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Tailoring the optical and hydrophobic property of zinc oxide nanorod by coating with amorphous graphene

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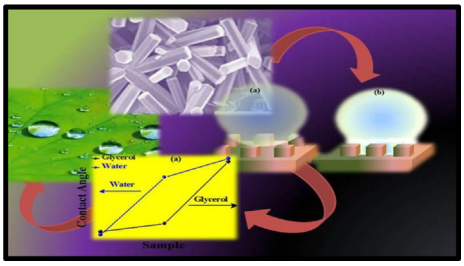
HIGHLIGHTS

- ZnO nanorods were chemically synthesized on both glass and silicon substrates.
- ZnONR were coated with chemically synthesized amorphous graphene (a-Gs).
- Detail optical studies were carried out with UV–vis spectroscopic analysis.
- Detail studies on hydrophobic properties were carried out using Owen's method.
- Improvement of hydrophobic properties of ZnONR by coating with a-Gs.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc oxide (ZnO) nanorods were synthesized at room temperature on potassium permanganate activated silicon and glass substrate by simple chemical method using zinc acetate as precursor.

To modify the surface energy of the as prepared ZnO thin films the samples were coated with amorphous graphene (a-G) synthesized by un-zipping of chemically synthesized amorphous carbon nanotubes (a-CNTs). All the pure and coated samples were characterized by x-ray diffraction, field emission scanning electron microscope, Raman spectroscopy, and Fourier transformed infrared spectroscopy. The roughness analysis of the as prepared samples was done by atomic force microscopic analysis. The detail optical properties of all the samples were studied with the help of a UV-Visible spectrophotometer.

The surface energy of the as prepared pure and coated samples was calculated by measuring the contact angle of two different liquids. It is seen that the water repellence of ZnO nanorods got increased after they are being coated with a-Gs. Also even after UV irradiation the contact angle remain same unlike the case for the uncoated sample where the contact angle gets decreased significantly after UV irradiation. Existing Cassie-Wenzel model has been employed along with the Owen's approach to determine the different components of surface energy.

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1. Introduction

Since the advent of material science and technology development of hydrophobic surface was one of the most important topics among the researchers in this field. Hydrophobic surface is the surface where water shows contact angle over 90° [1]. The hydrophobic surface has many important applications by mimicking so-called lotus effect that includes various engineering applications, such as self-cleaning, anti-bio-fouling, anti-icing, anti-corrosion, drag reduction at micro and macro scales and textiles, waterproof devices, micro channels, and other non-wetting related applications and others [2–6]. Hydrophobic materials have now found its' importance in different coating industries due to its' low degree of wetting. Hydrophobicity provides a gateway to find the key of protection, for the most sensitive and valuable properties of the surfaces, which can be easily affected by environmental factors such as rain, dirt, etc.

In general the wetting behavior of a surface may be explained by two different equilibrium states: In Cassie-Baxter model the contact angle hysteresis (difference between advancing and receding contact angles), which provides an indication of drop stickiness on the surface is less. On the contrary Wenzel state provides high hysteresis though under both the condition surface may show super hydrophobic nature [7].

Among different material, zinc oxide (ZnO) nanostructures like nanorod, nanoflower, nanospikes etc. have shown its potential as hydrophobic material [8]. ZnO is regarded as one of the most promising inorganic semiconductor towards optoelectronic and hydrophobic applications like photo detector, sensors, solar cellsor light-emitting diodes [9–11] due to its numerous useful properties, like wide direct band gap (3.37 eV for bulk) and a large exciton binding energy (60 meV), low crystallization temperature, high chemical stability, good charge carrier mobility (to overcome charge transport limitations in organic–inorganic hybrids) abundance in the earth's crust, cheap synthesis and non-toxic nature [12]. There are reports of producing hydrophobic ZnO surface by varying roughness, nanostructures or other chemical treatments [13]. Also there are some scattered reports of developing ZnO-carbon hybrid super-hydrophobic surface where carbon exists in its one dimensional, graphitic tubular form i.e. carbon nanotube (CNT). CNT is another material where lotus effect is reported to be present most acutely. However so far the CNT used is the crystalline CNT which needs complex synthesis condition like high pressure, temperature, catalyst etc, also when one achieves all these ideal condition the yield is poor. From this point of view our previously reported amorphous CNT (a-CNTs) is the best substitute that can be easily synthesized with very good yield [14]. Also in our other work we have shown how these a-CNTs can be easily unzipped (which is one of the most common method for the production of graphene) to produce amorphous graphene (a-Gs) with equal high yield [15].

So far the authors are concerned existing literature remains silent regarding the development of ZnO-a-Gs hybrid surface for the application in hydrophobic coating. Thus keeping this in mind here the development of ZnO-a-Gs hydrophobic surface has been reported for the first time. Detail optical properties of the as prepared samples were studied and different optical constants were calculated in order to show the effect of a-Gs coating on these parameters. This simultaneous study of optical and hydrophobic properties of ZnO is important due to the fact that the hydrophobicity or more fundamentally the surface energy of a material is directly related to surface roughness. On the other hand enhanced surface roughness can reduce the reflectance of the material thus modifying other fundamental phenomena like transmittance and absorbance. All these in turn affect the dielectric properties of the material. Thus a proper tailoring of these two properties simultaneously can give rise to a new novel hydrophobic opto-electronic material. The surface energy was calculated by measuring contact angle of two known liquids using well-known Owen's method. Also the effect of UV irradiation on hydrophobicity of the surface and the advantage of amorphous graphene coating regarding this has been discussed in detail.

2. Experimental and characterization

The different precursor and accessory materials, like Potassium Permanganate ($KMnO_4$), n-hexanol, zinc acetate dihydrate [$(CH_3COO)_2$ Zn, $2H_2O$], Ammonium hydroxide (NH_4OH), Ammonium chloride (NH_4Cl), Ferrocene ($C_{10}H_{10}Fe$), Hydrochloric acid (HCl), Hydrofluoric acid (HF), all the materials are purchased in analytical graded and used without further purification.

2.1. Synthesis of zinc oxide nanorod

In a typical set of experiment cleaned glass and silicon substrates placed in a narrow necked bottle are first activated with $KMnO_4$ solution (0.08 g KMnO4 with 100 ml water). Into 20 ml of this solution 50 μl n-hexanol was added. The solution was then shacked for several times in order to make the mixture homogeneous followed by subsequent heating at 80 °C for 30 min and left at room temperature. The $KMnO_4$ treated substrates were cleaned with DI water.

For the preparation of zinc precursor solution, 14 g of zinc acetate ($ZnAC_2$) were mixed with 60 ml water and kept into a Petri dish into which the activated substrates were immersed. Then 25 vol% NH_4OH was added drop wise into the system and the mixture was stirred continuously. The solution readily turns slurry white and then with excess addition of NH_4OH it again became transparent. The substrates were remained undisturbed into this clear solution for 18 hours and washed with DI water and heated for 30 min at 60 °C.

2.2. Preparation of amorphous graphene

The detail experimental for synthesizing a-CNTs was described in our previous work [14]. Briefly, NH_4Cl and ferrocene were taken in 2:1 weight ratio and thoroughly mixed in a mortar followed by open atmosphere heating for 30 min in an oven at 225 °C. The naturally cooled black product was then washed by diluted HCl and de-ionized (DI) water successively for several times to remove the residue amount of iron content if any. The black filtered was finally dried at 70 °C for 18 h. For production of a-Gs certain amount of as synthesized a-CNTs were dispersed into 60 ml ethanol and ultrasonicated for 2 h.

The ZnO thin films were coated with a-Gs by simply spin coating techniques. Two different samples were prepared along with uncoated ZnO by varying the number of coating. For sample Z1 number of coating is 5 and for Z2 it is 20.

All the uncoated and coated samples were characterized by X-ray diffraction (XRD, BRUKER D8 Advance) analysis using a Cu-Kα radiation (0.154056 nm) over a scanning angle (2θ) ranges from 20° to 70°. Field emission scanning electron microscope (FESEM, Hitachi, S-4800), atomic force microscopy (AFM, NT-MDT), Raman Spectrophotometer (Witec, excitation wavelength $\lambda_{ex}=532$ nm), Fourier Transformed Infrared Spectrophotometer (Shimadzu FTIR-8400S) and UV–vis spectrophotometer (JASCO V-750) study.

The surface energy of the samples was calculated from contact angle measurement of two different liquids by conventional method.