SYNTHESIS AND CHARACTERIZATION OF HYDROPHOBIC SURFACE USING METAL OXIDES THIN FILMS

Abstract

Hydrophobic surfaces play vital role in the solving the technological problems such as marine fouling, anticorrosion and drag reduction. For the synthesis of Nanoparticles such as Zinc Oxide (ZnO), Copper Oxide (CuO) and Ferrous Oxide (Fe_2O_3) Solution Combustion Method was used. Spin coating method was used to prepare hydrophobic surfaces. ZnO, CuO and Fe2O3 was mixed separately with Polystyrene (PS) and THF solution then magnetically stirred to get uniform dispersion of particles and heated to form gel. This gel was further spin coated on to the glass substrate to form ZnO/PS, CuO/PS and Fe_2O_3/PS thin films. Synthesized films were measured for Water Contact Angle (WCA) and Sliding Angle (SA) and further characterized for Energy Dispersive X-Ray Spectroscopy (EDX) and Scanning Electron Microscope (SEM). P-XRD of nanoparticles showed the hexagonal wurtzite ZnO structure, monoclinic CuO structure and cubic Fe_2O_3 structure with crystallite size of 12.5, 14.59 and 12.88 nm. Water Contact Angle for ZnO/PS, CuO/PS and Fe_2O_3/PS films was found to be 101.77°, 96.48°and 93.97° and Sliding Angle was found to be 24.23°, 25.24°and 27.53°. EDX analysis showed that presence of 0.18 wt % Zinc, 0.07 wt% Copper, 0.13 wt% Iron, 1.22 wt % Oxygen, 98.43 wt% carbon and 0.24 wt% Silica contents on the surfaces. SEM micrograph of ZnO/PS, CuO/PS and Fe_2O_3 /PS films showed the nanoparticles have been uniformly dispersed in the PS matrix and particle size was found to be 24, 27 and 28 nm.

Keywords: ZnO, CuO, Fe_2O_3, Solution Combustion Method, Water Contact Angle.

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I. INTRODUCTION

Hydrophobic surface is the one which repels the water the naturally occurring hydrophobic surface is the lotus leafs. To make surface as hydrophobic surface chemistry plays a very important role in the wettability, which gives interrelationship between solid, liquid and gas [1]. Investigation of the surface wettability properties has been one of the most attractive research areas in the past decades because of the numerous industrial applications such as self-cleaning, anti-corrosion, anti-fouling anti icing and oil/water separation [2]. The two main parameters which have significant impacts on the wettability properties are chemical composition and topographical features of the surface [3]. The common method fabrication the hydrophobic surface includes first creating a rough hierarchical structure and then modifying the surface with a low surface energy material [4]. On the basis of this principle, various elegant approaches have been proposed for the preparation of hydrophobic surfaces such as chemical deposition, chemical etching, layer-by-layer deposition, sol–gel, anodic oxidation, electro-spinning and lithography etc [5, 6].

Zinc Oxide (ZnO) has attracted great interest for many unique physical & chemical properties in the optical, electrical, magnetic, piezoelectric, & ferroelectric field. In addition, ZnO nanomaterials have become a hot topic of research & exploration because of its excellent stability & photocatalytic activity used in the field of biomimetic super hydrophobicity [5-7]. Copper (Cu) and Copper oxide has attracted great research interest due to its good mechanical workability, excellent electrical & thermal conductivity, which has a wide range of applications in human life & industry across many fields of electrical, construction, machinery manufacturing and transportation [8-10]. Iron oxide nanoparticles usually are deposited or dispersed in other materials such as polymer, textile, sponge, even bamboo. This strategy is beneficial to remain stability, dispensability, magnetism and other functions [11-13]. Polystyrene is preferred as the host matrix because of its unique properties for studying the optical properties of the nano composite. With Introduction of filler such as nano powders into polymeric matrices can change the optical, electrical & mechanical properties of the polymers [14-16].

II. EXPERIMENTAL DETAILS

1. **Synthesis of Nano Materials:** Zinc nitrate (Zn $(NO_3)_2$, 99%), Citric Acid ($C_6H_8O_7$, 99%), Cupric Nitrate (Cu $(NO_3)_2$, 99%), Ferric Nitrate (Fe $(NO_3)_2$, 99%), Glass substrate, Tetrahydrofuran $(CH_2)_4O$ & Polystyrene were used. Distilled water was used throughout the experiments. Zinc Nitrate, Cupric Nitrate and Ferric Nitrate are taken beakers and mixed with calculated amount of citric acid then it mixed with distilled water to form the solution and stirred until the particles get dissolved then it is placed in the muffle furnace for 15-20 mins at 500°C. A redox reaction takes place in furnace giving out the Zinc Oxide, Copper oxide and Ferrous Oxide Nano powders.

2. **Preparation of Thin Films:** Glass substrates was cleaned with soap, alcohol & acetone for 15 minutes & with distilled water & then dried in a stream of air. 1 gm polystyrene was dissolved in 10 ml of THF solution then heated & stirred for 30 minutes to get homogenous solution [17] Metal oxides like ZnO, CuO and Fe2O3 nano crystalline powder were added then stirred for 15 minutes to get metal oxides dispersed in the solution then gel is formed.

Before coating spin coater is calibrated to get uniform coating all over substrate then with speed controller knob 2000 rpm & 90 seconds time was set. Then glass substrate is placed on stand. The gel prepared was poured on the glass substrate then allowed spun for required set conditions [18-21]. Gel gets spread on the glass substrate centrifugally to form ZnO/PS, CuO/PS and Fe2O3/PS thin films.

3. Characterization

- **Powder X-Ray Diffraction (P-XRD):** P-XRD is a method in which the crystal structure of the synthesized nanoparticles is analyzed to check they are in the nano form. For the analyzation cu k α source was used and the scanning range was 2θ from 20° to 80°.

- **Water Contact Angle:** Water contact angle measuring was carried out on using sessile drop test method for the prepared thin films to test for the hydrophobicity [22].

- **Energy Dispersive X-Ray Spectroscopy (EDX):** The Energy Dispersive X-ray (EDX) technique is being utilized to analyze the elemental composition of a specimen. EDX suggests quick & efficient characterization technique that attains elemental information at high resolutions.

- **Scanning Electron Microscope (SEM):** Scanning electron microscope gives the surface morphology of the nano particles or thin films by scanning surface with high energy beam electrons.

III. RESULTS AND DISCUSSIONS

1. **Powder X-Ray Diffraction:** XRD pattern of ZnO nano Nanoparticles is shown in Figure 1(a). XRD peaks of corresponds to the hexagonal wurtzite ZnO structure according to the JCPDS card No 36-1451 with 2θ peaks at 32° (100), 34° (002), 36.10° (101), 47.52° (102), 56.59° (11 0), 62.96° (103), 68.70° (112) & 73.12° (201) was observed. XRD pattern of CuO Nanoparticles is shown in Fig 1(b). XRD peaks of CuO Nanoparticles corresponds to the monoclinic CuO structure according to the JCPDS card No 05-0661 with 2θ peaks at 32.98° (110), 35.2° (111), 38.62° (111), 47.52° (202), 56.59° (202), 62.96° (202), 66.70° (113) & 67.12° (022) was observed and XRD pattern of Fe2O3 Nanoparticles is shown in Fig 1(c). The XRD peaks [23-26] of Fe2O3 Nanoparticles corresponds to the cubic Fe2O3 structure according to the JCPDS card No 84-0311 with 2θ peaks at 31°(102), 33.93°(104), 35.44°(110), 43.21°(113), 49.97°(024), 54.10°(116), 56.98°(018) & 63.12°(214) was observed [27-29]

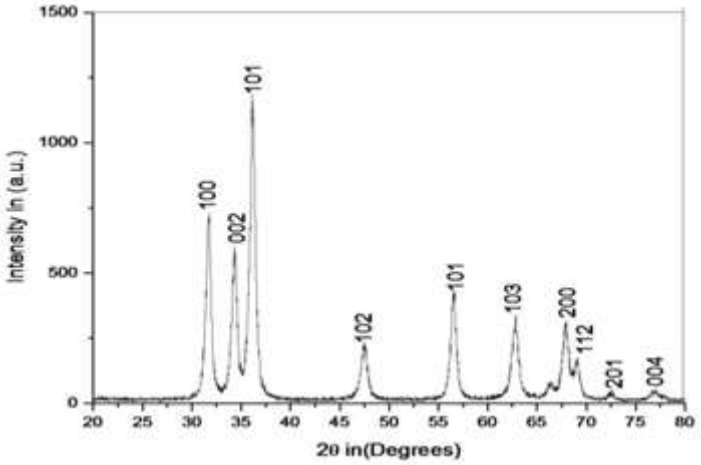

Figure 1a: P-XRD pattern of ZnO Nanoparticles

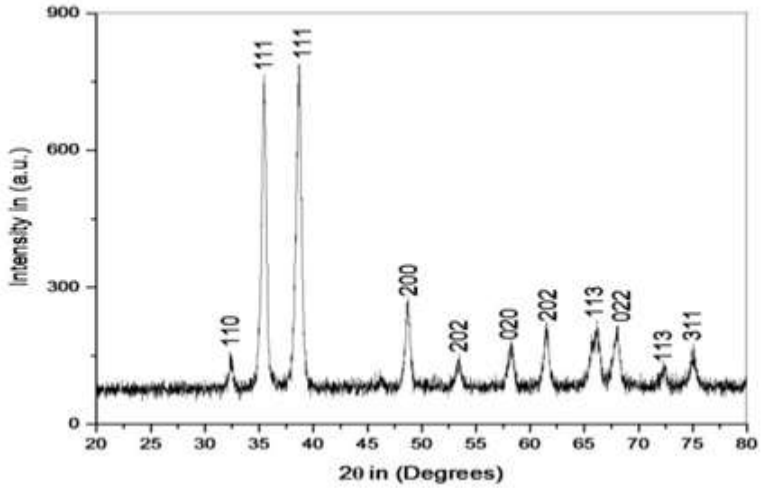

Figure 1b: P-XRD pattern of CuO Nanoparticles

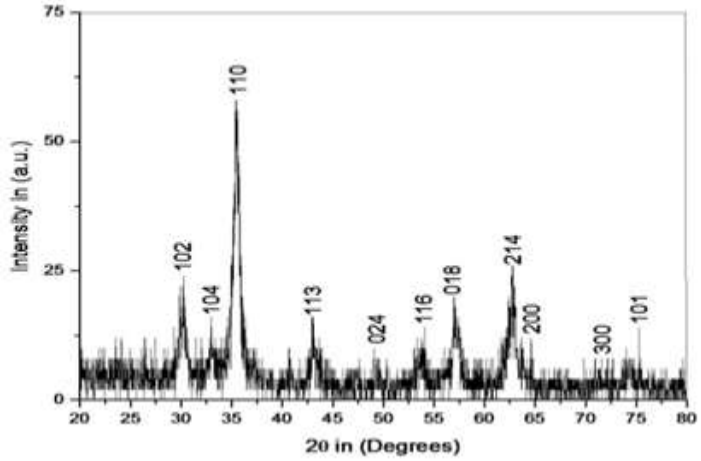

Figure 1c: P-XRD pattern of Fe_2O_3 Nanoparticles

The crystallite size was calculated from Scherrer Equation (1) given by

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where D = Crystallite size, λ = wavelength of X-ray = 1.5 A° = 1.5×10^{-10} m,
β= full width at half maximum (FWHM) and θ= angle of diffraction
The crystallite size for ZnO, CuO and Fe_2O_3 Nanoparticles was 12.5 nm, 14.59 nm and 12.88 nm and it was calculated by using Eqn. 1.

2. **Water Contact Angle Measurement:** In this test substrates were placed on the stand and DI water was used with approximately 2-7µL water droplet is placed on the substrate through syringe and left for few seconds and then with help of camera images are captured and then contact angle was measured [30-33]. The water contact angle for ZnO/PS, CuO/PS and Fe2O3/PS film was 101.77°, 96.48°, and 93.97° respectively. Contact angle for ZnO/PS film is shown in Fig 2 (a), contact angle for CuO/PS film is shown in Fig 2(b) and contact angle for Fe2O3/PS film is shown in Fig 2 (c) and similarly sliding angle was calculated by tilting the glass slide. Sliding for ZnO/PS, CuO/PS and Fe2O3/PS film was 24.23°, 27.53°and 29.36° respectively [34-36].

Figure 2a: ZnO/PS film

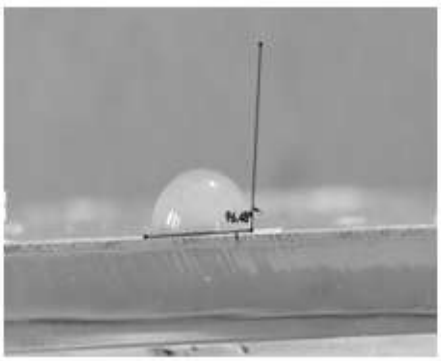

Figure 2b: CuO/PS film

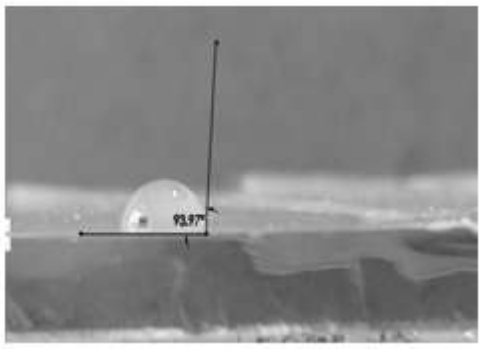

Figure 2c: Fe_2O_3/PS film

3. **Energy Dispersive X-Ray (EDX) Analysis of Films:** EDX of ZnO/PS is shown in Fig 3(a). which shows that the Zinc, Oxygen, Carbon & Silica content in the film which contains 1.22 wt % oxygen, 0.18 wt % zinc, 98.43 wt% carbon & 0.17% of silica. Some small peaks of silicon are also observed which is obvious as the film is deposited in Si/SiO2 substrate. EDX of CuO/PS is shown in Fig 3(b) which shows that the copper,

oxygen, carbon & silica content in the film which contains 19.90 wt% oxygen, 0.07 wt% copper, 79.80 wt% carbon & 0.24% of silica [37-39]. Some small peaks of silicon are also observed which is obvious as the film is deposited in Si/SiO2 substrate. EDX of Fe2O3/PS is shown in Fig 3(c). Which shows that the main elements of the ferrous oxide & polystyrene film were iron, oxygen & carbon & the film contained 3.66 wt% oxygen, 0.13 wt% iron & 96.21 wt% carbon.

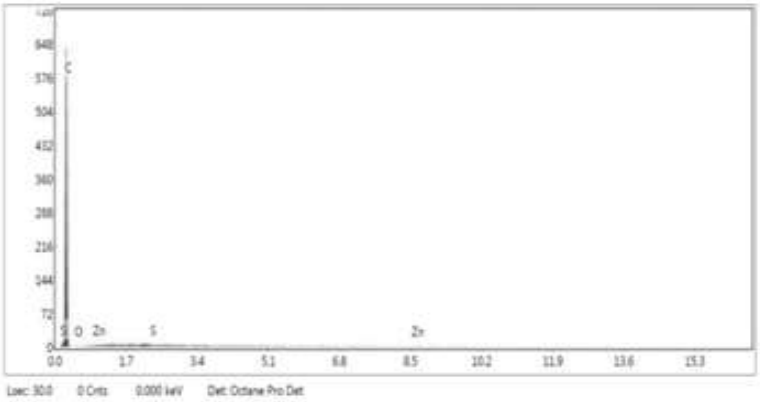

Figure 3a: EDX image of ZnO/PS film

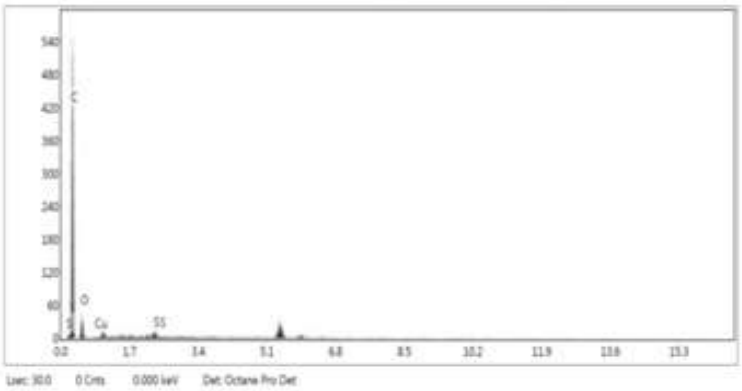

Figure 3b: EDX image of CuO/PS film

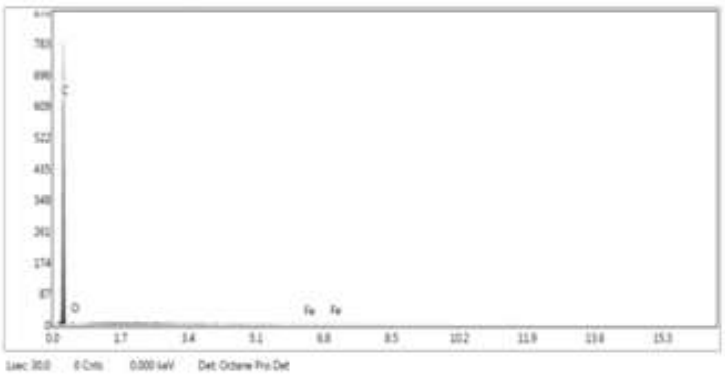

Figure 3c: EDX image of Fe2O3/PS film.

4. **Scanning Electron Microscopy:** Figure 4.1(a) shows the SEM image of ZnO/PS film Surface with magnification of 500 µm. There are voids on the surface because of non-uniform distribution of nano crystalline powder. Small particles on the surface give the presence of the ZnO. The particle size was found to be 24 nm. Fig 4.1(b) shows the SEM image at 50µm. it was smooth surface because of high focused beams melts the polymer surface. Most of the nanoparticles were buried in the coating layer by evaporating the solvent & particle size was found to be same [40].

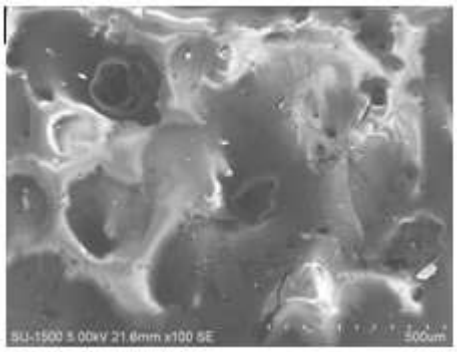

Figure 4.1a: SEM image of ZnO/PS at 500 µm

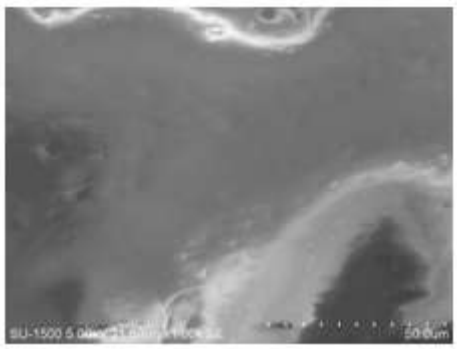

Figure 4.1b: SEM image of ZnO/PS at 50 µm

EM images of CuO/PS film surface is shown in Fig 4.2(a) at magnification 500 µm. It was found that the surface has irregular patterns & there are void on the surface because of improper distribution. Small particles on the surface give the presence of the CuO & rough surface because of presence of the nanoparticles present on the surface which results in the droplet formation on the surface. The particle size was found to be 27 nm. Fig 4.2(b) SEM images at magnification 50 µm. it was found smooth because of high focused beams melts the polymer surface & particle size was found to be same [41].

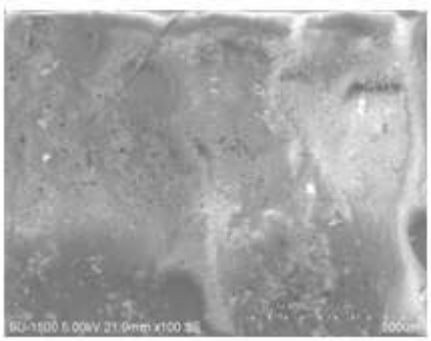

Figure 4.2a: SEM image of CuO/PS at 500µm

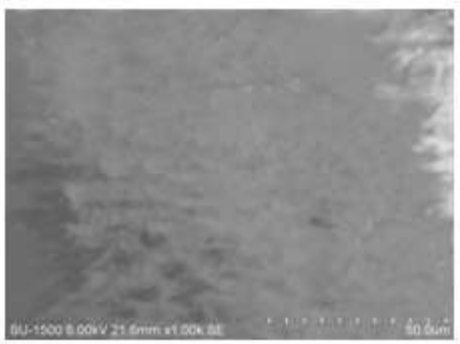

Figure 4.2b: SEM image of CuO/PS at 50 µm

SEM image of Fe_2O_3/PS film surface is shown in Fig 4.3(a) at magnification 500 µm. It was found that the surface has voids on the surface due to the Small particles on the surface gives the presence of the Fe_2O_3& roughened surface may be cause for the hydrophobicity. The particle size was found to be 28 nm. In Fig 4.3(b) shows SEM image at magnification 50 µm. it was found nearly smooth surface due to high focused electrons

melts the polymer surface. In fact, there can be seen very few nanoparticles on the surface showing a very disperse morphology which shows that the most of nanoparticles was buried in the coating layer upon evaporating the solvent [42-45]

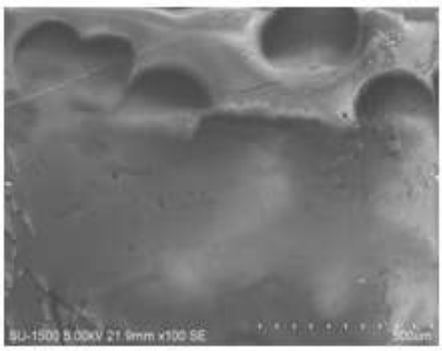

Figure 4.3a: SEM images of Fe_2O_3/PS at 500 µm

Figure 4.3b: SEM images of Fe2O3/PS at 50 µm

IV. CONCLUSIONS

Three different Metal Oxides Nanoparticles ZnO, CuO & Fe2O3 are synthesized through a simple solution combustion method. Hydrophobic surfaces are made by ZnO/PS, CuO/PS & Fe2O3/PS has been made through spin coating method on the glass substrate. Water contact angle of 101.77°, 96.48°, & 93.97° have been obtained. Sliding angle of 24.23°, 25.24°, & 27.53° have been obtained. XRD results of ZnO, CuO & Fe2O3 powder confirmed nano crystalline powder, crystalline size of 12.5 nm, 14.59 nm & 12.88 nm respectively has been obtained. EDX results of hydrophobic surface gave presence of various elements on the surface like Zn, Cu, Fe, O, C & Si with weight 0.18%, 0.07%, 0.13%, 1.22%, 98.43% & 0.24% respectively on the ZnO/PS, CuO/PS & Fe2O3/PS surfaces. SEM results gave the surface morphology of the prepared samples. It was found that presence of ZnO, CuO & Fe2O3 particles on the surface & particle size was found to be 24 nm, 27 nm & 28 nm.

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