

A Microwave-Assisted Process for Coating Polymer and Glass Surfaces with Semiconducting ZnO Submicron Particles

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ABSTRACT: A new method for coating glass slides with ZnO particles with an average size of 200 nm is proposed in the current article. The coating was performed under microwave radiation. Two main morphologies are found for the ZnO crystals that are deposited on glass slides. The first morphology is that of a very dense coating of ZnO hexagonal rods growing perpendicular to the glass surface. The second is the growth of ZnO flower-like particles. In addition to coating the glass by ZnO particles, we also report on coating other polymers [poly(methyl methacrylate) plate, polycarbonate beads, Nylon 6,6 beads, and

polypropylene beads) by ZnO. The morphology obtained for ZnO coated on polymers is different from that detected for coating ZnO on glass. The unorganized coating of ZnO rods on polymers has been observed. The coated glass slides were characterized by X-ray diffraction, volumetric titration, EDS, scanning electron microscope, and optical measurements (DRS and transmittance spectroscopy). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1773–1780, 2009

Key words: microwave; coating; polymer; glass; ZnO nanoparticles

INTRODUCTION

Recently, the preparation and characterization of materials with unique optical and electronic properties have been an active area of investigation. ZnO crystals are among the most interesting and studied materials. ZnO is a semiconductor (II–IV) with a band gap of 3.3 eV at 300 K and an excitation binding energy of 60 meV at room temperature. It has superior electronic and optical properties and is currently in use or being considered for use in electro-optical devices^{1–7} as a piezoelectric transducer,^{8–10} a varistor,^{8,11,12} a phosphor,⁸ a UV and microwave absorber,^{1,10} and a gas sensor.^{8,13–15} It is also used to make transparent conducting films.^{8,16} ZnO has many advantages over numerous other semiconductors such as Si, GaAs, CdS, and GaN because of its low cost, it is also environmentally friendly, and is more resistant to radiation damage. ZnO can be grown by using a variety of techniques, including vapor-phase transport,^{17,18} sol–gel methods,^{18,19} hydrothermal growth,^{20,21} melt growth,²² chemical vapor deposition,²³ electrochemical deposition,^{24–27}

laser ablation,²⁸ sputtering,²⁹ molecular beam epitaxy,^{30,31} and spraying arc-discharge.³² All these methods yield high-quality ZnO and afford control over the orientation of the crystal grown and its exposed face, and, therefore, over its physical properties.

Various crystal shapes of ZnO can be achieved. Liang et al. and Xu et al. have synthesized submicron and nanotowers.^{33,34} Lao et al. prepared ZnO nanobridges and nanonails.³⁵ Gao and Wang prepared mesoporous polyhedral cages and shells formed by the textured self-assembly of ZnO nanocrystals.³⁶ Jung et al. prepared ZnO rods, spheres, hexagonal discs, cups, and flower-like crystals.³⁷ ZnO nanotubes have been prepared by Xu et al.³⁸ Many flower-like and branched ZnO crystals were also prepared by Zhang et al. and by Sounart et al.^{39,40} There are also hundreds of other research works where ZnO crystals have been prepared with different shapes and morphologies.

One of the challenges is to achieve an oriented growth of the ZnO crystals on substrates. An example of such a growth is described in Refs. 41 and 42. In most of the known methods, it takes ZnO crystals a few hours to grow. In the current work we present a method that enables the growth of organized ZnO crystals on a glass substrate within 5 min by means of microwave radiation.

The idea of using microwaves to accelerate chemical reactions is not new, and the theory of dielectric

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heating by microwaves is described by Gabriel and coworkers.⁴³ Komarneni et al. prepared Pt and Ag nanoparticles by this method.⁴⁴ Tsuji et al. synthesized Au@Ag core-shell (an Au core with an Ag shell) nanoparticles⁴⁵ and Ag nanorods and nanowires by using a Pt catalyst and poly(vinyl pyrrolidone).⁴⁶ Palchik et al. used this technique for the preparation of nanoparticles of metal chalcogenides.⁴⁷ There is also some other work where ZnO particles were prepared by using microwaves.^{48–51} However, as far as we know, no substrates in general, and no glass slides in particular, were coated by ZnO using microwaves. Moreover, there are almost no reports on metallic or ceramic particles that were deposited on substrates by means of microwaves. Only recently have two articles reported on the coating of poly(methyl methacrylate) and stöber silica by silver nanoparticles using microwaves.^{52,53} The current article extends these studies to semiconducting nanoparticles. Moreover, this article shows that a good coating can be obtained when using a domestic microwave oven, which is a multimode apparatus, while previous attempts⁵⁴ were made using a single-mode microwave oven. This shows that unfocused microwave can form a good and homogeneous coating layer. The procedure of preparing a ZnO layer on glass slides, which is described in this article, has several advantages over other techniques. First, it has already been mentioned that the time of the reaction is very short (5 min). Second, well-oriented, high-purity ZnO particles were grown on the glass substrates. Third, the procedure that is described here can be used not only to coat glass with ZnO particles but also to coat the ZnO on a large variety of substrates (glass, silica, different polymers).

EXPERIMENTAL

The coating procedure

All the reagents were of the highest commercially available purity, purchased from Aldrich, and used without further purification. Poly(methyl methacrylate) slides (PMMA), polycarbonate chips (~ 2 mm in diameter) (PC), and Nylon 6,6 chips (~ 2 mm in diameter) were supplied by PALRAM (Israel) and were used as obtained. The glass pieces were regular microscope slides purchased from Yancheng Rongkang Glassware (Cat. No. 7102; Nanjing, China).

A 100-mL flask was loaded with a glass slide (4 cm × 1.5 cm, ~ 1 g weight), 30 mL distilled water, 10 mL ethanol, and 10 mL poly(ethylene glycol) ($M_w = 400$ g/mol). The solvent mixture was purged by argon for 30 min to expel the oxygen from the solution. $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ (1.1 g; 0.1M) was completely dissolved in the solution, and the solution became slightly cloudy (other concentrations of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$

have also been used). After the dissolution of the $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$, 0.5 mL of ammonium hydroxide was added, and the solution became cloudy. The solution was stirred, with the addition of more ammonium hydroxide, until the solution became completely clear. Next, the solution was irradiated by microwaves for 5 min. At the end of the reaction, the glass slides were washed thoroughly with water and ethanol and dried overnight in vacuum. We could detect that the glass slide underwent modification because it turned white. Five reactions were carried out. The $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ concentrations in these experiments were 0.01, 0.02, 0.03, 0.05, and 0.1M. As the amount of deposited ZnO on glass increased, the glass became less transparent and the white color was dominant.

In addition to the glass coating, a few polymers were also coated by ZnO according to the same process as described above. The concentration of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ in the coating process of the three polymers was 0.1M. The coated polymers were PMMA slides, PC chips, and Nylon 6,6 chips. The purpose of polymer coating by ZnO was to compare the ZnO morphologies formed on glass with those created on the polymers. Such a comparison will help us to understand the mechanism of ZnO growth on the substrates, under microwave radiation.

Characterization methods

The X-ray diffraction (XRD) patterns of the product were measured with a Bruker AXS D* Advance powder X-ray diffractometer (using Cu $K\alpha = 1.5418$ Å radiation). The HR-SEM images were obtained by using a JEOL-JSM 7000F scanning electron microscope operating at 2 and 15 kV accelerating voltages. The sample was placed on double-sided conducting carbon tape supported by a copper plate. The samples were sputter-coated with gold prior to imaging, to enhance the conductivity of the sample. This sputtering of the gold should be done to enlarge the quality of the images. It should be noted that the gold particles are very small (~ 15 nm) and uniform and cannot be seen in the images that are presented in this article. Volumetric titration was done by dissolving ZnO on the glass in nitric acid and titrating it with EDTA.

RESULTS AND DISCUSSION

We have already commented that the coating of the glass slides by ZnO particles using higher concentrations of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ produced less transparent slides. The results of the titrations were as follows: coating of glass prepared from 0.01M and 0.02M of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ gave 0.05 wt % ZnO. A solution of 0.03M and 0.05M of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ yielded 0.06 wt %

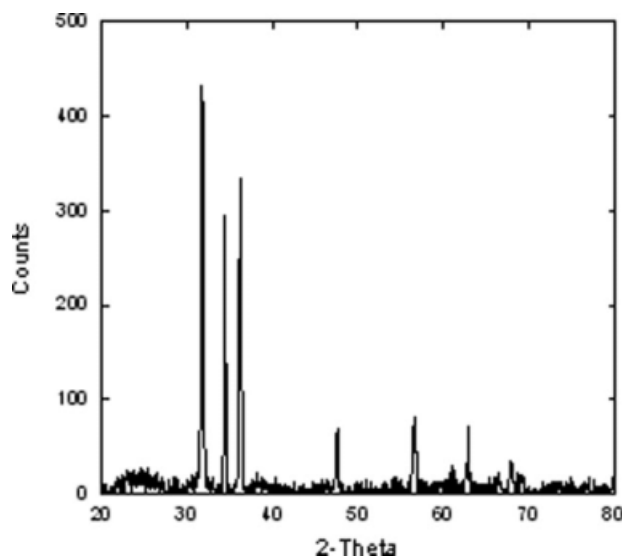


Figure 1 The XRD pattern of ZnO particles coated on glass slides by microwave radiation.

ZnO, and 0.1M of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ led to 0.13 wt % ZnO on the glass slides.

X-ray diffraction studies

The XRD of ZnO crystals deposited on glass slides (Fig. 1) was measured to obtain information about

the nature of the product, its crystal structure, and its purity. The diffraction peaks match well the database of power diffraction files: 01-089-0510, for a polycrystalline hexagonal wurtzite crystal structure of ZnO ($a = 3.24982 \text{ \AA}$, $c = 5.20661 \text{ \AA}$) (space group $P6_3mc$) with no preferred orientation.

In ZnO crystals, the reflections were received from the following atomic planes: (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104), (203) in the following 2θ angles: 31.78, 34.43, 36.26, 47.55, 56.61, 62.88, 66.40, 67.97, 69.11, 72.59, 76.99, 81.41, and 89.65, respectively. No diffraction peaks of any impurities were observed.

Morphology of ZnO coated on glass and polymers

Figure 2(a) displays the HR-SEM image of ZnO particles coated on glass slides, obtained from a 0.1M solution of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$. We observed a glass coated with a very dense layer of ZnO hexagonal, rod-like particles with an average diameter of 210 nm, perpendicular to the glass surface. The density of the ZnO rods on the glass surface was $\sim 11 \text{ rods}/\mu\text{m}^2$. About 60% of the rods are perpendicular to the glass surface and the other $\sim 40\%$ of the rods are at an angle to the surface of the glass. There are some areas on the glass surface where the ZnO rods reach a higher density of $\sim 16 \text{ rods}/\mu\text{m}^2$. The density of

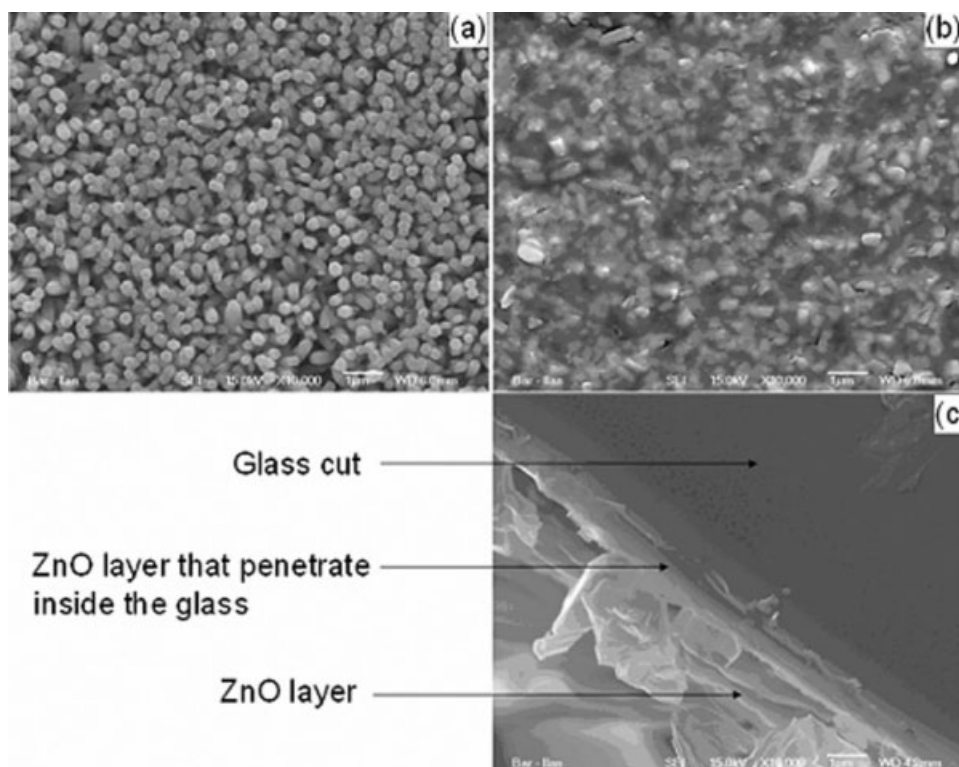


Figure 2 HR-SEM of (a) ZnO particles on the glass slide after reaction with 0.1M of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$. Average particle size is 210 nm. (b) ZnO-coated glass slide after brushing. (c) An image of the cross-section of a cut of the ZnO-coated glass slide.

the ZnO rods was calculated by counting the number of rods per unit area. In such areas, 100% of the rods are perpendicular to the glass surface. It can be concluded from this result that as a higher density of the ZnO rods is formed on the glass surface, more ZnO rods are perpendicular to the glass surface. In an attempt to check how strongly the ZnO particles are attached to the glass slides, the ZnO-coated glass slide was brushed with a piece of paper, becoming more transparent. The HR-SEM of the brushed ZnO-coated glass slide is presented in Figure 2(b), which illustrates that the ZnO particles melt on the glass, and even after brushing many ZnO particles still remained on the glass. Figure 2(c) depicts the HR-SEM of a cross-section measured by cutting the ZnO-coated glass slide and measuring it at 90°C to the surface. Figure 2(c) shows that ZnO particles have penetrated the glass slide, where an ~ 700 nm ZnO layer is observed.

As mentioned above, the diameter of the ZnO particles was ~ 210 nm. An attempt was made to reduce their diameter, and for this purpose the concentration of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ was decreased from 0.1M to 0.03M. It was assumed that diminishing the $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ concentration would lead to smaller ZnO particles. However, the decrease in the concentration did not lead to smaller particles but rather to

a different morphology of ZnO. Using a concentration of 0.03M yielded a flower-like morphology of ZnO [Fig. 3(b,c)]. When the concentration of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$ was decreased to 0.01M, small, incomplete flower-like particles were obtained [Fig. 3(a)].

In contrast to the deposition on glass slides where the ordered coating of the ZnO was observed, on polymers, rods of ZnO were formed, although no organization of the rods on the surfaces was observed. Figure 4 illustrates ZnO particles that were deposited on the different polymers (PMMA, polycarbonate, Nylon 6,6, and polypropylene). On the surface of PMMA two kinds of ZnO particles were formed: small hexagons with an average size of 110 nm, and plate-like flat particles with an average length of 205 nm and an average width of 85 nm. All the particles lay on the surface without any order. On the surface of PC, a large amount of unordered rods with an average length of 665 nm and an average width of 195 nm was observed. On Nylon 6,6, the amount of deposited ZnO particles was much lower than on PC. The size of the rods on Nylon 6,6 was 400 nm in length and 130 nm wide. The picture [Fig. 4(d)] of ZnO deposited on PP was different from the other polymers. A ZnO particle that resembles short rods, with an average size of 330 nm, was melted into the PP beads.

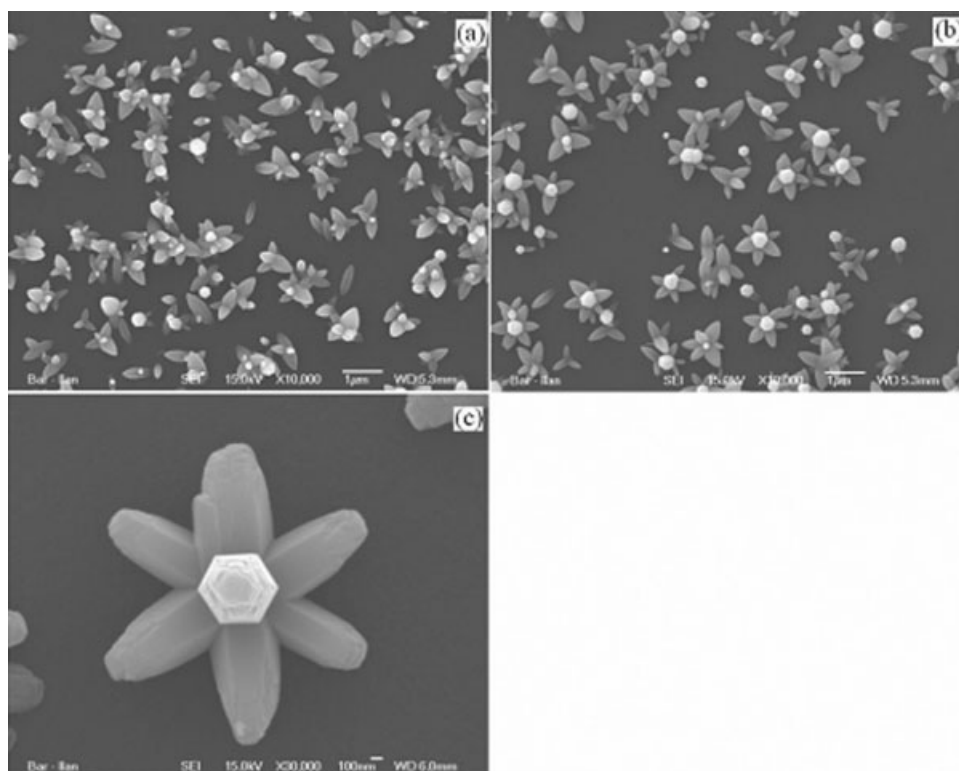


Figure 3 HR-SEM of (a) ZnO coating on a glass slide carried out in an 0.01M concentration of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$. (b) ZnO coating on a glass slide carried out in a 0.03M concentration of $\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2$. (c) Enlargement of ZnO flowers that crystallize on the glass surface.

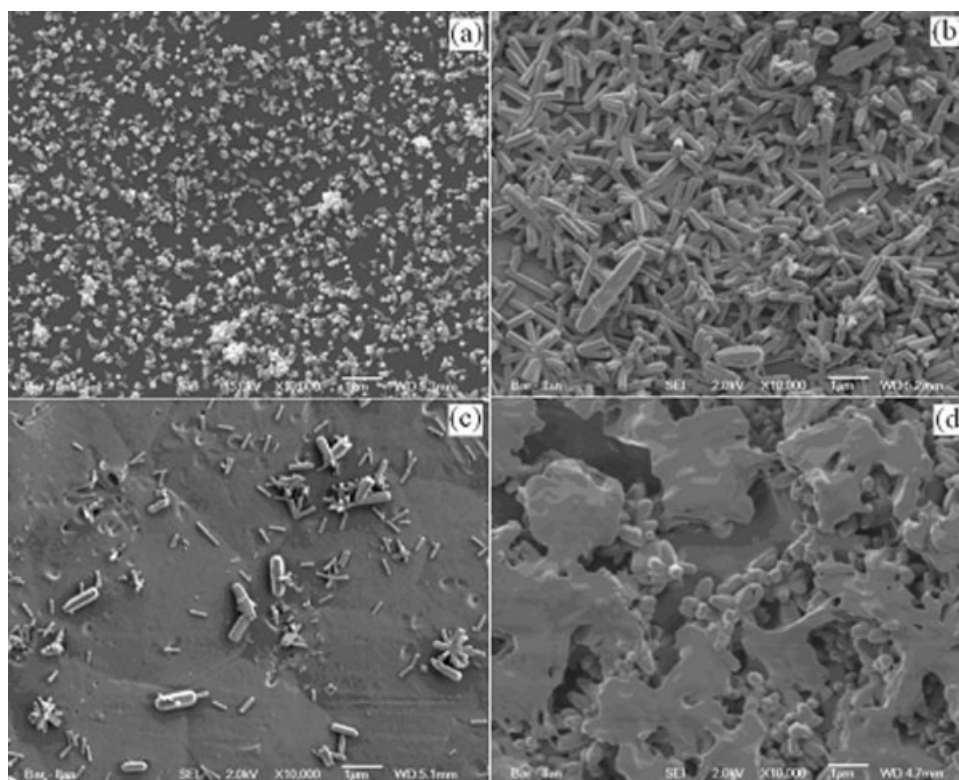


Figure 4 HR-SEM of (a) ZnO coating on PMMA, (b) on PC, (c) on Nylon 6,6, (d) on PP.

Optical measurements of the ZnO-coated glass

DRS (diffused reflection spectroscopy)

DRS is a technique that collects and analyzes scattered electromagnetic radiation. It is used for the measurement of fine particles and powders as well as rough surfaces. In a DRS spectrum, the x -axis is a wavelength and the y -axis is an $F(R)$ function. $F(R)$ is named the Kubelka Munk function and is defined as⁵⁵

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}$$

where R is the reflection, ranging from 0 to 1, K is an absorbance coefficient, and S is a scattering coefficient of the material at a given wave length. As is seen from the Kubelka Munk function, a peak will be observed when the reflection (R) is low, or in other words, the absorbance (K) will be large. Figure 5(a) represents a DRS spectrum of ZnO-coated glass. We observed that as larger amounts of ZnO were deposited on the glass, the intensity of the peak assigned to the glass at 300 nm was weaker, and the peak attributed to ZnO was stronger (at 360 nm). The expanded DRS spectrum in the region of 350–400 nm is also shown [Fig. 5(b)], where it can be seen that ZnO particles with different morphologies

demonstrate $F(R)$ peaks at slightly different wave lengths. The dense coating of ZnO rods that are perpendicular to the glass present a peak at 365 nm. ZnO flower-like particles show a peak at 359 nm, and the absorption of ZnO small tripods and tetrapods appears at 352 nm.

Transmittance measurements

The transmittance spectra of ZnO-coated glass slides are depicted in Figure 6. As can be seen, the uncoated glass transmits about 90% of the light in the visible region and totally blocks UV radiation. As expected, the transmittance of these slides decreased as a function of the amount of ZnO deposited on them. The dense coating of ZnO rods that are perpendicular to the glass surface, received from a 0.1M solution of zinc acetate, transmits about 35% of the visible light (violet curve). On the other hand, the glass coated by ZnO flowers (tetrapods or tripods) transmits 60–80% (red and orange curves) of the visible light. This is reasonable in light of the many empty spaces between the flowers. In addition, at least one distinct absorption peak of ZnO can be observed at around 360 nm. The absorption peak shows a blue shift from that of bulk ZnO (380 nm) crystals.⁵⁵ Such a blue shift has been observed in Refs. 50 and 56. It is possible that the slight

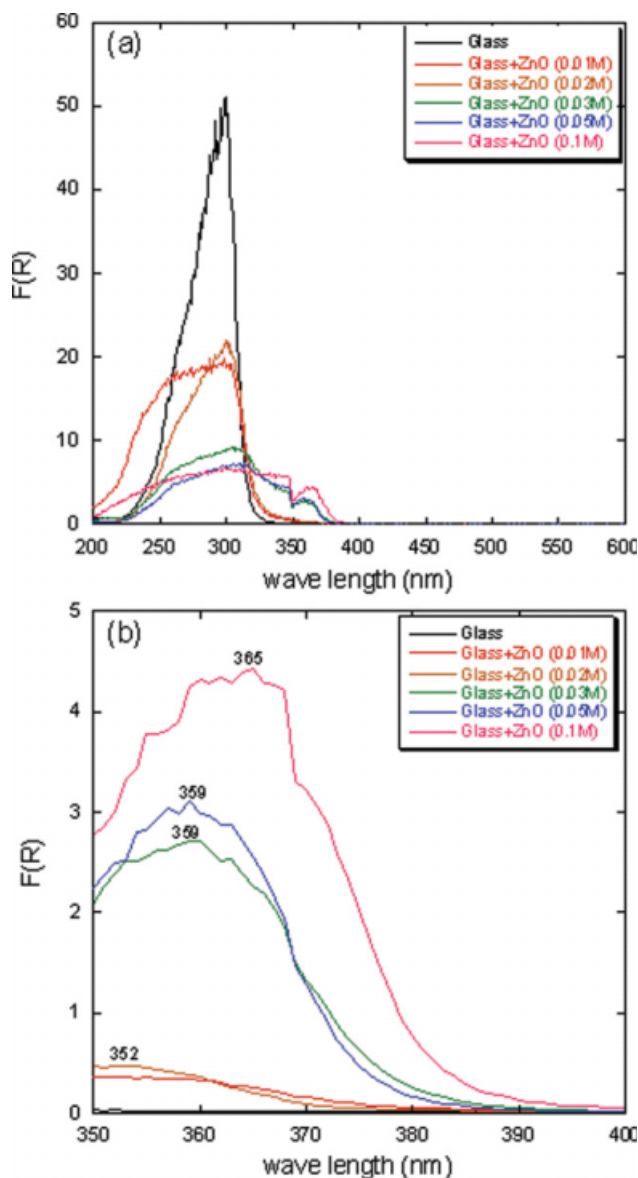
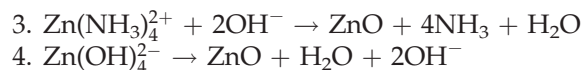
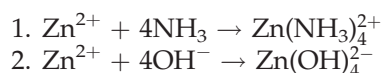


Figure 5 (a) DRS spectrum of glass coated with ZnO particles obtained from a solution of zinc acetate at different concentrations. (b) Expanded wavelength region of the DRS of ZnO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

difference in the spectra of the different ZnO morphologies obtained on glass is due to the different densities of these coatings.

Proposed mechanism of the reaction

The process of receiving ZnO from Zn^{2+} ions is well known from the literature.⁵⁷ In general, in an aqueous solution, in the presence of ammonia, $Zn(NH_3)_4^{2+}$ and $Zn(OH)_4^{2-}$ are the intermediates, and the reactions following their formation are 3 and 4



The proposed mechanism should answer two main questions. First, why the deposition of the ZnO crystals on the polymers are unordered, while ordered layers of ZnO (flower-like crystals or rods that are perpendicular to the glass surface) are observed on the glass? Second, what conditions cause the ZnO rods to grow perpendicular to the glass surface, and when and why do we obtain ZnO flower-like particles? The answer to the first question is that glass, in contrast to polymers, can be negatively charged in a basic environment (by the removal of the proton from the silanol group on the glass surface).⁵⁸ The $Zn(NH_3)_4^{2+}$ complexes are attracted to the charged surface of glass and then react to give ZnO. Actually, the (001) plane is a polar face of ZnO, which is Zn terminated and positively charged and is complexed with the negatively charged surface of glass. Such a complexation causes the attachment of ZnO crystals to the glass surface in such a way that the polar face is parallel to the surface of glass. Because ZnO crystals grow along the *c*-axis^{59,60} [i.e., perpendicular to the (001) and the (00-1) planes], the crystals of ZnO will grow perpendicular to the glass surface.

However, such an explanation does not explain the formation of ZnO flower-like crystals on the surface of glass. This can be explained by a secondary nucleation process. When the ZnO rod grows on the surface of glass in an upright direction, a secondary nucleation starting from the interface between the glass and ZnO crystal occurs.⁴⁰ The ZnO crystal has six faces (ZnO is a hexagon), and therefore, from

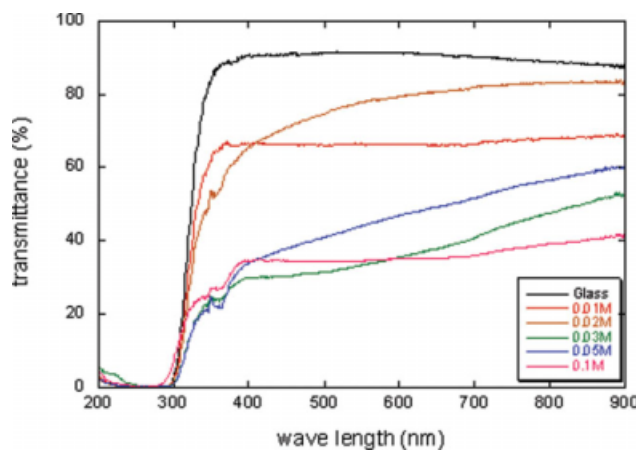


Figure 6 Spectral transmittance of uncoated glass slide (black curve) and ZnO-coated glass slides received in various concentrations of zinc acetate solution where the reaction was carried out (red, orange, blue, violet, and green curves). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

each face another ZnO rod will grow, forming a flower-like ZnO crystal.

The answer to the second question is that at a high concentration of zinc acetate, many nucleation centers are formed on the glass surface. Therefore, the ZnO particles are very close to each other, and a dense layer of rods that are perpendicular to the glass surface appears. In other words, at a high concentration of zinc acetate, there is no space for ZnO particles to grow except in the upright direction. Thus, steric hindrance dictates the growth direction of the ZnO crystals. However, for a low concentration of zinc acetate, the amount of nucleation centers of ZnO on the glass surface is low. Therefore, around each ZnO particle there is a lot of free space, and the secondary nucleation of ZnO can occur. This will lead to the formation of flower-like shapes.

CONCLUSIONS

In this work, a simple and short (5 min) method of coating glass slides by ZnO particles is shown. The particles of ZnO are usually hexagonal rods with an average diameter of ~ 210 nm. In addition, by using a low concentration of zinc acetate ZnO leads to the growth of ZnO flower-like particles. The difference in morphologies between ZnO deposited on glass from high concentration of zinc acetate (perpendicular to the glass surface ZnO hexagonal rods) and ZnO obtained from low concentration of zinc acetate (flower-like crystals) is due to steric hindrance that dictates the growth direction of the ZnO crystals. In contrast to glass, on polymers ZnO does not form a homogeneous layer of perpendicular particles, but rather a very unordered layer of ZnO rods that lie on the polymer surface. This fact led us to assume that the growth of ZnO rods on glass surface is dictated by the ability of the glass surface to be charged.

The amount of ZnO nanoparticles found on the surface of polymers was almost equal to that found on glass. However, a remarkable difference was observed in the orientation of the ZnO submicron crystals on glass and polymers. While on glass, the perpendicular growth of the ZnO rods was observed, on polymers (flat and curved surfaces), a nondirected growth is detected. This difference is attributed to the glass being a charged surface.

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