ZnO NANORODS GROWN ON PLASTIC PVC SUBSTRATE FOR ENVIRONMENTAL APPLICATION

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Abstract: *In this work, the hydrothermal growth of ZnO nanorods (NRs) on plastic PVC substrate is presented. It was shown that ZnO NRs with high density and high crystallinity can be successfully grown by implementing saturated nutrition solution of zinc nitrate hexahydrate ($Zn[NO_3]_2{\cdot}6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) without the assistance of a seed layer. The morphologies of the ZnO nanorods investigated by scanning electron microscope (SEM) demonstrated hexagonal structures. The crystallinity of the ZnO NRs was studied by photoluminescence (PL) spectroscopy. The as-grown ZnO NRs were then utilized for photocatalytic degradation of methylene blue.*

Keywords: ZnO nanorods; Hydrothermal method; Plastic substrate; Methylene blue.

1. INTRODUCTION

Nowadays, semiconductor nanostructures have attracted a lot of interest and are widely used in the construction of optoelectronic devices. Zinc oxide (ZnO) has been recognized as one of the most important n-type II–VI semiconductors because of their interesting optical and electrical properties. Besides unique properties such as direct wide band gap (3.37 eV), and large exciton binding energy (~ 60 MeV), ZnO is one of just several oxides that can be grown as a crystalline material at relatively low temperatures on various substrates including conductive substrates such as Au, Ag, Cu, ITO, FTO, etc. and non-conductive substrates such as amorphous glasses, fabric, and paper, etc.. As a result, ZnO nanostructures have been intensively applied in a wide range of applications such as: in dye-sensitized solar cells, chemical and biological sensors, piezoelectric, and thermoelectric devices [1–5].

In general, the fabrication of ZnO nanostructures can be done by using different techniques such as spray pyrolysis, sputtering, MOCVD, and hydrothermal method. Among those methods, hydrothermal method has been widely used due to its low temperature and low-cost fabrication process, and can be applied in different kinds of substrates such as GaN, Si, sapphire, ITO and FTO. However, due to the big difference in lattice mismatch between ZnO and substrates. Therefore, prior to the hydrothermal growth of ZnO, a seed layer of ZnO or a thin layer of Ag or Au is normally required to support the growth of ZnO nanostructures [6]. This results in a complex, multi-step fabrication process of hydrothermal method.

In this paper, ZnO nanorods (NRs) have been successfully synthesized on a low-cost plastic PVC substrate using a one step, simple, seedless, low temperature hydrothermal method. Without implementing a seed layer, ZnO NRs with high density, high crystallinity was still obtained. The surface morphology of the as-grown ZnO NRs was characterized by scanning electron microscopy (SEM) and their optical properties were studied using photoluminescence spectroscopy (PL). The as-grown ZnO NRs were then utilized for photocatalyst degradation of methylene blue (MB).

2. EXPERIMENTAL

The plastic PVC sheet was purchased from our local market. The plastic PVC sheet was cut into small pieces for substrate preparation. The substrates were first ultrasonically cleaned with acetone, ethanol, and deionized (DI) water sequentially. Then, the as-

prepared substrates were emerged into an equivalent saturated solution of 80mM zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and of 80mM hexamethylenetetramine ($C_6H_{12}N_4$) (Sigma Aldrich: http://www.sigmaaldrich.com). The substrates were placed in the solution with the temperature maintained at 90oC in 3 hours. Afterwards, the substrates were again rinsed with DI water to remove residual salts from the surface before being air-dried. The geometrical area for ZnO NRs growth was of approximately 4.5 cm x 10 cm.

Methylene Blue (MB), 95% pure, was purchased from Sigma Aldrich. 20 mg/L MB solution was prepared by dissolving a proper amount of MB with fresh DI water with fixed pH of 7.0.

For the photodegradation analysis, the prepared MB solution with concentration of 20 mg/L was transferred to a petri disk. An UV-C lamp was implemented as an irradiation source. The UV source was put 10 cm above the petri disk. All experiments were done at room temperature. The ZnO NRs sample was immersed completely in the solution without stirring. The setup was covered with a black box to avoid the influence of interfering light such as sun light or surrounding lamp light. The photocatalytic setup of the reaction is shown in Figure 1. The MB solution was collected for absorbance measurement every 10 min. The absorbance spectra of the solution with respect to time sample were determined with an UV VIS spectrophotometer.

The morphology of the sample surface was examined by scanning electron microscopy (SEM) (Nova NanoSEM 450). The crystallinity of the ZnO NRs was characterized by Photoluminescence (PL) spectrometry. The PL measurement was performed using a continuous wave HeCd laser operated at 325 nm as an excitation light source and a Princeton spectrometer (SP 2500i).

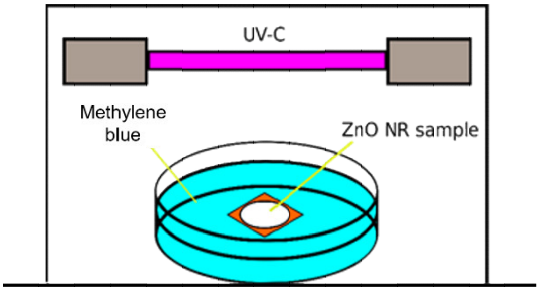


Figure 1. *Schematic setup for photocatalyst of methylene blue.*

3. RESULTS AND DISCUSSION

The chemistry of the hydrothermal growth of ZnO nanocrystals is well reported elsewhere [7–9]. $Zn(NO_3)_2 \cdot 6H_2O$ provide Zn^{2+} ions required for building up the ZnO NRs while $C_6H_{12}N_4$ hydrolyzes to produce formaldehyde and ammonia. Ammonia further hydrolyzes into OH^- and NH_4^+. The OH^- ion forms a complex compound with Zn^{2+} and then it decomposes into ZnO under given reaction conditions. In this work, a saturated concentration of $Zn(NO_3)_2 \cdot 6H_2O$ and $C_6H_{12}N_4$ was utilized to support the growth of ZnO without the assistance of a seed layer. The growth mechanism was attributed the fact that when the solution is saturated, the number of ion Zn^{2+} and OH^- is drastically increased. This resulted in the significant enhancement of ZnO nuclei which then formed a thin layer of ZnO on the surface. This thin layer can act as a seed layer to release the elastic strain resulted from the lattice mismatch between ZnO and the PCB surface. Subsequently, ZnO NRs began to grow on the surfaces without strain and defect. With this precursor concentration value, high density ZnO NRs can be obtained without implementing an additional ZnO seed layer.

Figure 2a shows the real images of ZnO NRs grown on the plastic substrate. As clearly seen in the figure, ZnO nanostructures were grown successfully on the plastic substrate. The surface morphology of the as-grown ZnO NRs is demonstrated in Figure 2b. The SEM image demonstrates that without the assistance of a seedlayer ZnO NRs with typical hexagonal structure still can grow with high density, and with well vertical alignment. The rods' diameter ranges from 50 nm to 500 nm.

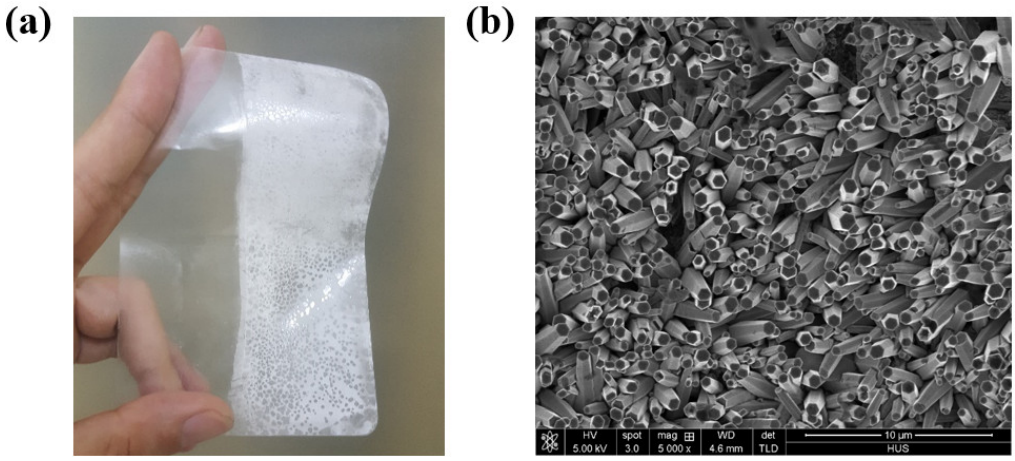


Figure 2. *(a) Optical image and (b) SEM images of ZnO NRs grown on plastic substrate.*

Figure 3 shows the room temperature PL spectra of the ZnO NRs, which contain a narrow UV emission peak and a weak broad green emission band. Centering at 384 nm (3.3 eV), the UV emission peak corresponds to the near-band-edge emission and free exciton peak of ZnO. On the other hand, the broad green emission band of the visible region is located at 570 nm (2.18 eV) and can be attributed to the intrinsic defects or oxygen vacancies in the ZnO, such as the single and double ionized oxygen vacancies. Also, the higher intensity in the UV emission band compared to that in the green emission band indicates the high crystallinity of the as-grown ZnO NRs which were seedless synthesized from the method.

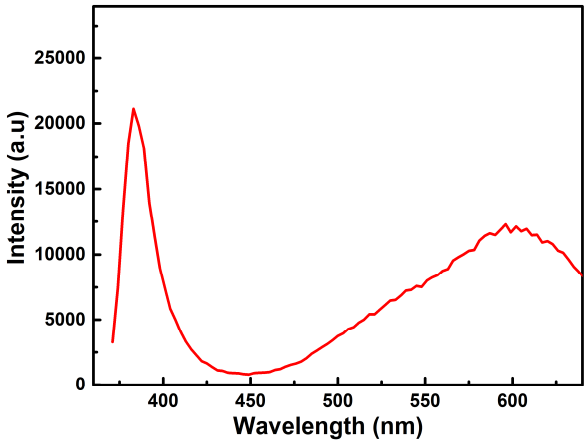


Figure 3. *Photoluminescent spectrum of the as-grown ZnO NRs on glass substrate.*

The photocatalytic activity of the as- synthesized ZnO NRs was investigated using the photodegradation of methylene blue under UV-C light irradiation. One PVC plastic sample with ZnO NRs grown on top were place within 20 mg/L MB solution without stirring. The MB solution was collected for absorbance measurement every 10 min.

Figure 4a demonstrates the absorbance intensity of MB solution with respect to treatment time. As clearly seen from the figure, the absorbance intensity was significantly reduced with the treatment time increased. The photodegradation efficiency of ZnO with respect to time is shown in Figure 4b. The percentage degradation was calculated using the equation. $Degradation = (A_0 - A_t)/A_0 \times 100\%$ where A_0 and A_t are the absorbance values at the initial stage and at time t, respectively. That means more than 25 % of all of the organic dyes studied were degraded within 60 min under UV-light irradiation. With similar MB concentration and similar active area of ZnO NRs, the degradation efficiency of the as-grown ZnO NRs after 60 min is compatible with that of ZnO NRs grown on Si substrate by multi-step chemical bath deposition, and Carbothermal Reduction Vapor Phase Transport techniques [10]. Note that, in this published work, the Si substrate was deposited by a thin layer of ZnO prior to implementing the synthesized technique. Note that, in this work, the ZnO NRs were grown on the cost-effective PVC substrate by only one-step, seedless hydrothermal method. The high catalytic activity of the as-grown ZnO NRs may be attributed to the crystallinity of the ZnO samples.

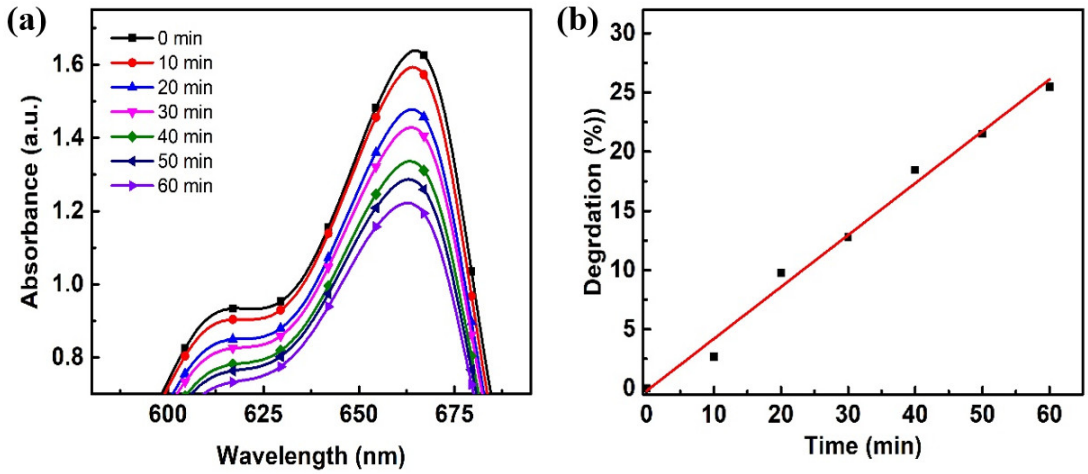


Figure 4. *(a) The absorbance spectra of the Methylene Blue solution corresponding with treatment time; (b) The degration of Methylene Blue as a function of time.*

4. CONCLUSION

In this study, ZnO NRs grown on low-cost effective PVC plastic substrates were obtained by using a seedless, one-step hydrothermal method. The SEM and the PL spectra have confirmed the high-crystallinity, high-density of the as-grown ZnO NRs. The as-grown ZnO NRs were then utilized for MB photocatalytic photodegradation. The results shows that after only 60 min, more than 25 % of MB was degradated which is compatible with published work. This gain confirms the potential of the as-grown ZnO NRs for environmental applications.

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REFERENCES

[1]. F. Yi *et al.*, "*Simple fabrication of a ZnO nanorod array UV detector with a high performance,*" Phys. E Low-dimensional Syst. Nanostructures, **vol. 61**, pp. 180–184, (2014).

[2]. J.Chen, Xingbin Yan and Qunji Xue, "*ZnO Nanorod Arrays Applied as Broad-Spectrum Sensors for Detecting Various Volatile Organic Solvents,*" Nanosci. Nanotechnol. Lett., **vol. 4**, (2012).

[3]. H. L. *et al.*, "*Electroluminescence from ZnO-nanorod-based double heterostructured light-emitting diodes,*" Appl. Phys. Lett., **vol. 103**, p. 123504, (2013).
[4]. L. Huang *et al.*, "*ZnO nanorods grown directly on copper foil substrate as a binder-free anode for high performance lithium-ion batteries*," Int. J. Electrochem. Sci., **vol. 11**, pp. 8439–8446, (2016).
[5]. H. H. Mai, V. T. Pham, V. T. Nguyen, C. D. Sai, C. H. Hoang, and T. B. Nguyen, "*Non-enzymatic Fluorescent Biosensor for Glucose Sensing Based on ZnO Nanorods,*" J. Electron. Mater., **vol. 46**, pp. 3714–3719, (2017).
[6]. M. Willander, O. Nur, S. Zaman, A. Zainelabdin, N. Bano, and I. Hussain, "*Zinc oxide nanorods/polymer hybrid heterojunctions for white light emitting diodes,*" J. Phys. D. Appl. Phys., **vol. 44**, (2011).
[7]. J.-M. Jang, J.-Y. Kim, and W.-G. Jung, "*Synthesis of ZnO nanorods on GaN epitaxial layer and Si (100) substrate using a simple hydrothermal process,*" Thin Solid Films, **vol. 516**, pp. 8524–8529, (2008).
[8]. Y. Sun, D. J. Riley, and M. N. R. Ashfbld, "*Mechanism of ZnO nanotube growth by hydrothermal methods on ZnO film-coated Si substrates,*" J. Phys. Chem. B, **vol. 110**, pp. 15186–15192, (2006).
[9]. V. Errico, G. Arrabito, S. R. Plant, P. G. Medaglia, R. E. Palmer, and C. Falconi, "*Chromium inhibition and size-selected Au nanocluster catalysis for the solution growth of low-density ZnO nanowires,*" Sci. Rep., **vol. 5**, p. 12336, (2015).
[10]. A. P. P. da Rosa *et al.*, "*Photoelectrocatalytic Degradation of Methylene Blue Using ZnO Nanorods Fabricated on Silicon Substrates,*" J. Nanosci. Nanotechnol., **vol. 20**, pp. 1177–1188, (2019).

TÓM TẮT

ỨNG DỤNG THANH NANO ZnO MỌC TRÊN ĐẾ NHỰA PVC

Trong nghiên cứu này, thanh nano ZnO được tổng hợp trên đế nhựa PVC bằng phương pháp thuỷ nhiệt trong môi trường dung dịch bão hoà gồm Kẽm nitrate hexahydrate ($Zn[NO_3]_2{\cdot}6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) không sử dụng lớp mầm. Thanh nano ZnO được tổng hợp với mật độ dày và độ kết tinh cao. Kết quả ảnh hiển vi điện tử quét (SEM) cho thấy, thanh nano với hình thái lục giác đều. Độ kết tinh của thanh nano ZnO được đánh giá bằng phổ huỳnh quang. Thanh nano ZnO được ứng dụng làm mất màu xanh methylene.

Từ khóa: Thanh nano ZnO; Phương pháp thuỷ nhiệt; Đế nhựa PVC.

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