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Investigation of Structural and Morphological Properties of Zno Nanoflowers on Biocompatible Polymeric Substrate

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Abstract

In this study, acrylic acid (AA) biocompatible hydrogels were prepared and used as a polymeric substrate for zinc oxide (ZnO) nanoflower. Acrylic acid hydrogels were synthesized by free radical polymerization technique. ZnO nanoflowers on hydrogels (ZnO/PAA) were prepared for the first time in literature by Chemical Bath Deposition technique at a very short deposition time (30 minutes). Structural and morphological properties of ZnO nanoflowers on PAA hydrogels were examined by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Field Emission Scanning Electron Microscopy – Energy Dispersive of X-Ray (FESEM-EDX) respectively. Distribution of ZnO nanoflower on PAA hydrogels was determined by using elemental mapping. The XRD patterns showed that ZnO nanoflowers were fully formed on hydrogels. The FT-IR spectrum proved the characteristic absorption peaks of ZnO. FESEM images showed that the homogeneous morphology of ZnO nanoflowers. Nanoflowers were synthesized with an average size of 700 nm. XRD, FT-IR spectroscopy and FESEM-EDX analysis evidenced the successful synthesize of novel ZnO/PAA biocompatible nanocomposite hydrogels.

Keywords: Poly Acrylic acid, Hydrogel, Chemical Bath Deposition, ZnO nanoflower.

1. INTRODUCTION

Nanotechnology is the refer of working at the scale of individual molecules through science and technology around the world. According to the surge of a relevant number of publications, a great deal of interest on ZnO nanostructures is increasing recently. ZnO is mostly used in optoelectronic applications due to its wide band gap (Eg-3.3eV at 300 K) and large exciton binding energy (60 meV). Among different metal oxide nanoparticles, ZnO nanoparticles have great importance owing to their wide application areas such as chemical sensor, storage devices, bio-sensor, gas sensors, optoelectronic devices and window materials for solar cells. Various synthesis methods have been developed to grow a variety of ZnO nanostructures, including, nanoparticles, nanoflowers, nanowires, nanotubes, nanorods, nanobelts, etc [1-6].

A three dimensional (3D) networks of polymers made of both natural and synthetic materials dominating high number of flexibility is called hydrogels. In physical conditions, they are able to contain high amount of water and they can be characterized easily, it makes them an ideal material for variable applications. Hydrogels have characteristics properties like a desired functionality, reusability, reversibility, sterilizability and biocompatibility [7-10]. Due to these properties, hydrogels were selected as a substrate for nanoflower like ZnO particles.

There are only a few reports about deposition of ZnO nanoparticles on biocompatible hydrogels [11-13]. Due to its high specific surface area, excellent hydrophobicity and oxidizing ability, ZnO has been widely used to inhibit the growth of microorganisms. Reducing ZnO particles to nanoscale provides them ability to kill bacteria rapidly [14]. In this case, the use of ZnO nanoparticles together in biocompatible polymeric substrate should be improved to enhanced antibacterial property.

In these reports, ZnO nanoparticles deposition lasts about 24 hours. In the present work, ZnO/PAA biocompatible nanocomposite hydrogels were deposited via Chemical Bath Deposition (CBD) Technique. CBD is a cost effective and simply applicable technique. ZnO nanoparticle deposition by CBD can be carried out in a very short time compared to other methods. ZnO/PAA biocompatible nanocomposite hydrogels were successfully deposited at a very short deposition time like 30 minutes. Shorter deposition time provides energy efficiency and time saving.

2. EXPERIMENTAL SECTION

Synthesize of two types of hydrogels (PAA and ZnO/PAA) and characterization of obtained materials were described in this section.

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2.1. Materials

Acrylic Acid (AA) (Sigma), N,N'methylenebisacrylamide (N,N'-MBAAm) (Sigma) and ammonium per sulphate (APS) (Sigma) were used for synthesized hydrogels. Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ (Sigma), ammonia solution (%28 v/v) (Merck) and distilled water were used for preparation of ZnO nanoflower on PAA hydrogels.

2.2. Synthesize of PAA hydrogels

The poly acrylic acid hydrogel solution containing monomer (acrylic acid), initiator (APS), crosslinking agent (N,N'-MBAAm) and solvent (distilled water) were poured into PVC straws and heated in a temperature-controlled water bath (at 80 °C) for 2 h. Then, the PVC straws were removed from bath and cut into cylindrical discs (3-4 mm in length) with a knife in same shape, and the hydrogels were dried in air before kept in vacuum oven (35 °C) [15].

2.3 Synthesize of flower-like ZnO on PAA substrates

0.1M Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ solution was prepared in distilled water of 100 ml. Then, it was stirred with a magnetic stirrer. The pH of the solution was fixed to 10 while the solution was stirred, with adding ammonia solution (%28 v/v) drop by drop. After the bath was prepared, swollen cylindrical disc hydrogels substrates were thrown into the solution. The bath solution was stirred by temperature-controlled magnetic stirrer at 85°C in optimized minimum deposition time. The obtained samples were washed with distilled water and dried at room temperature [16-17]. Schematic diagram of general experimental procedure was seen in Fig.1.

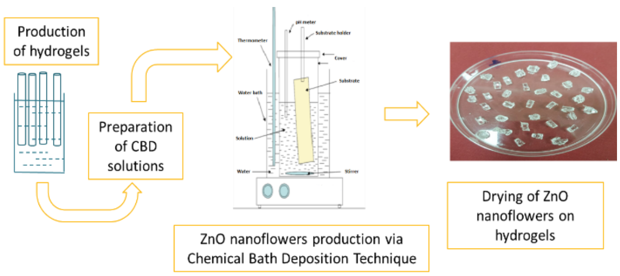

Figure 1. Schematic diagram of ZnO nanoflowers on PAA hydrogels production.

2.4 Characterization of ZnO Nanoflowers on Poly Acrylic Acid Hydrogels

The synthesized ZnO nanoflower on PAA hydrogels were primarily investigated by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Field Emission Scanning Electron Microscopy (FESEM) for structural and morphological analysis. The crystal structure of the PAA hydrogel and ZnO nanoflower on PAA hydrogel were investigated by Panalytical Empyrean X-ray diffractometer using CuK_α (λ=1.5405 Å) radiation in the 2θ range 20°- 60°. The presence and absence of the ZnO nanoflower vibrational modes were examined by FT-IR (Perkin Elmer, Spectra 100). The wave number range is 400-4000 cm^{-1}. ATR mode was used and each spectrum was scanned 4 times and worked at a resolution of 4 cm^{-1}. FESEM was used to confirm the size and shape of the ZnO nanoflowers on hydrogels. FESEM samples were prepared by coated with 2 nm of gold/palladium using a Qourum Sputter coater, and imaged using a Zeiss Supra 40 VP FESEM at a working distance of 9 mm and at 15 kV. Elemental amounts and distributions of ZnO nanoflowers were shown by EDX and mapping images respectively.

3. RESULTS AND DISCUSSION

The X-ray measurements of the PAA hydrogel and ZnO nanoflower on PAA hydrogel were taken at the room temperature at 45 kV and 40 mA. In Fig. 2, XRD patterns of PAA hydrogel and ZnO nanoflower on PAA hydrogel have been given comparatively. According to XRD results, PAA hydrogel has amorphous structure. ZnO nanoflower on PAA hydrogel has polycrystalline nature. ZnO nanoflowers has matched completely with the hexagonal structured ZnO (ICDD: 98-003-1052). The XRD patterns showed that ZnO nanoflowers were fully formed on PAA hydrogels.

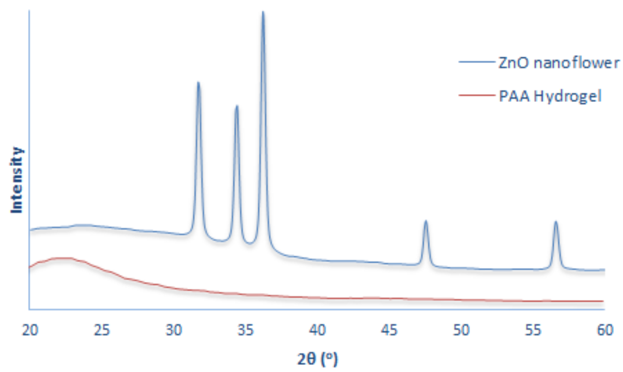

Figure 2. XRD patterns of PAA hydrogel and ZnO nanoflowers on PAA hydrogel.

FT-IR spectroscopy is performed in order to quickly establish the presence or absence of the various vibrational modes present in synthesized structures. FT-IR functional groups of PAA and ZnO/PAA hydrogels were given in Fig. 3 and Table 1.
The spectrum of interference pattern obtained in FT-IR images clearly shows that the characteristic absorption peaks of Zn-O 2000 cm^{-1}, 2152 cm^{-1} and 3835 cm^{-1} [18]. Swelling and water retention properties of PAA hydrogels exhibits by electrostatic interactions and H-bonding between the COO^- groups. FT-IR results demonstrated of chemical interactions between ZnO and polymer.

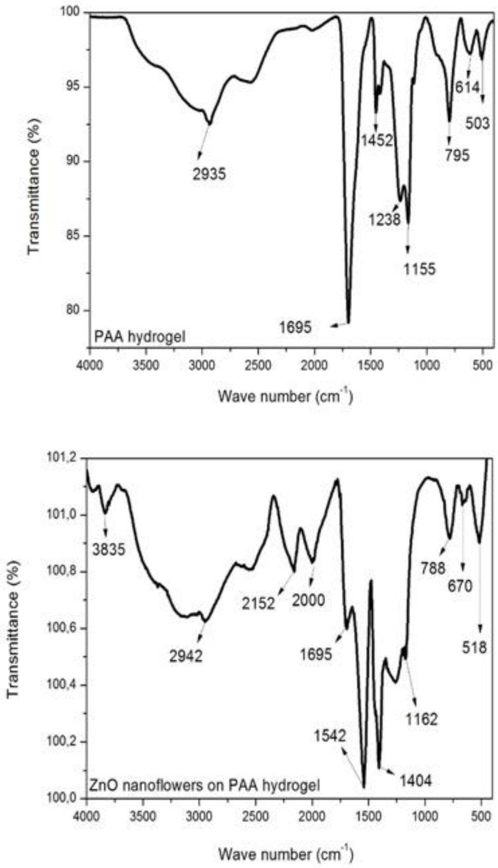

Figure 3. FT-IR spectra of PAA hydrogel and ZnO nanoflowers on PAA hydrogel.

Table 1. FT-IR functional groups of PAA and ZnO/PAA hydrogels.

Functional Groups	Wave Number (cm^{-1})	
	PAA Hydrogel	ZnO/PAA Hydrogel
Zn-O groups	-	3835, 2152, 2000
C-H stretching	2935	2942
C=O stretching	1695	1695, 1542
C=C stretching	1452	1404
C-O stretching	1238, 1155	1162

The morphological structures of hydrogels were imaged by FESEM. It was defined the distribution of ZnO nanoflowers on polymer surface clearly. Fig. 4 showed that homogenous ZnO distribution on PAA hydrogel surface at 3kx magnification. Also, morphological differences were seen before and after deposition of ZnO nanoflowers at 1kx magnification.

The observed size and shaped of ZnO nanoflowers were seen in Fig. 5. ZnO nanoflowers were obtained on PAA hydrogels by using CBD technique at minimum deposition time without any breaks and splits. ZnO nanoflowers distributed on hydrogel's surface smoothly.

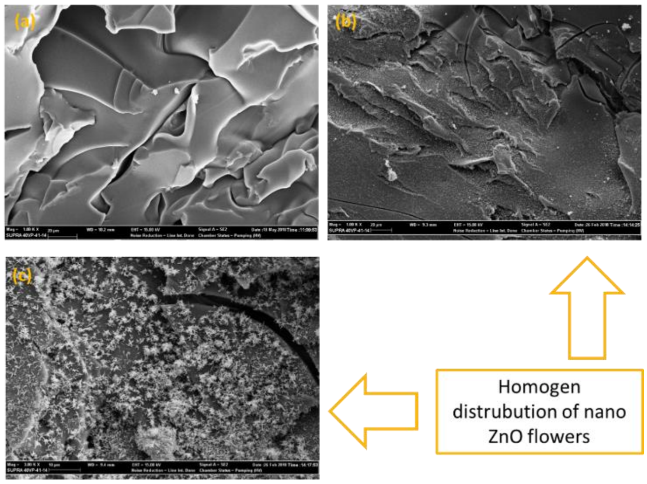

Figure 4. SEM images of (a) plain PAA hydrogel (1kx), (b) ZnO nanoflowers on PAA hydrogel (1kx) and (c) SEM image ZnO nano flowers on hydrogel (3kx).

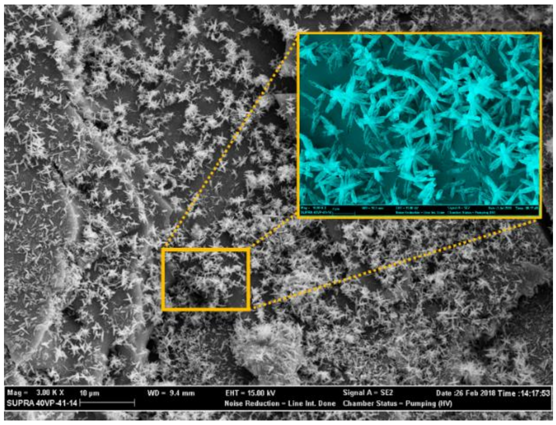

Figure 5. SEM image of ZnO nanoflowers on PAA hydrogel.

The elemental amount of C, O and Zn were determined by EDX analysis. Amount of elements on PAA and ZnO/PAA hydrogels were given in Table 2. According to the Table 2, the O and Zn amounts were increased of after deposition.

Table 2. Amount of elements on PAA and ZnO/PAA hydrogels

Elements	PAA Hydrogel	ZnO/PAA Hydrogel
C	57.96 %	39.36 %
O	42.04 %	45.45 %
Zn	-	15.19 %

Elemental mapping images of ZnO nanoflowers on hydrogel were given in Fig. 6. Zinc distribution was clearly seen in flower structures (in red color).

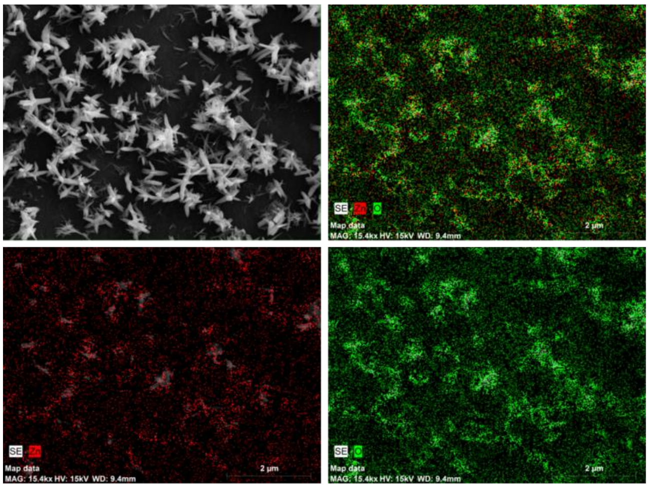

Figure 6. Elemental mapping images of ZnO nanoflower on PAA hydrogel.

4. CONCLUSIONS

ZnO/PAA biocompatible nanocomposite hydrogels were synthesized via a cost effective and simple method by using CBD technique. The effect of ZnO nanoflowers on structural and morphological properties of PAA hydrogels was investigated. Chemical bath solution at pH 10 triggered the interactions between hydrogel and ZnO nanoparticles strongly in 30 minutes. The XRD patterns showed that ZnO nanoflowers were fully formed on PAA hydrogels. The FT-IR spectrum proved that the characteristic absorption peaks of Zn-O were at 2000 cm^{-1}, 2152 cm^{-1} and 3835 cm^{-1}. FESEM images showed that the homogeneous morphology of ZnO nanoflowers. Nanoflowers were synthesized with an average size of 700 nm. XRD, FT-IR spectroscopy and FESEM analysis evidenced the successful synthesize of ZnO/PAA biocompatible nanocomposite hydrogels. In comparison with studies in literature, ZnO nanoparticle deposition were carried out in a very short time via CBD. The further studies can be done on antibacterial property of ZnO/PAA hydrogels, due to its ability to kill bacteria rapidly.

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