of ZnO colloidal spheres prepared were investigated by the UV-VIS spectrum measurement on normal incident angle. The plots demonstrated a clear existence of absorption peak (known as PBG) on the wave transmission.

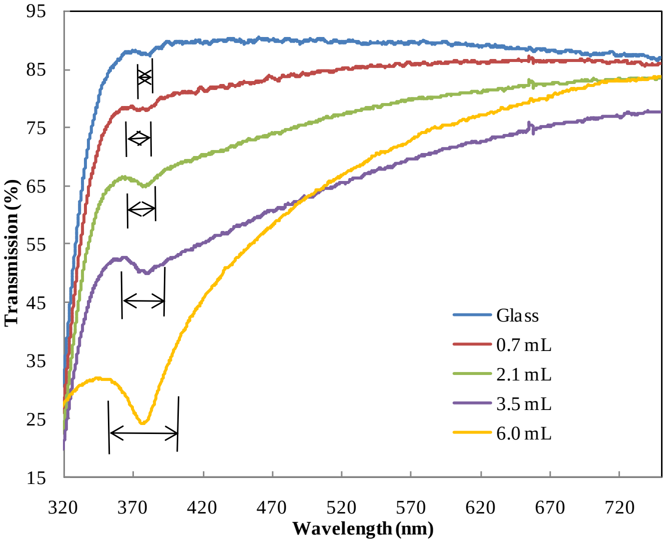


Figure 3 Transmission spectra from wavelength 320 nm to 750 nm of samples prepared with different amount of ZnO colloidal suspension

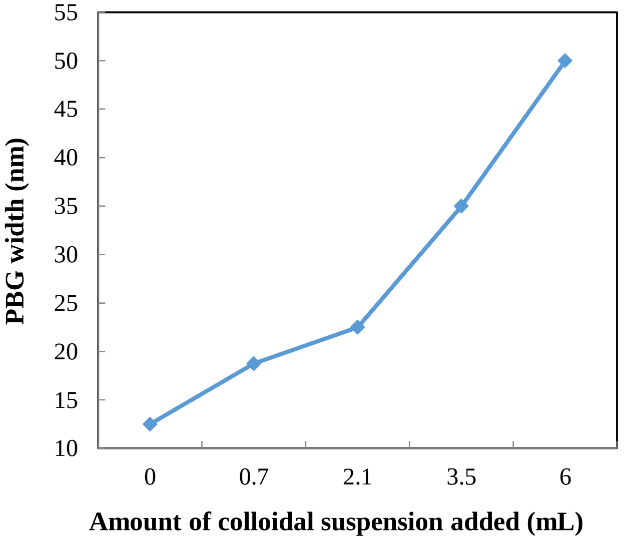


Figure 4 Plot of stop band width exhibited with amount of ZnO colloidal suspension coated

Different amounts of ZnO colloidal suspension coated samples were composed to analyze the PBG exhibited by the colloidal spheres. Colloidal spheres samples obtained from self-assembly by sol-gel method indeed show the sign of PBG.

PBG were obtained in all the samples at wavelength around 340-400 nm, near ultraviolet (NUV) and violet region. Figure 3 illustrated the increment of PBG width in higher amount of ZnO colloidal suspension coated samples. The PBG is not clearly shown in the glass sample; it started to broaden from 0.7 mL ZnO colloidal suspension coated sample up to 6 mL colloidal suspension coated sample. The PBG width of each sample was measured and shown in Figure 4. As the amount of ZnO colloidal suspension coated on samples was increased, the crystal of colloidal spheres will be overlapped together, creating acomposite film layer which forbids the light propagation over a wider range of wavelength and angles.

The effective PBG width was broadened by the presence of larger concentration of ZnO colloidal spheres produced.[2,25,26] This idea was further experienced by Wang and Yuan [25] where sample composed of colloidal crystal spheres of different sizes heterostructure were found to result in a wider broadened PBG and additive photonic bandgap properties. The colloidal spheres diameter has an important relationship with the exhibited PBG position.[27] The wavelength of the specular peak remarkably matched well with the diameter of the colloidal spheres produced.

It had been reported by Xie *et al*., where the PBG position have a blue shift as the diameter of colloidal spheres decrease.[24] The colloidal spheres produced in our experiment are not significant enough to distinguish the PBG position in the transmission spectra. From Figure 3, the PBG positions were obtained at 340–400 nm for colloidal spheres size of 150 - 250 nm. This is nearly consistent with the result obtained by Seelig *et al*., where the PBG position has a relation 2 times of ZnO spheres diameter.[10]

Thermal annealing plays an important role in controlling the optical properties of ZnO colloidal spheres. The PBG exhibited by the colloidal spheres can be tuned by manipulating thermal annealing process. Deng, *et al*., demonstrated the manipulation of both particle size and effective refractive index by varying the annealing temperature.[28] Annealing process may eventually cause the evaporation of chemically absorbed water molecules or moistures in the colloidal spheres structure. Arvind *et al*., also stated that a proper selected annealing temperature could produce a matter of viscous flow causing the colloidal spheres to bound together forming a closer pack structure.[29]

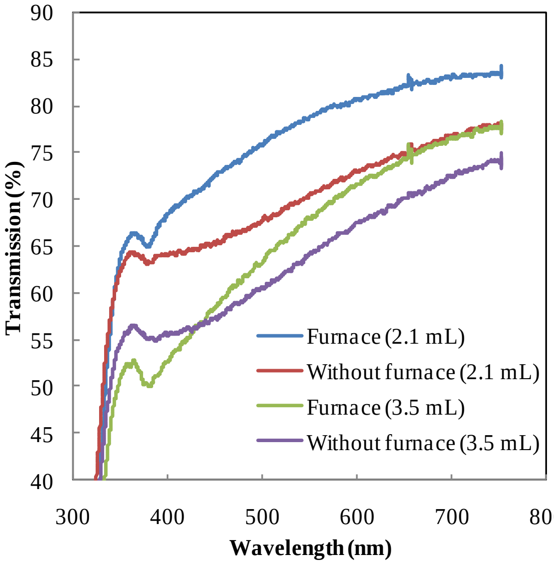


Figure 5 Transmission spectra from wavelength 300 nm to 800 nm of colloidal spheres samples treated with annealing and without annealing process. (The description are listed respectively according from top to bottom plots)

Figure 5 illustrates the effect of thermal annealing on the PBG of sample with different amounts of ZnO colloidal suspension coated. Samples treated with annealing process exhibit sharp peak absorption of PBG on the transmission spectra, whereas broaden and attenuation of PBG were obtained for samples without annealed. The sharp peak of PBG exhibited might be caused by the disorder introduced during the thermal annealing process[28] or it may be due to looser coating caused by larger spheres separation. These may create the existence of more disorder and cracks in the colloidal structure.[30]

3.3 Electrical Properties of Colloidal Spheres Based Thin Film

In order to study the electrical properties of ZnO colloidal spheres, spin coating process was repeated 30 times to deposit 21 mL of colloidal suspension on the glass substrate. This was to ensure the formation of thin film based structure of colloidal spheres for current-voltage measurement. The structure properties of the as-prepared thin film is shown in Figure 6. A closely packed colloidal spheres structure is clearly seen. The colloidal spheres particles size was found to be in the range of 150–250 nm with an approximate 2.5 µm in the thickness.

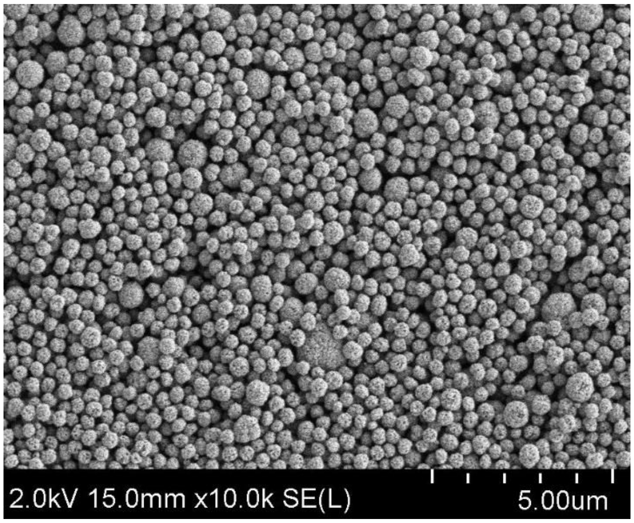


Figure 6 FESEM image at 10 kx magnification of ZnO colloidal spheres based thin film prepared by 30 times spin coating process

An aluminum contact was then deposited on top of the ZnO colloidal spheres thin film by sputtering method, to create an electrical connection known as contact metallization as shown in Figure 7. Our aim is to form a low resistance and fairly ohmic contact, the current-voltage measurement was then conducted to study the electrical properties of ZnO colloidal spheres based thin film and the relationship is shown in Figure 8.

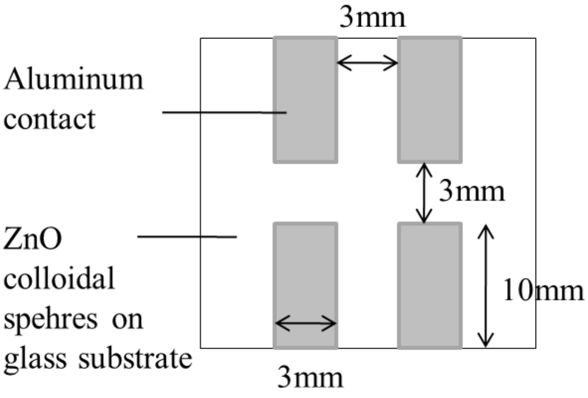


Figure 7 ZnO colloidal spheres based thin film structure prepared in our experiment

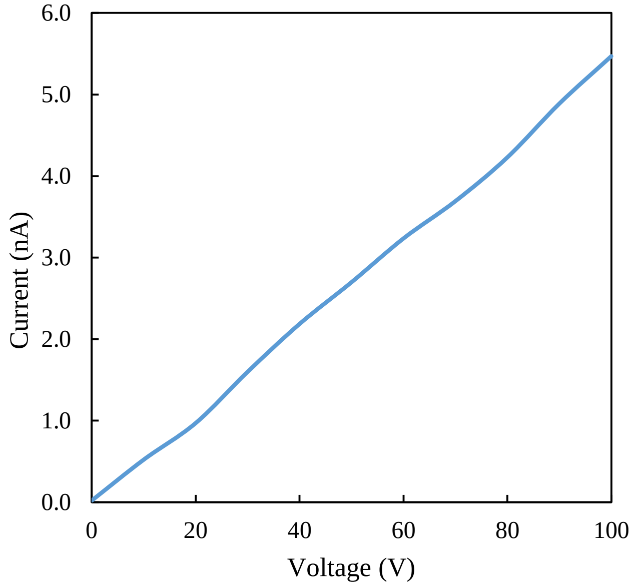


Figure 8 Current-voltage measurement for ZnO colloidal spheres based thin film

The resistivity of colloidal spheres based thin film was resulted at 4.5 x 10^6 Ωcm. The current obtained is ranged in nano ampere regime, which considered being a poor conductivity thin film. It was reported that the resistivity of undoped ZnO thin film range up to 10^7-10^8 Ωcm. The reduction of resistivity can be achieved by carefully control the substrate temperature during the deposition process.[31] Furthermore, the resistivity of ZnO thin film can be dramatically decreased by introducing different dopant.[32]

Study had shown that hydrothermally synthesized or grown ZnO crystals showed rather high resistivity, which is due to the solvents used can be readily contributed to charge compensation in the defective lattice.[33] Hence, it is to believe that self-compensation in the lattice of ZnO originating from its native defects or hydrogen impurities are the major problem to enhance the conductivity of ZnO.[34,35]

■4.0 CONCLUSION

In conclusion, ZnO colloidal spheres structures were successfully prepared on glass substrate by sol gel method. The size of colloidal spheres can be controlled by varying the amount of supernatant used. The PBG were revealed for all samples transmission spectra in our experiment. However, the crystal structures yet to achieve the desired completely closely packed and perfectly well-ordered. The preparation of supernatant shall be further studied in order to produce monodisperse colloidal spheres structures. Investigation on the thermal annealing process should be further explored to improve the optical properties of colloidal spheres in wider range of wavelength. Electrical conductivity of ZnO colloidal spheres based thin film was obtained to fall under nano ampere-regime with a biasing voltage up to 100 V. The fundamental study of electrical properties of ZnO nanostructure is essential for developing the future applications in nanoelectronics.

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