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INVESTIGATION OF STRUCTURAL, MORPHOLOGY AND SELF-CLEANING PROPERTIES OF GO:AG, GO:SI AND GO:ZN NANO-COMPOSITES THIN FILMS SYNTHESIZED BY SPRAY PYROLYSIS TECHNIQUE

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Abstract

A wide variety of approaches have been explored by researchers in the attempt to attain a system with controllable wetting properties. The hydrophilic surfaces can be used in anti-fogging applications, biomedical, filtration, heat pipes, and many others. hydrophilic surface has strong affinity to water whereas hydrophobic surface repel water. In this research, the synthesis of graphene oxide- silver, graphene oxide- silica and graphene oxide-zinc nano-composite were done by spray pyrolysis method in order to investigate their self-cleaning properties. The nano-composite thin films were characterized by X-ray diffraction (XRD), field-emission transmission electron microscope (FE-SEM) . The xrd results confirm the formation of desired thin films. Atomic force microscope (AFM) was used to calculate the thickness and RMS value of thin films. RMS values for GO, GO:Ag, GO:Si and GO:Zn thin films were 17.57, 185.78, 125.64, 37.23 nm, respectively. According to the results of contact angle and AFM images, GO:Zn thin film has the lowest roughness and therefore the lowest contact angle and a relatively good hydrophilic surface.

Keywords: GO:Ag Nano-Composite, GO:Si Nano-composites, GO:Zn Nano-Composite, Thin Film, Self-Cleaning Properties

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Introduction

Graphene is a 2D one-atom-thick carbon structure that has a structure similar to the honeycomb lattice [1-4]. Graphene oxide is an oxidized derivative of graphene that is generated by the oxidation of graphite powder. The most common method of producing the graphene oxide is Hummers method [5-7]. However, these nano-particles tend to accumulate during the synthesis process, which eventually results in loss of their properties at nano-meter level. Since graphene oxide has a large surface area, it can be used as a substrate for nanoparticles. Composition and decoration of graphene oxide surface with metallic nano-particles and metal oxide such as Au, Ag, Zn, Pd, or nano-particles of semiconducting oxides such as ZnO and TiO2 improves the performance of these materials for applications such as mechanical strength materials, biochemical and electrochemical sensors, photocatalysts, lithium-ion batteries and solar cells [8-9].

Nano-composites made of nano-particles placed on carbon substrates such as graphene oxide [10-13] have been one of the topics of interest to recent research in science and engineering. These carbon substrates have a very higher surface area than volume, making them suitable for a variety of practical applications [14]. In 2006, Roff et al. reported the first graphene nano-composite (graphene-polystyrene composite) [15]. According to their results, disruption of graphene with polystyrene increased the electrical conductivity of the composite. In the study, we intend to prepare the GO:Ag, GO:Si and GO:Zn nano-composites thin films by spray pyrolysis method and investigate self-cleaning properties of these nanocomposite.

Preparation Method of Nano-Composites Thin Films

- **Preparation of GO:Ag Nano-Composite thin film**

For preparation of GO:Ag nano-composite thin film, at first Graphene oxide (GO) colloid was dispersed in the ultrasonic bath for 0.5 hour. Silver diamine hydroxide solution (Ag(NH3)OH) (40M) was prepared using ammonia, silver nitrate and deionized water (DI). GO:Ag nano-composite was prepared by mixing the Ag(NH3)OH solution and graphene oxide solution and stirred for 0.5 hour. The final solution (figure 1) was then stirred in the oil bath at 70-80°C for 30 min. It was centrifuged with DI water to remove the additional materials.

Figure 1: The solution of Go:Ag nanocomposite

- **Preparation of GO:Si Nano-Composite thin film**

For preparation the solution of GO:Si nano-composite thin film, at first ethanol and 10ml of graphene oxide were mixed and stirred. Tetra Ethyl Ortho Silicate (TEOS) (2 ml) was added to the GO solution and stirred (Figure 2). The obtained solution was diluted by adding DI water and aged at room temperature for 1 day.

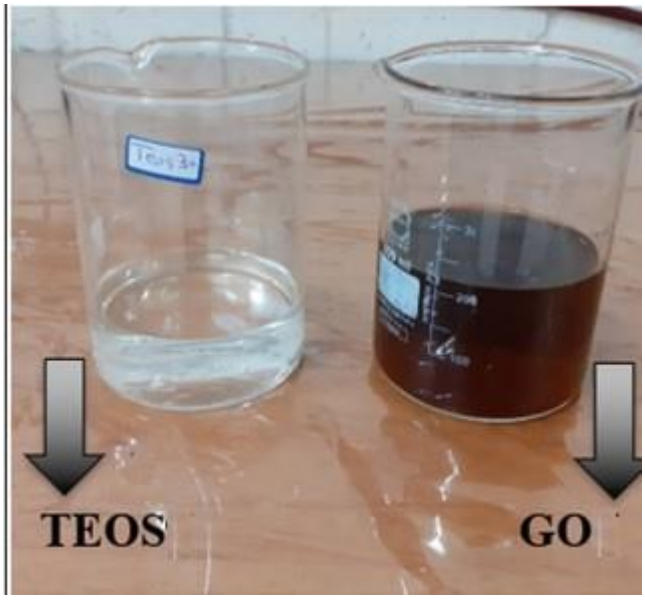

Figure 2: The solution of Go:Si nanocomposite

- **Preparation of GO:Zn Nano-Composite thin film**

For preparation solution of GO:Zn nano-composite thin film, at first graphene oxide (GO) was dispersed in the ultrasonic bath for 0.5 hour. Hexa Methylene TetrAmine (HMTA) solution (0.2 M) and zinc acetate solution (0.2 M) were prepared and mixed with GO solution for 15 min. The final solution was placed in oil bath at temperature of 90°C for 3 hours and then centrifuged 3 times with DI water to remove excess solvents (figure 3).

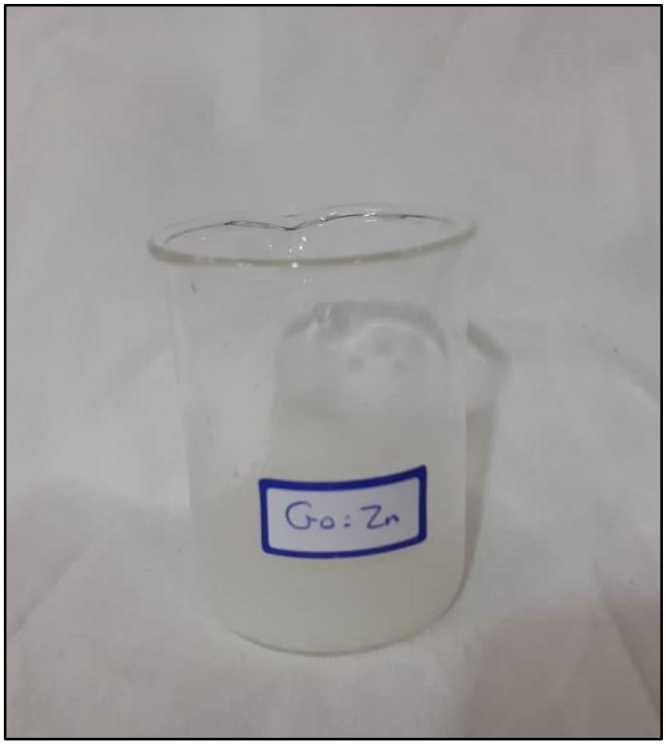

Figure 3: The solution of Go:Zn nanocomposite

- **Preparation of nano-composite Thin films using Spray Pyrolysis device**

At first, the glass substrates were washed by acetone. Then, the substrates were placed in the ultrasonic bath for 0.5 hour. In order to prepare the thin film using spray pyrolysis device, 35 ml of each of GO:Ag, GO:Si and GO:Zn solutions were sprayed by compressed air as carrier gas. The nozzle distance was selected about 30-40cm. The deposition rate was chosen of 2-2.5. The hot plate temperature was set as 150°C for GO:Ag thin film [16,17] and 400°C for GO:Si and GO:Zn thin films [18,19]. The thickness of GO, GO:Ag, GO:Si and GO:Zn thin films is equal to 180.1, 182.3, 154.6, 132.8 nm, respectively. The film thickness was measured using Z- height scan of AFM microscope. The prepared thin films were shown in figure 4.

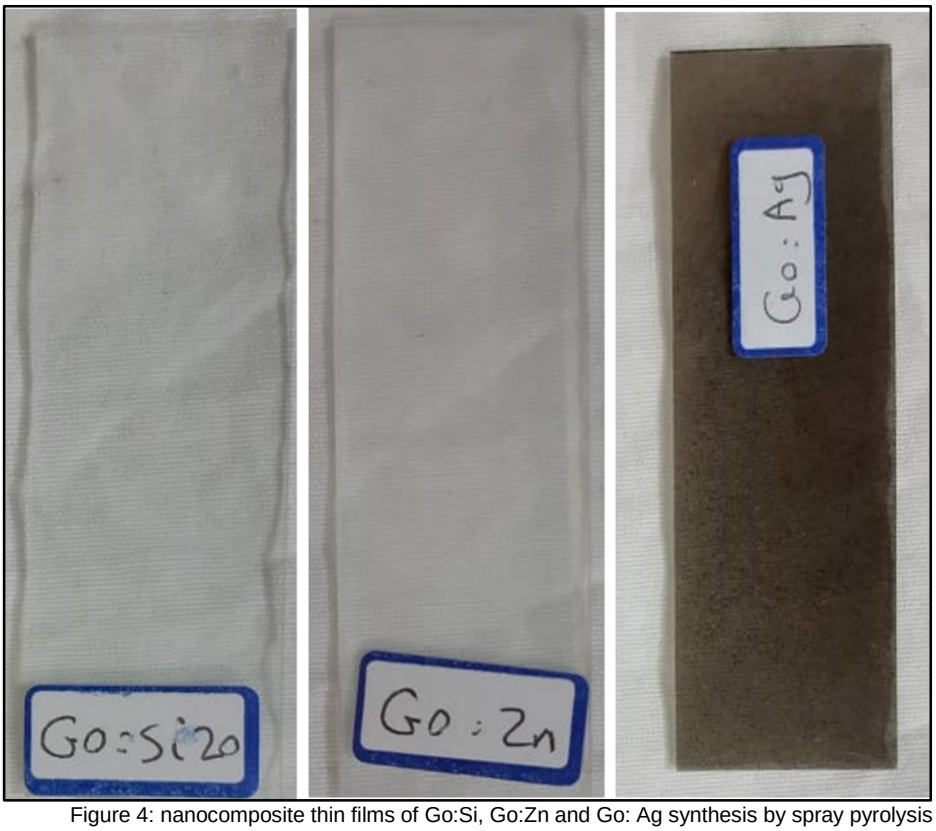

Figure 4: nanocomposite thin films of Go:Si, Go:Zn and Go: Ag synthesis by spray pyrolysis

Characteristics

X-ray diffraction (XRD) device, D8 Advance Bruker YT model was used to confirm the composite structure of the synthesized thin layers, using CuKα radiation at λ = 1.5418Å at 2θ values between 5◦ and 80◦. Field emission scanning electron microscope (FESEM), MIRA3 TESCAN-XMU model was used to investigate the surface morphology of the obtained layers. Atomic force microscopes (AFM) (manufactured by Ara-research Company) were used to examine the surface topology of the layers. The measurement of contact angle of water droplets on thin layers under ambient conditions at 25° C was performed to measure the self-cleaning properties of the samples. Water droplets were placed in 3 different positions for each sample and its mean was considered as the contact angle.

Results and Discussion:

X-ray Diffraction (XRD) analysis

XRD method is used to characterize the presence of functional groups at the surface of sample. Figure 5 shows the X-ray diffraction (XRD) spectrum for GO, GO:Ag, GO:Si and GO:Zn nanocomposite thin films. XRD pattern of the graphene oxide (GO) thin film prepared by spray pyrolysis shows that the sample lacks the other phases, indicating a diffraction peak at an angle of about 2θ=10° corresponding to the plate (001). In the XRD spectrum of GO:Ag in addition to the peaks of graphene oxide and reduced graphene oxide, further diffraction peaks at the 2θ angles of 38, 44.1, 64.3, and 77.3 are seen, that are related to the planes of (111), (200), (220), and (311), and demonstrate the fcc cubic structure of undoped Ag (JCPDS file no. 04-0783). In X-ray diffraction spectrum of GO:Si thin film is shown in Figure 5. As shown in the X-ray diffraction

spectrum of GO:Si nano-hybrids, a broad peak is seen at angles of 23.45, that is relevanted to the silica structure (SiO2) and corresponds to (JCPDS File no. 47-1301). The presence of this broad peak indicates that the silica structure is amorphous and there is poor arrangement in the graphene sheets along their agglomeration directions. In other words, these structures are composed of stacked multilayer graphene sheets, which can be clearly seen in FESEM images [20-21].
Graphene oxide peak in GO:Zn thin layer almost disappeared and the broad diffraction peak appeared at the 2θ = 25° related to the (002) plane of the layers of reduced graphene oxide (rGO). Very small diffraction peaks for ZnO layer with the planes of (100), (002), (101), (102), (110), (103) and (112) can be seen that correspond with standard data for wurtzite structure of ZnO (JCPDS 36-1451) [22]. As shown in the Figure 5, the formation of graphite particles (at 2θ = 25) can be attributed to the high amount of GO in GO:Zn thin layer, due to the agglomeration of graphene sheets.

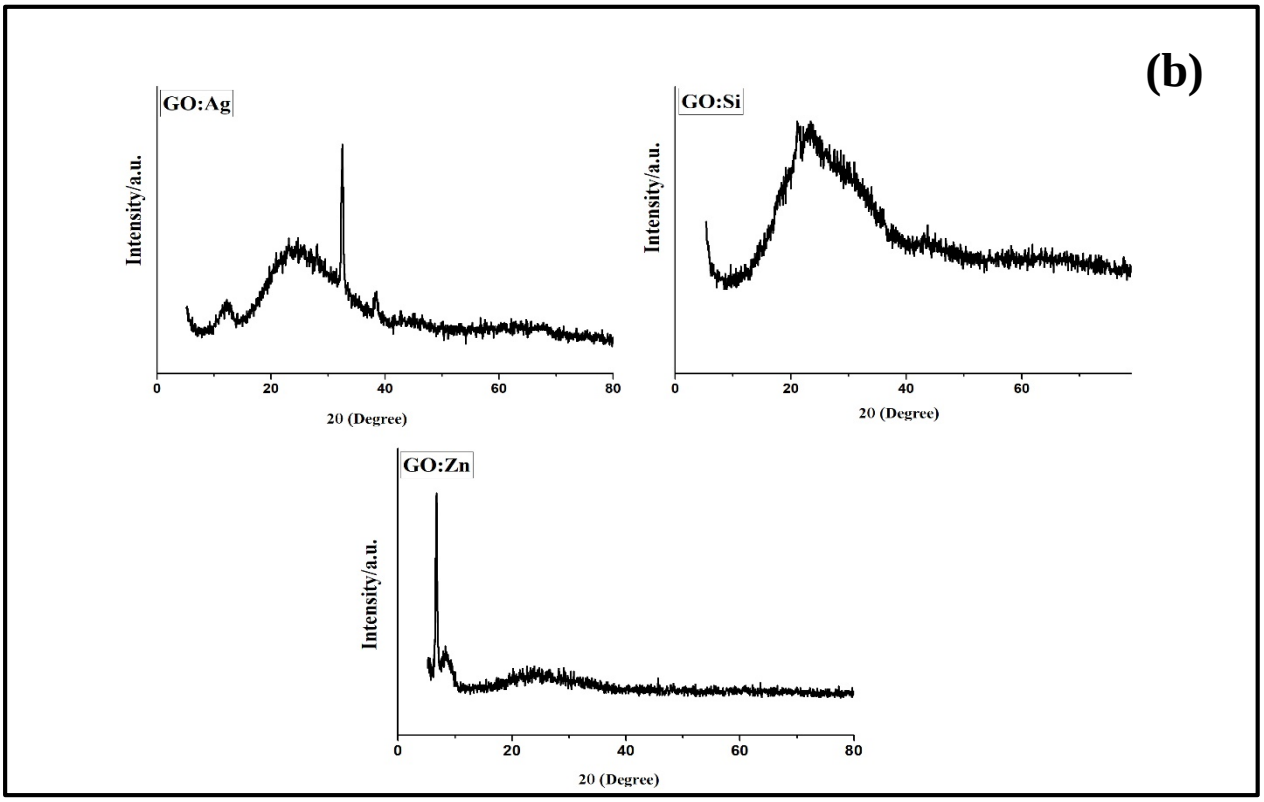

Figure 5. X-Ray Diffraction Spectrum of (a) GO thin film (b) GO:Ag, GO:Si and GO:Zn nanocomposite thin films Prepared by Spray Pyrolysis Method.

FESEM Analysis

Field emission scanning electron microscope (FESEM) was used to analyze the morphological appearance and size distribution of GO:Ag, GO:Si and GO:Zn nanocomposite thin films.

FESEM images of GO:Ag, GO:Si and GO:Zn thin films are shown in Figure 6. FESEM images of GO:Ag thin film composite confirm not only the results of XRD spectroscopy, but also show that the Ag nano-particles are heterogeneously formed. Different sizes and shapes of Ag nano-particles, such as polyhedral and spherical shape are clear on the GO surface that can be observed in the Figure. As shown in the Figure, the accumulated Ag nano-particles are randomly accumulated on GO sheets with the average size between 10 nm and 50 nm [23-24].

In FESEM images of GO:Si, small white particles are seen, which are related to SiO2 nano-particles on the graphene oxide surface and are very small in size and below 50 nm. The surface roughness increased after the decoration of the surface of GO plates with SiO2 nano-particles. Nucleation and growth of spherical SiO2 nano-particles on GO surface occurs due to the reactions of hydrolysis and condensation of TEOS with oxygen groups present on graphene oxide plates [25-27].

As expected in FESEM figures of GO:Zn thin film, the structure of this composite is crust-like after reaction in the presence of GO, given the 3D cross-sectional nature of ZnO particles, which tends to homogeneously precipitate on the surface of GO sheets. The average size of the almost spherical nano-particles of ZnO on GO sheets is between 10 nm to 30 nm.

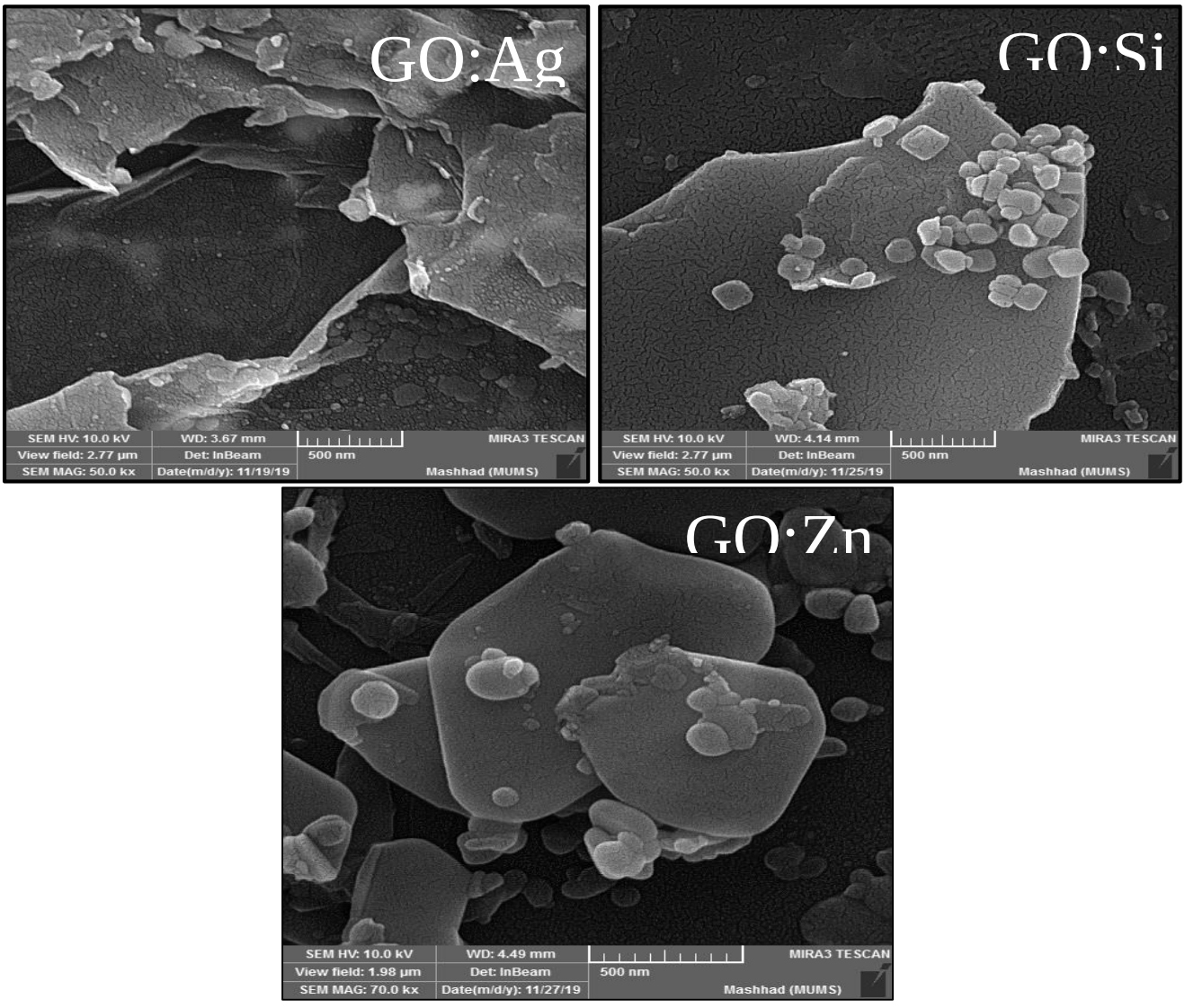

Figure 6. FESEM Images of GO:Ag, GO:Si and GO:Zn thin films Prepared by Spray Pyrolysis Method.

AFM analysis

Atomic force microscope (AFM) was used for imaging the topography of GO, GO:Ag, GO:Si and GO:Zn thin films prepared by spray pyrolysis method. The results are reported in Figure 7. In AFM microscope, the force between the sample surface and the scanning needle, which causes the cantilever to bend, is measured by the detector. According to Figures 6 and 7, GO:Ag, GO:Si and GO:Zn nano-composites have the heterogeneous morphology. The graphene oxide (GO) sheets have covered the surface and GO sheets are randomly accumulated. Lateral dimensions of graphene oxide sheets are about a few micrometers. Silver, silica and zinc nano-particles are randomly scattered in the form of prominent peaks on the surface. Also, AFM microscope can be used to measure the mean surface roughness. Root Mean Square Roughness (RMS) is measured by calculating the deviation of elevation between peaks and troughs in a particular region. The more deviation indicates the higher surface roughness. According to AFM results, RMS values for GO, GO:Ag, GO:Si and GO:Zn thin films were 17.57, 185.78, 125.64, 37.23 nm, respectively. According to RMS results, GO:Ag thin film has the highest surface roughness and GO:Zn sample has the lowest surface roughness [28-30].

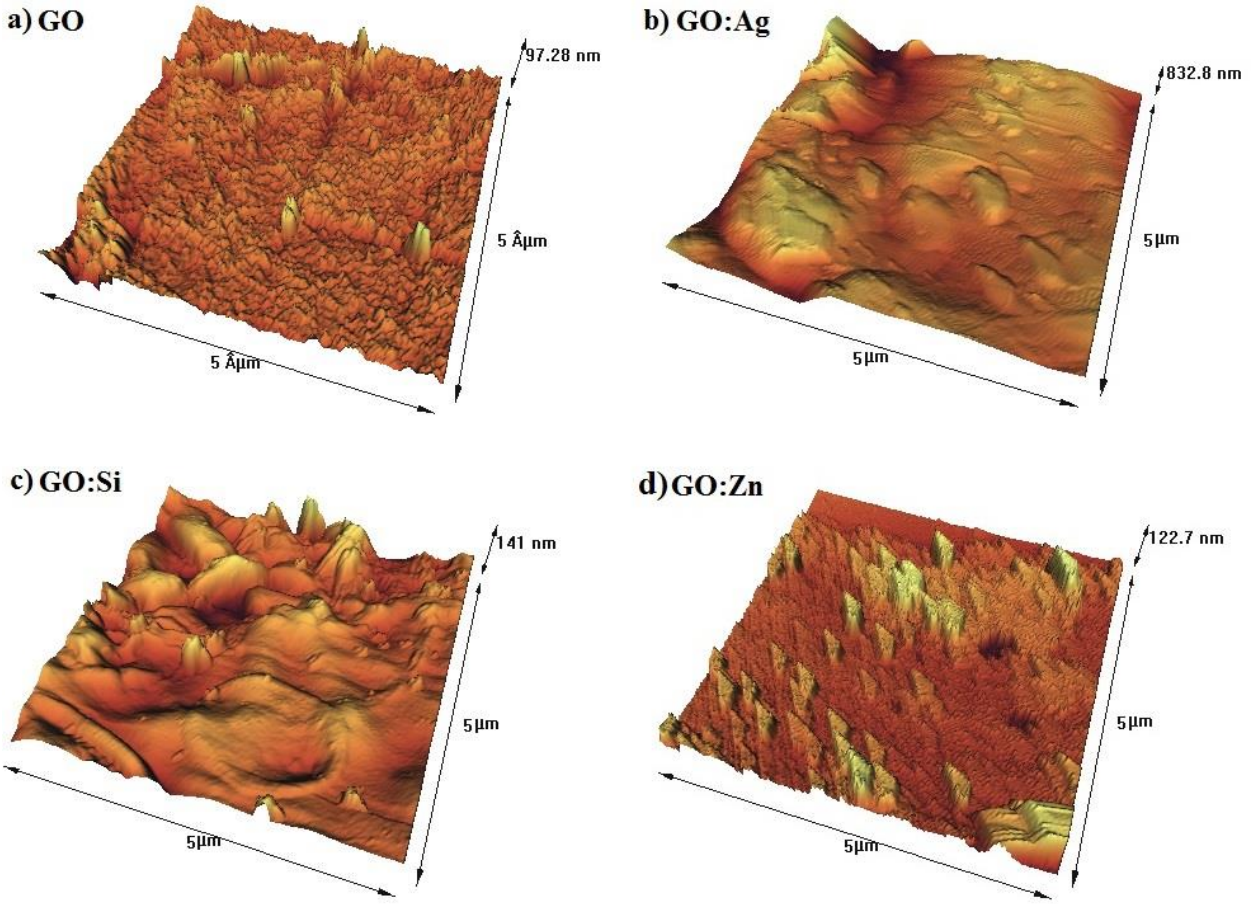

Figure 7. AFM Images of a) GO, b) GO:Ag, c) GO:Si and d)GO:Zn thin films Prepared by Spray Pyrolysis Method.

Contact Angle

The self-cleaning properties depends on the contact angle (CA) between water drop and surface of the sample. Hydrophilic surfaces have the contact angle (CA) less than 90° and very high surface energy. Hydrophobic surfaces have CA more than 90° and very low surface energy [12]. In this study, the contact angle of GO:Ag, GO:Si and GO:Zn thin films was measured by AM-7013MZT, Dino-Lite, Taiwan. Imaging of a 1µl water droplet with a magnification of 50 was done at room temperature and the results are shown in Figures 8 and 9. The CA of water droplet with the surface of thin films in GO:Ag, GO:Si and GO:Zn samples are 63.7, 54.6 and 30.4°, respectively. The contact angle of all samples is less than 90°, indicating the surface hydrophilicity of these samples. The different parameters such as the amount and type of impurity, surface homogeneity and surface roughness affect the contact angle. Among these parameters, the surface roughness is very important that affecting the interaction between the liquid and the surface. The higher the surface roughness leads to greater CA. As it can be seen in AFM images, GO:Ag nano-composite has the

highest RMS and the highest CA . GO: Zn thin film has the lowest roughness and thus the lowest contact angle and a relatively good hydrophilic surface. As we know, Silicon oxide is hydrophobic but in the GO:Si sample the Si nano-particles content is very low and therefore it does not cause much change in the CA.

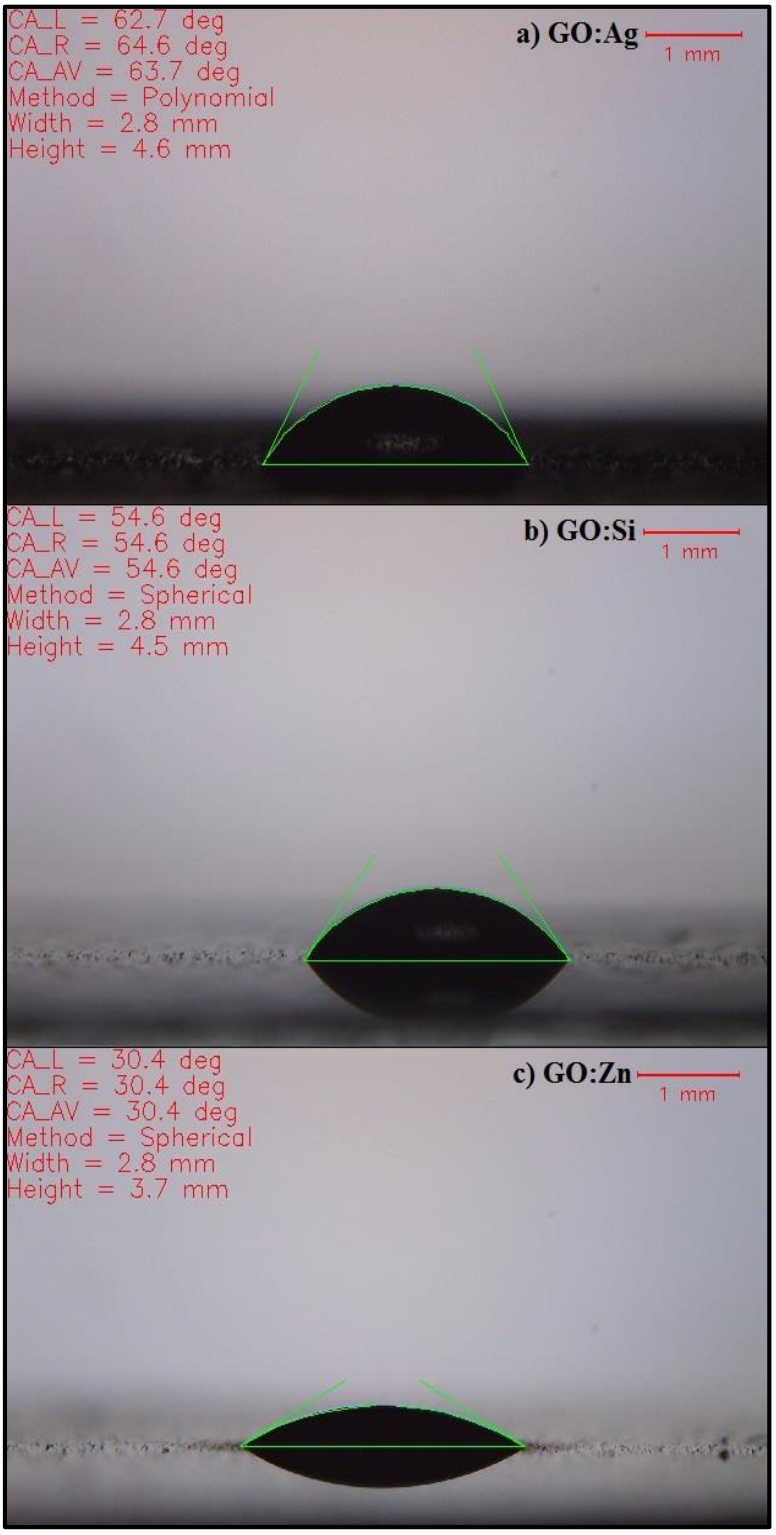

Figure 8. Contact Angle of a) GO:Ag, b) GO:Si and c) GO:Zn thin films prepared using spray pyrolysis method.

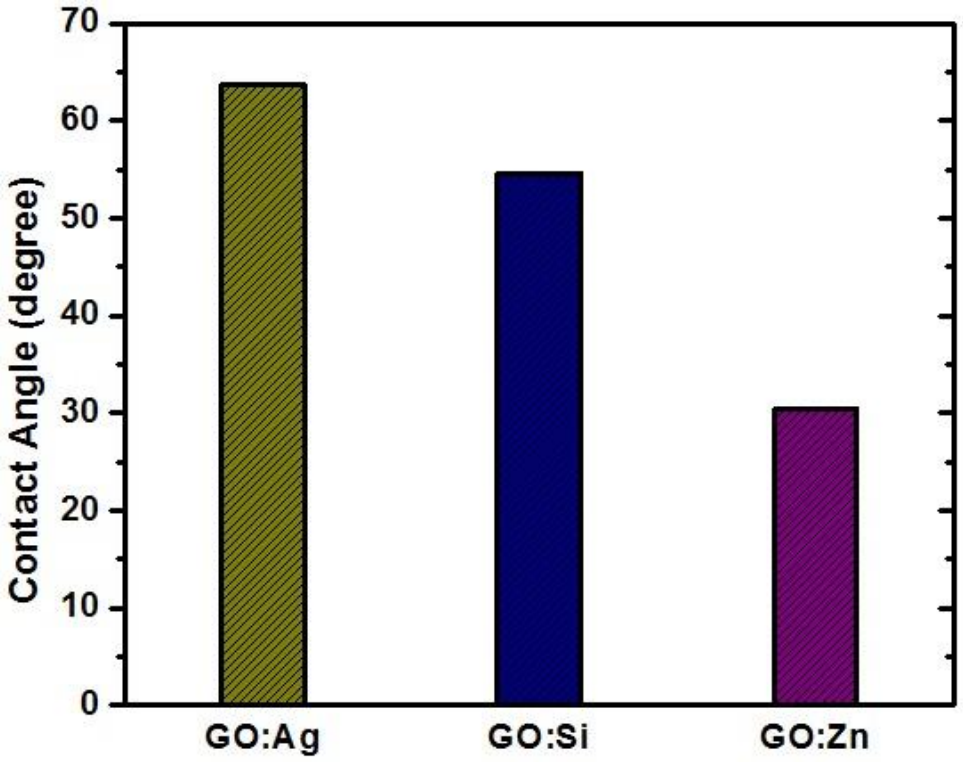

Figure 9. Comparison of Contact Angle of GO:Ag, GO:Si and GO:Zn thin films prepared using spray pyrolysis method.

Conclusions

In this paper, the sol containing GO:Ag, GO:Si and GO:Zn nano-composites thin films were prepared using a simple method and were deposited by spray pyrolysis technique. The results of XRD spectrum show that in addition to the peaks of GO, further diffraction peaks are seen, that are related to the Ag, Si and Zn nano-particles. The presence of GO sheets, Ag, Si and Zn nano-particles is also clearly evident in FESEM and AFM images. According to Figures of FESEM and AFM, GO:Ag, GO:Si and GO:Zn nano-composites thin films have the heterogeneous morphology. Among the studied samples, GO:Zn nano-composite thin film, which has the lowest roughness according to AFM results, also has the lowest CA and is a relatively good hydrophilic surface.

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