Hydrophilic and Superhydrophilic Self-Cleaning Coatings by Morphologically Varying ZnO Microstructures for Photovoltaic and Glazing Applications

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ABSTRACT: Transparent, superhydrophilic materials are indispensable for their self-cleaning function, which has become an increasingly popular research topic, particularly in photovoltaic (PV) applications. Here, we report hydrophilic and superhydrophilic ZnO by varying the morphology for use as a self-cleaning coating for PV applications. Three different ZnO microstructures, such as ZnO nanorods (R-ZnO), ZnO microflowers (F-ZnO), and ZnO microspheres (M-ZnO), were developed by hydrothermal methods. The surface morphology by using X-ray diffraction (XRD), wettability behavior by using water contact angle (WCA) measurements, structural and optical properties by using photoluminescence (PL), Raman, and UV–vis spectrophotometry, and defect estimation by using X-ray photoelectron spectroscopy (XPS) of the ZnO nanostructured films were systematically investigated. XRD confirmed the formation of the hexagonal wurtzite structure of ZnO. The average crystallite sizes of prepared R-ZnO, F-ZnO, and M-ZnO were found to be 28.95, 11.19, and 41.5 nm, respectively. The band gap values of ZnO nanostructures were calculated from the UV–vis absorption spectrum and found to be 3.6, 3.3, and 3.1 eV for R-ZnO, F-ZnO, and M-ZnO, respectively. The WCAs for R-ZnO and F-ZnO were 20.2 and 11.19°, respectively, while M-ZnO behaved like a superhydrophilic material having a WCA of 2.8°.

1. INTRODUCTION

Deposited dust or organic contaminants on photovoltaic (PV) glass covers reduce solar photon flux reaching a PV cell via spectral absorption and reflection losses. This optical loss reduces PV power that can vary between 2 and 50% depending on local climate, dust composition, dust particle concentration, surface morphology of PV glass, and employed dust mitigation techniques.1–3 Prominent dust impact on the PV module is found in arid or semiarid areas, such as the Middle East and North Africa, and in the most cleaned area U.K., up to 5% soiling losses are possible due to dust accumulation. PV installed capacity in the world is likely to be more than doubled in a few years, and PV is installed faster than any other renewable energy technologies. Thus, the effect of dust deposition to improve the PV system efficiency is significant.

Manual, automated, electrostatic, electrodynamic, and self-cleaning are the different applied techniques to clean a soiled PV device. Except for self-cleaning, other types are time-consuming, costly, and hazardous to the environment and corrode the solar panel frame.4 Two different self-cleaning methods are presently available, which include photocatalytic hydrophilic and hydrophobic types.5 The hydrophobic coated surface shows a water contact angle (WCA) greater than 150° and low surface energy, while the hydrophilic coated surface shows a water contact angle ≤ 90° and high surface energy.5 A water contact angle (WCA) greater than 150° shows superhydrophobic properties, whereas a WCA less than 5° shows superhydrophilic properties.6,7 Suspended water, dirt, or any pollutant rolls down spontaneously due to the nonequilibrium thermodynamic state from a superhydrophobic surface.4,8,9 They are also capable of reducing the formation of corrosion and ice and drag reduction. On the other hand, a hydrophilic or a superhydrophilic surface spreads water droplets to form a film throughout itself, thereby allowing light waves to pass through and diminish any pollutants through a photocatalysis reaction. For antisoiling purpose, the superhydrophilic surface provides 2.5 times higher efficiency than the superhydrophobic coating.10,11 The wetting behavior of the hydrophobic and hydrophilic coatings is a combined effect of its surface topography and microstructure, surface free energy, and the chemical composition. Semiconductive metal oxide has the ability to be used as a self-cleaning coating.

Zinc oxide is one of the important semiconductors, often selected as a doped material due to its wide band gap of 3.37 eV with a large excitation binding energy of 60 meV, low cost, nontoxicity, and optical and photochemical properties. ZnO
surfaces display better photocatalytic performance in the degradation of hazardous dye molecules in both basic and acidic media. Also, ZnO is bio-safe and biocompatible and thus acts as an environmentally benign coating.27 Zinc oxide has been extensively investigated due to its promising applications in short-wavelength lasing; gas sensors,13 catalysts,14 PV cells,15 transparent conductors,16 and piezoelectric materials.17 photodiodes,18 transistors,19 and varistors.20 ZnO nanostructures have been synthesized in different morphologies such as nanowire arrays,21,22 nanorods,23 nanotubes, nanoflowers, and nanosheets24 using physical and chemical methods for self-cleaning applications. Various techniques have been utilized to prepare ZnO nanostructured films for self-cleaning applications such as magnetron sputtering,25 spray pyrolysis, thermal oxidation, reactive evaporation,22 vapor phase epitaxy, electrodeposition, sol–gel method,26 solid-state reaction, and chemical deposition.27 However, to support the high demand for low-cost mass production of hydrophobic/hydrophilic ZnO nanostructured surfaces for PV applications, a hydrothermal process is efficient. ZnO nanostructures prepared by hydrothermal methods have excellent crystalline quality, high surface area, chemical and thermal stability, low growth temperature, and are environmentally safe (water used as a solvent) with a strong possibility of scaling up.26

The surface of ZnO can be hydrophobic or hydrophilic depending upon the physical and chemical properties of ZnO/water interfacial interactions. ZnO is introduced to prepare a superhydrophobic, with a WCA of 158° and a sliding angle of about 6°, Zn coating on a steel substrate.24 The ZnO hydrophobic coating was prepared on borosilicate glass, amorphous quartz, single-crystal sapphire, lanthanum aluminate, and yttria-stabilized zirconia substrates using thermal evaporation methods,25 which are also suitable for mechanical and oxidation resistance applications. A flexible self-cleaning nanofiber membrane using an oleic acid-coated ZnO nanowire structure had WCA > 150°, which closely resembled the nanoscale tubular randomly oriented crystalloids on a lotus leaf.21

Pesika et al. reported that the surface of a ZnO single-crystal is relatively hydrophilic.28 Photocatalytic self-cleaning ZnO on cellulosic fibers was prepared by an ambient temperature sol–gel process.29 A composite ZnO/TiO2 film possesses superhydrophilicity with a water contact angle of less than 5° without UV irradiation.30

Switching wettability by the transformation between the oxygen-vacant state (hydrophobic) and the oxygen-rich state (hydrophilic) is possible with ZnO.30 Using hydrothermal method, prepared ZnO nanorod array film showed hydrophilic (water contact angle of 9.6°) nature which became superhydrophobic (water contact angle of 156.2°) after being exposed to octa decanethiol solution23 ZnO shows hydrophobicity and superhydrophobicity at normal conditions, which can be UV-cured to obtain hydrophilic properties.31

The surface roughness of hydrophobic and superhydrophobic surfaces can limit the transparency of that surface. Surface roughness is higher than one-quarter of a wavelength of a visible hindrance to achieving transparency in visible light.32–34 However, for PV applications, a transparent self-cleaning coating is paramount.

In this contribution, we describe a facile synthesis of morphologically varied hydrophilic and superhydrophilic ZnO microstructures without UV treatment for self-cleaning techniques of PV and glazing applications. ZnO microflowers (F-Zno), nanorods (R-Zno), and microspheres (M-Zno) were developed on an ITO glass substrate.

2. RESULTS AND DISCUSSION

2.1. Morphological Analysis. The X-ray diffraction (XRD) profile of as-prepared samples is presented in Figure 1, which revealed that all of the diffraction peaks are indexed to the hexagonal wurzite structure of ZnO (space group P63mc, JCPDS card number 36-1451), ensuring its identity. The sharp diffraction peaks indicate good crystallinity. Using Scherrer’s equation $D = \frac{K \lambda}{\beta \cos \theta}$, the crystallite sizes of R-ZnO, F-ZnO, and M-ZnO were calculated to be 41.5, 28.95, and 11.19 nm, respectively.

Figure 2a–c displays the field-emission scanning electron microscopy (FESEM) micrographs of the three different morphologies of as-prepared ZnO microstructures. The FESEM analysis revealed that the growth of as-grown nanorods R-ZnO, rod assembled flowerlike structures F-ZnO, and porous microspheres M-ZnO can be varied by merely changing the surfactant, hydrothermal reaction conditions, and calcination process. ZnO has a tendency to form rods as the growth is dominated unidirectionally, thereby forming rod-shaped morphology of ZnO (Figure 2a). Cetyl trimethyl ammonium bromide (CTAB) on the other hand behaves not only as a growth promoter but also as a soft template for the formation of flowerlike morphology of ZnO by providing active sites (CTAB-conjugated growth units) along the circumference of ZnO nuclei, which help in the adsorption of growth units and altering its surface energy, eventually allowing the low-temperature radial growth of uniformly distributed F-ZnO microstructures (Figure 2b). The uniformly distributed individual crystalline nanorods were ~1 μm long with an average diameter of 20 nm. The flowerlike sample has a diameter ranging from 2 μm. By changing the surfactant to urea with subsequent calcination of the zinc hydroxide carbonate (ZHC) precursor, ZnO microspheres were formed with highly porous nanosheets. The decomposition of ZHC resulted in evaporation of H2O and CO2 during calcination, resulting in the formation of ZnO with a porous surface (Figure 2c). All three samples maintained their morphologies even after undergoing aging with postannealing at 350 °C on a glass substrate as shown in Figure 2d–f.
and M-ZnO. The WCA was found to be 20.2, 11.19, and 2.8° for surfaces with R-ZnO, F-ZnO, and M-ZnO, respectively. All contact angles were measured with a 5 μL water droplet at ambient temperature. The results clearly indicate hydrophilic surfaces for rods and superhydrophilicity in the cases of flower- and microsphere-assembled surfaces. These results could arise due to the crystallinity and microstructural changes that occur by the synthesis of these microstructures. Due to the abundance in the number of troughs between the microstructures, the surface’s roughness is increased, and the wettability is largely affected, thereby following Wenzel’s model.

2.3. Optical Property Analysis. The optical transmission and absorption behavior of different ZnO morphologies fabricated on a glass substrate was observed by using UV–vis–near infrared (NIR) spectroscopy analysis as shown in Figure 4. Band gaps of R-ZnO, F-ZnO, and M-ZnO were obtained by calculation from the Tauc plot as 3.6, 3.3, and 3.1 eV. The slight shifting in band gap arises due to changes in morphologies, defects, and grain sizes. It was clearly hinted that the morphology of the microstructures could efficiently control the transmittance, absorbance, and optical band gap. Reduced band gap can enhance its electrical property, thereby decreasing resistance. \( V_0 \) acts as an electron donor, forming acceptor states near the valence band. When the concentration of the \( V_0 \) is high enough, \( V_0 \) states overlap with the valence band, pushing it upward toward the conduction band. With an increase in \( V_0 \), there is an increase in the number of energy states above the valence band and hence an increase in the band gap narrowing. Thus, in our case, various morphologies

Figure 2. FESEM images: before annealing; (a) R-ZnO, (b) F-ZnO, and (c) M-ZnO and after annealing at 350 °C (d) R-ZnO, (e) F-ZnO, and (f) M-ZnO

Figure 3. Water droplet contact angle measurement: (a) water drop before coming into contact with the surface and after coming into contact with the ZnO-coated glass substrate; (b) nanorods (R-ZnO), (c) microflowers (F-ZnO), and (d) porous microspheres (M-ZnO).
of ZnO display different energy band gap values because they have different concentrations of V₀.

2.4. X-ray Photoelectron Spectroscopy (XPS) Analysis for Defect Estimation. XPS analysis is further done to determine the presence of surface defects. Figure 5 demonstrates the comparison of the O 1s region of the XPS spectra of various morphologies of ZnO: (a) R-ZnO, (b) M-ZnO, and (c) F-ZnO. Previous studies have reported that the peak around ~530.05 eV (O₁) is due to oxygen in the Zn-O matrix and the peaks centered around ~531.06 to ~531.58 eV (O₂) generally originate from the surface defects in the ZnO structure especially oxygen vacancies. After Gaussian fitting of peaks for each sample, the total areal percentage clearly indicated that the presence of defects arising from the oxygen vacancies in ZnO porous microspheres (58.2%) is the highest as compared to flowerlike ZnO (32.2%) and ZnO nanorods (20.2%). This result confirms the proposed reason for higher wettability in porous microspheres than in flower and rod morphologies.

3. CONCLUSIONS
We report self-cleaning microsphere ZnO (M-ZnO), nanorod ZnO (R-ZnO), and flower ZnO (F-ZnO) morphologies developed by a hydrothermal process on a glass substrate at ambient conditions for antisoiling of PV applications. The structural and morphological properties were studied by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM). The optical and wetting properties were investigated by UV−vis spectrophotometry and water contact angle measurement, respectively. Stable morphologies were obtained even after performing aging with postannealing at 350 °C on the glass substrate. Single-crystal rods had a diameter of 20 nm, which changed to 5−7 μm for flower structures. M-ZnO behaved as a superhydrophilic material as it had a WCA of 2.8°, which was the lowest compared to R-ZnO and F-ZnO having WCAs of 20.2° and 11.19°, respectively. M-ZnO had a band gap of 3.1 eV and more than 80% average visible (380−780 nm) transparency. Hydrophilic R-ZnO and F-ZnO had optical band gaps of 3.6 and 3.3 eV, respectively, which support their use in self-cleaning applications.

4. EXPERIMENTAL SECTION
4.1. Material Synthesis. 4.1.1. Synthesis of ZnO Rods (R-ZnO) and Flowerlike Structures (F-ZnO). All chemicals were of analytical grade and were used as purchased (Sigma-Aldrich) without any further purification process.
For the synthesis of flowerlike ZnO microstructures (F-ZnO), 50 mL of a transparent solution of Zn(NO$_3$)$_2$.H$_2$O (0.2 M) was steadily added to 50 mL of a transparent solution of 1.2 M NaOH and 0.01 M CTAB under vigorous stirring in an ice bath for 1 h. The resulting solution was transferred in a 100 mL capacity autoclave with a Teflon liner and maintained at 90 °C for 5 h. After the hydrothermal reaction was complete, the autoclave was allowed to cool down to room temperature. The white precipitate obtained was harvested by centrifugation and then thoroughly washed with distilled water and ethanol several times. The final white product was dried at 80 °C in air for 10 h. The same experiment as mentioned above was repeated for the synthesis of ZnO microrods (R-ZnO) in the absence of CTAB.

For the synthesis of ZnO microspheres, a hydrothermal reaction with subsequent calcination was conducted. In a typical synthesis process, optimized amounts of Zn(NO$_3$)$_2$.H$_2$O, urea (CO(NH$_2$)$_2$), and trisodium citrate (Na$_3$C$_6$H$_5$O$_7$) in a ratio of 1:1:0.1 were steadily dissolved in 100 mL of deionized water under vigorous stirring to form a transparent solution. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at a hydrothermal temperature of 120 °C for 5 h. After the hydrothermal reaction was complete, the autoclave was allowed to cool down to room temperature. The precipitate was harvested by centrifugation and was washed thoroughly with deionized water and ethanol several times. The final white precipitate was dried at 80 °C in air for 10 h. The same experiment as mentioned above was repeated for the synthesis of ZnO microrods (R-ZnO) in the absence of CTAB. The as-prepared ZnO samples were dissolved in DI water (0.5 wt %) and ultrasonicated, and finally, the solution was drop-cast onto the surface of the glass substrate placed on a hot plate (100 °C). The film was dried by evaporating out the solvent and was subjected to postannealing at 350 °C for 2 h. After completing the fabrication of the device, it was subjected to various characterization techniques.

4.3. Material Characterization. The crystal phases of the materials were determined by X-ray powder diffraction (XRD) using a Bruker D8 ADVANCE diffractometer with Cu Kα radiation and were matched with the standard values using the Joint Committee on Powder Diffraction Standards (JCPDS) database. The morphology of the sample was obtained using JSM-7600F JEOL field-emission scanning electron microscopy (FESEM). Raman spectroscopy analysis was carried out to evaluate structural defects and various modes in the prepared sample, and the spectrum was recorded using an Alpha 300 M confocal micro-Raman spectrometer equipped with a YAG laser.
laser (532 nm). Furthermore, the optical properties were analyzed by studying the photoluminescence (PL) spectrum recorded at room temperature using a fluorimeter (FS-2, Scinco) equipped with a Xe-arc lamp having an excitation wavelength of 350 nm. UV–Vis spectroscopy analysis was carried out to evaluate the band gap and the transmission properties of the prepared samples with the help of a LAMBDA 1050 UV/vis/NIR spectrophotometer. Finally, to understand the wettability property of these materials and surface energy, which is an essential parameter for self-cleaning application in solar panels, contact angle measurement was conducted by using a contact angle meter (optical tensiometer).

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**Notes**
The authors declare no competing financial interest.

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