

Low-temperature growth of well-aligned zinc oxide nanorod arrays on silicon substrate and their photocatalytic application

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Abstract: Well-aligned and single-crystalline zinc oxide (ZnO) nanorod arrays were grown on silicon (Si) substrate using a wet chemical route for the photodegradation of organic dyes. Structural analysis using X-ray diffraction, high-resolution transmission electron microscopy, and selected area electron diffraction confirmed the formation of ZnO nanorods grown preferentially oriented in the (001) direction and with a single phase nature with a wurtzite structure. Field emission scanning electron microscopy and transmission electron microscopy micrographs showed that the length and diameter of the well-aligned rods were about ~350–400 nm and ~80–90 nm, respectively. Raman scattering spectra of ZnO nanorod arrays revealed the characteristic E₂ (high) mode that is related to the vibration of oxygen atoms in the wurtzite ZnO. The photodegradation of methylene blue (MB) using ZnO nanorod arrays was performed under ultraviolet light irradiation. The results of photodegradation showed that ZnO nanorod arrays were capable of degrading ~80% of MB within 60 minutes of irradiation, whereas ~92% of degradation was achieved in 120 minutes. Complete degradation of MB was observed after 270 minutes of irradiation time. Owing to enhanced photocatalytic degradation efficiency and low-temperature growth method, prepared ZnO nanorod arrays may open up the possibility for the successful utilization of ZnO nanorod arrays as a future photocatalyst for environmental remediation.

Keywords: ZnO, nanorods, XRD, photodegradation

Introduction

Increased industrialization is posing a threat to human health in the form of environmental pollution. Environmental remediation of organic pollutants by photocatalytic degradation using wide bandgap semiconductors has attracted considerable attention in recent times.^{1–4} Further, these materials, in a nanostructured form, exhibit enhanced properties and therefore have potential application such as the fabrication of nanodevices. Various semiconductors, including zinc oxide (ZnO) and titanium dioxide (TiO₂), are being used in photocatalytic application because they have a low-cost, high-photosensitivity, nontoxic, and environmentally friendly nature.^{5,6} ZnO is established to be a more efficient photocatalyst than TiO₂ because of its high surface reactivity, owing to its large number of active surface defect states. It has also been shown that ZnO has high reaction and mineralization rates⁷ because of its more efficient hydroxyl ion production.⁸ When ZnO is irradiated with ultraviolet (UV) light, electrons are excited from the valence band to the conduction band and electron–hole pairs are created. These electron–hole pairs activate the surrounding chemical species and then promote the chemical reactions.^{9,10} As photocatalytic activity of metal

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oxide nanostructures depends on the surface area and surface defects, one-dimensional nanostructures such as nanowires/nanorods are ideal candidates for the application in photocatalysis, because they offer a larger surface-to-volume ratio than nanoparticulate thin films.¹¹

Photocatalysis using suspended nanoparticles is an efficient method for removing pollutants in a liquid. However, the successive removal of the nanoparticles from the liquid can be cumbersome and includes an additional process step. Also, freely suspended nanoparticles can enter the human body through skin pores and may lead to health-related problems.¹² Therefore, it is advantageous if the nanoparticulate photocatalyst is attached to a support. The importance of catalyst support has been discussed by Pozzo et al,¹³ who observed an inverse relationship between the adhesion of a catalyst to a support and its photocatalytic activity. Thus, ZnO nanorods, which can be strongly attached to any type of substrates through proper surface treatment before seeding,¹⁴ might be an attractive choice for photocatalytic applications. Various one-dimensional ZnO nanostructures, such as nanobelts, nanowires, nanorods, and nanotubes,¹⁵⁻¹⁸ have been reported in literature. Several methods have been employed for synthesizing ZnO nanorods, such as thermal evaporation, chemical vapor deposition, physical vapor deposition, and electrochemical processes.¹⁹⁻²² However, these methods require vacuum conditions, a high temperature, sophisticated equipment, and other rigid experimental conditions, which may increase the cost. Comparatively, the solution approach is more attractive for its simplicity, commercial feasibility, and good potential for large-scale production. Wet chemical synthesis has been proven to be a versatile approach for the growth of ZnO nanorod arrays, due to its convenience, simplicity in fabrication, environmentally friendly reactions, low temperature, large-scale production, and high crystalline quality.

In this work, ZnO nanorod arrays on an Si substrate were grown using a wet chemical route for the photodegradation of organic dyes. The presented work may open up the possibility for the successful utilization of ZnO nanostructures as a future photocatalyst.

Experiment

Well-aligned ZnO nanorod arrays were synthesized on the ZnO particles deposited on an Si (100) substrate using high purity analytical grade chemicals (Sigma-Aldrich, St Louis, MO, USA). To obtain the final product, a two-step low-temperature wet chemical method was followed. Initially, ZnO nanoparticles were synthesized by acetate route and

were used as a seed layer on an Si substrate. Afterwards, ZnO nanorods were grown on the seeded layers. ZnO nanoparticles acted as the nucleation center for the formation of ZnO nanorods on the Si substrate.

Preparation of the ZnO seed layer

ZnO nanocrystals to be used as the seed layer were synthesized by the acetate route. Prior to coating, Si substrate was cleaned ultrasonically for 10 minutes, first in acetone and then deionized water, to remove any impurity and oxide layer. In a typical synthesis procedure, 20 mM zinc acetate dihydrate ($\text{Zn}[\text{CH}_3\text{COO}]_2 \cdot 2\text{H}_2\text{O}$) and 10 mM sodium hydroxide (NaOH) solution in ethanol was mixed in a beaker and kept at 70°C for 2 hours under stirring, to produce a white suspension of ZnO seeds. Subsequently, the suspension was used to produce a seed layer on an Si substrate by a drop casting method. The coated Si substrate was dried at 200°C in an oven for 1 hour to attain better adhesion of the seed particles to the substrate.

Fabrication of ZnO nanorod arrays

A solution containing 0.2 M aqueous solution of zinc nitrate hexahydrate ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$) and 0.01 M hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) was prepared in a beaker. The seeded Si substrate described in the previous section was kept inverted (seeded surface facing downwards) inside the beaker. The reaction was allowed to take place for 2 hours at 70°C. Lastly, the Si substrate now with ZnO nanorods was thoroughly washed with deionized water to eliminate residual salts and dried in air at 80°C for 2 hours before characterization.

Various characterizations were carried out on the as-obtained product, such as X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with $\text{CuK}\alpha$ radiations ($\lambda=1.5406 \text{ \AA}$) operated at a voltage of 40 kV and current of 30 mA. XRD spectrum was recorded at a scanning rate of 0.5/minute in the range of $20^\circ \leq 2\theta \leq 80^\circ$. Morphology was studied using a field emission scanning electron microscope (FESEM), (JEOL, Tokyo, Japan) at an operating voltage of 15 kV. Energy dispersive X-ray spectroscopy (EDX) was used for ascertaining the elemental composition of ZnO nanorods. An FESEM (JEM-2100F; JEOL) operated at 200 kV was used for obtaining transmission electron microscopy (TEM) micrographs, selected area electron diffraction pattern, and high-resolution transmission electron microscopy (HRTEM) images. To prepare samples for TEM examination, ZnO nanorods were scraped off an Si substrate and then dispersed

in ethanol solution, followed by an ultrasonic treatment for 10 minutes. A minute drop of ZnO nanorod suspension was cast on to a carbon-coated copper grid and subsequently dried in air before transferring it to the microscope. Room temperature Raman spectrum was recorded using a Raman spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a 532 nm solid-state primary laser as an excitation source in the backscattering configuration.

Photocatalytic measurements of ZnO nanorod arrays

Methylene blue (MB) was used as the test contaminant for the photolysis experiments. A 10 μM aqueous solution of MB was prepared, into which the ZnO nanorod arrays substrate was dipped. A high-pressure mercury lamp (125 W) was used as a light source. The beaker containing MB and ZnO nanorod arrays was then placed under the UV light, with the nanorod surface facing the light source for photodegradation of MB. Optical absorption spectrum in the UV-visible region was recorded after every fixed time interval, to follow the degradation of the MB.

Results and discussion

The XRD pattern of the ZnO nanorod arrays grown on the Si substrate is depicted in Figure 1. It is clear from Figure 1 that the XRD peaks positions are very well matched with the standard PDF values (JCPDS, 36-1451). It is also seen from the figure that the relative intensities of these peaks are different from those of ZnO nanopowder,²³ as shown in the inset of Figure 1. On the basis of the XRD results, we

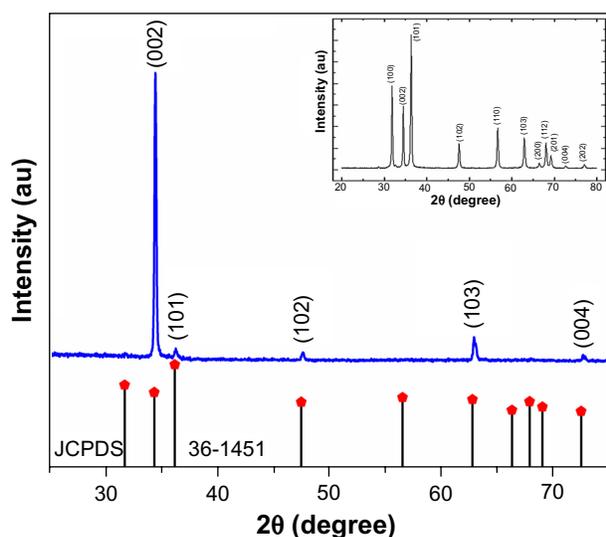


Figure 1 X-ray diffraction pattern of zinc oxide nanorod arrays. **Notes:** Inset shows the X-ray diffraction pattern of zinc oxide nanopowder. Standard pattern of zinc oxide (JCPDS 36-1451).

can conclude that the prepared nanorod arrays are highly crystalline, having wurtzite structure with preferable c-axis orientation. These nanorods are highly pure because no secondary phase was detected. The intensity of the (002) peak was observed to be very strong in comparison with other peaks. Trace amounts of other diffraction peaks, such as (101), (102), and (103), do not mean that some ZnO nanorods were grown in those directions, but c-axis ZnO nanorods were so randomly oriented that these diffraction planes happen to meet Bragg's law.²⁴

The morphological studies of vertically aligned ZnO nanorod arrays were carried out using FESEM, and the micrograph is shown in Figure 2A. The FESEM image (Figure 2A) of the sample shows that the product consists of nanorods with an average diameter of ~ 80 – 90 nm and length of about ~ 350 – 400 nm, respectively, and each individual ZnO nanorod has well-developed hexagon facets. The elemental composition of the sample determined by EDX analysis is presented in Figure 2C. Figure 2C shows the presence of only Zn and O peaks, which confirms that the nanorods are primarily made of ZnO.

Further microstructural studies of the ZnO nanorod arrays were carried out using TEM. The HRTEM image and its corresponding selected area electron diffraction pattern (inset) are shown in Figure 2B. It is also confirmed from Figure 2B that the synthesized ZnO nanorods are single crystalline with (001) growth direction. The interplanar spacing was found to be 0.262 nm, corresponding to the (002) plane of the hexagonal structure of ZnO, corroborating the XRD results.

Raman spectroscopy measurements were performed at room temperature to examine the structure, crystallization, and defects of the ZnO nanorod arrays. ZnO has a wurtzite structure and belongs to the C_6^4V space group with two formula units per primitive cell.²⁵ Group theory analysis, at the center of the Brillouin zone, suggests that the $A_1 + E_1 + 2E_2$ modes are Raman active.²⁶ Representative Raman spectrum of the ZnO nanorod arrays is shown in Figure 3. Only the E_2 high modes at 439 cm^{-1} and A_1 (LO) at 578 cm^{-1} were observed, which further confirms that the ZnO nanorod arrays are highly c-axis oriented because, in the present experiment, the incident light was normal to the substrate: ie, the incident light is parallel to the c-axis of the nanorods and the Raman signal was recorded in the backscattering geometry. In this configuration, only A_1 (LO) and E_2 modes are allowed and the other modes cannot be observed from the vertically aligned nanorods but can be observed from the tilted and randomly oriented nanorods, according to the Raman selection rules.^{27,28}

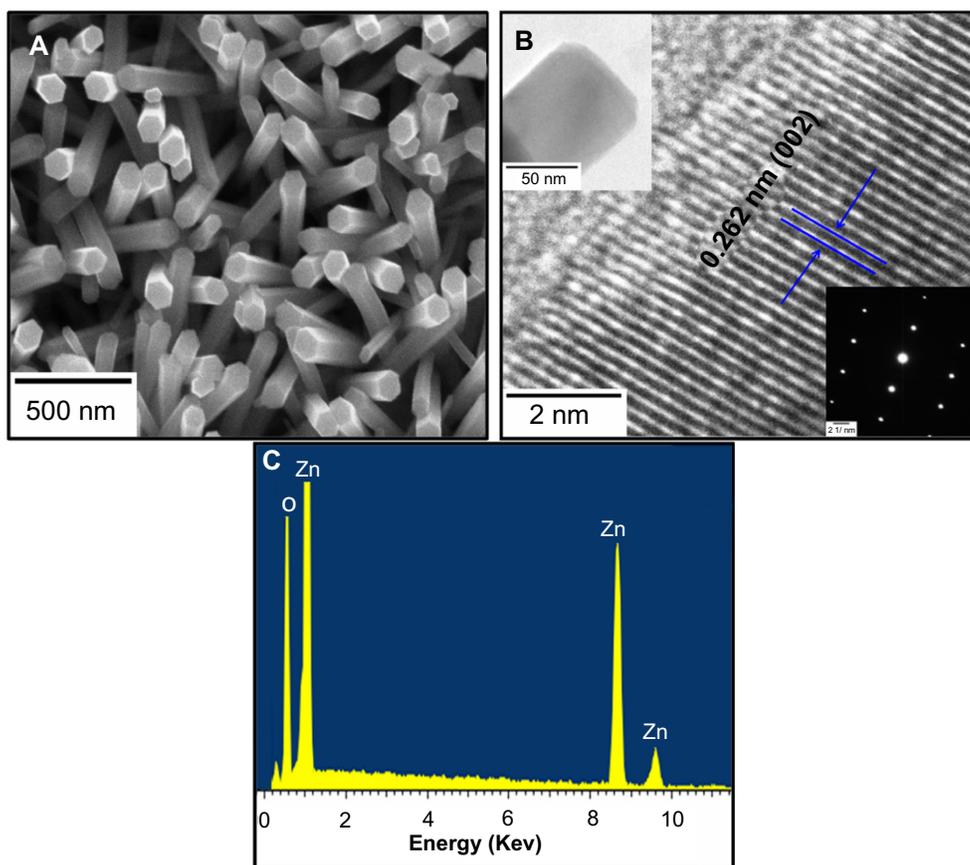


Figure 2 (A) Field emission scanning electron microscopy images of zinc oxide nanorod arrays. (B) High-resolution transmission electron microscopy image and (C) energy dispersive X-ray spectroscopy spectrum of zinc oxide nanorod arrays. Inset of (B) shows corresponding transmission electron microscopy and selected area electron diffraction pattern.

Photocatalytic properties of the ZnO nanorod arrays were examined by decomposition of MB. The characteristic absorption of MB at ~ 660 nm was chosen to monitor the photocatalytic degradation process. Figure 4 illustrates the time-dependent absorption spectra of MB aqueous solutions

during the UV light irradiation in the presence of ZnO nanorod arrays. As a control, the absorbance peak of the MB solution was monitored under two different conditions: 1) with a photocatalyst in the dark and 2) without photocatalysts under UV light illumination. The change in the absorbance

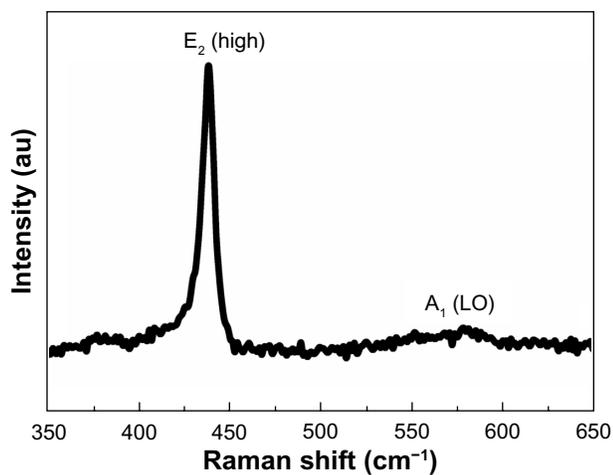


Figure 3 Room temperature Raman spectrum of zinc oxide nanorod arrays.

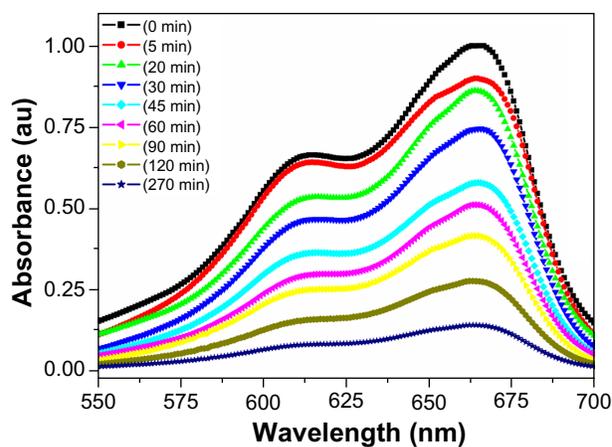


Figure 4 Ultraviolet-visible absorbance spectra of photodegradation of methylene blue with zinc oxide nanorod arrays.

peak of MB under these conditions is found to be negligible, indicating that there is no loss of MB without an irradiated photocatalyst. For ZnO nanorod arrays placed in MB solution, the maximum absorption of the MB solution was found to decrease with illumination time and disappeared almost completely after irradiation for about 270 minutes. This indicates that ZnO nanorod arrays show UV light photocatalytic properties in the degradation of MB.

Figure 5 shows the relative concentration (C/C_0) of MB as a function of time, where C is the concentration of MB at the irradiation time (t) and C_0 is the concentration of the dye before irradiation. After UV light irradiation for 270 minutes, more than 95% of MB is degraded in the presence of ZnO nanorods. This indicates that ZnO nanorods are an effective photocatalyst for the degradation of organic dyes.

Figure 6 shows the percentage degradation of MB as a function of irradiation time with ZnO nanorod arrays photocatalyst. The higher photocatalytic performance of ~80% was achieved within 60 minutes of photoirradiation for ZnO nanorod arrays, whereas after 270 minutes of illumination with UV light, MB was almost completely removed over ZnO nanorod arrays. By comparing the photocatalytic performance of the ZnO nanorod arrays obtained in this study with other reported nanostructures, ZnO nanorod arrays showed better photocatalytic properties. For example, Nipane et al²⁹ showed that ZnO nanorods degraded 50% of MB under UV light irradiation for 120 minutes of irradiation time, whereas about 90% of MB was degraded with ZnO nanocauliflowers. In the present work, ZnO nanorod arrays degraded ~92% of MB for 120 minutes, and for 270 minutes of UV light irradiation, MB was almost completely degraded. Therefore, the

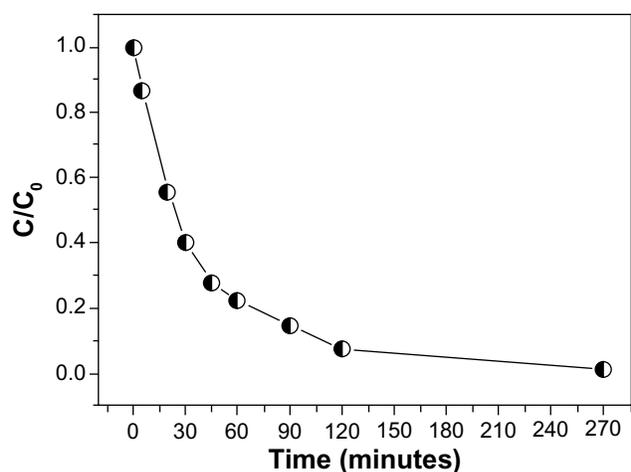


Figure 5 Temporal evolution of methylene blue absorption spectra with zinc oxide nanorod photocatalyst.

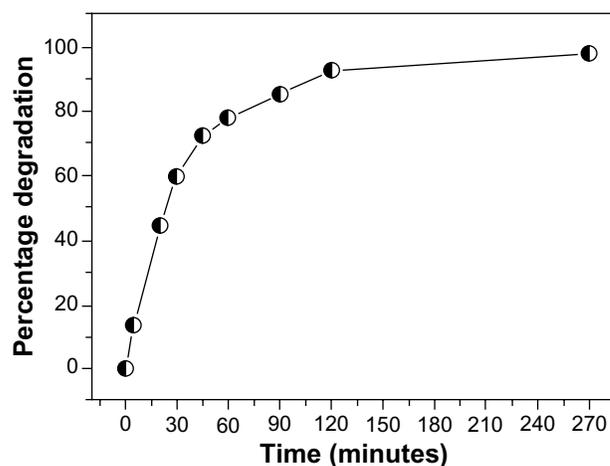
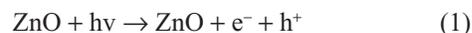


Figure 6 Percentage degradation of methylene blue as a function of irradiation time in the presence of zinc oxide nanorod arrays.

ZnO nanorod arrays obtained in the present work are more superior photocatalysts than others.

The photocatalytic activity of a catalytic material is influenced by several factors, such as carrier recombination, size of the particles, surface area, surface acidity, and presence of a higher number of hydroxyl groups. The enhancement of photocatalytic activity was most likely due to the relative increase of active morphological surface resulting from increased surface to volume ratio as well as the low recombination rate of the electron–hole pairs generated during optical exposure, owing to largely available surface states.

Photocatalytic degradation was generally operated by the action of hydroxyl radicals formed during the reaction.³⁰ The photocatalytic mechanism is proposed as follows: when the ZnO nanorod arrays are illuminated with light, electrons are excited from the valence band of ZnO to the conduction band, leaving a hole in the valence band. The hydroxyl groups present on the surface of the ZnO react with the photogenerated hole to produce hydroxyl radicals. Similarly, peroxide (O_2^-) is formed when the dissolved oxygen interacts with photogenerated electrons. This peroxide takes one proton to yield a superoxide (HO_2^-) followed by the formation of hydrogen peroxide ($H_2O_2^-$). A hydroxyl radical was also produced by the attack of a photogenerated electron to the hydrogen peroxide. These reactive radicals and intermediate species react with dye and degrade them into nontoxic organic compounds.





Conclusion

We have successfully grown well-aligned ZnO nanorod arrays on an Si substrate with a cheap, low-temperature, and environmentally friendly wet chemical solution route. XRD, HRTEM, and Raman analyses revealed the hexagonal wurtzite structure, single phase nature, and high crystalline quality of ZnO nanorod arrays. FESEM and TEM micrographs showed that the nanorods were typically of ~80–90 nm in diameter and ~350–400 nm in length, respectively. Raman measurements confirmed the characteristic peak of ZnO: ie, E_2 (high) mode for ZnO nanorod arrays. The photocatalytic properties of ZnO nanorod arrays toward MB under UV light irradiation were found to be attractive. The results of photodegradation show that ZnO nanorod arrays are capable of degrading ~80% of MB within 60 minutes of irradiation, whereas ~92% of degradation was achieved for 120 minutes. Upon prolongation of irradiation time to 270 minutes, MB degrades almost completely. Due to the excellent photocatalytic performance and easier preparation method, the prepared ZnO nanorod arrays are believed to have potential application in the containment of environmental pollution.

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Disclosure

The authors report no conflicts of interest in this work.

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