

Preparation and Extensive Characterization of Fullerenol C₆₀

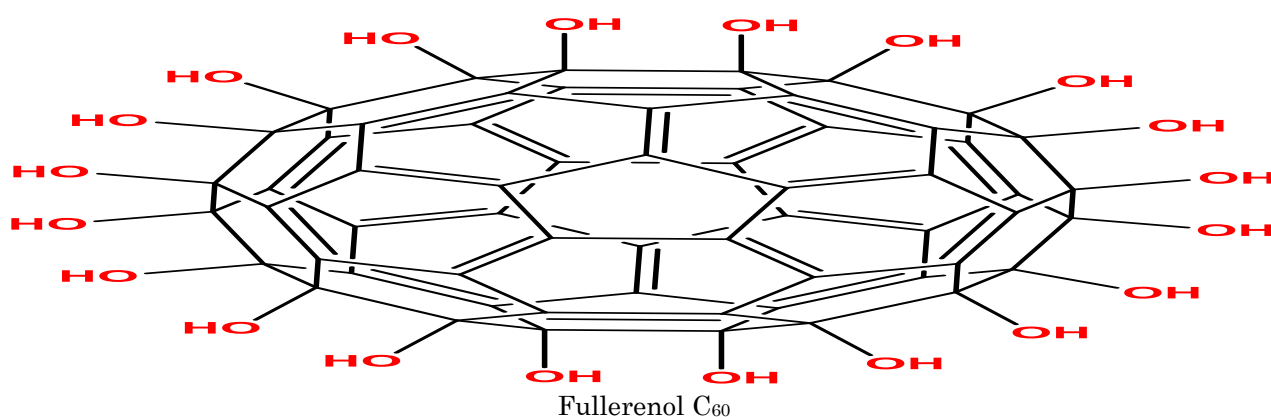
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Abstract

Recently, functionalization processes onto the outer surface of fullerenes such as C₆₀ and C₇₀ with various groups attracted large interesting from scientists, which including convert sp² hybridization carbon atoms to sp³ hybridization that aim for enhancing its solubility in an organic polar solvent. This work converts the fullerene C₆₀ successfully to hydroxyl functionalized fullerene which called fullerenol C₆₀.



The hydroxyl functionalized fullerene C₆₀ nano-product was characterized using FTIR, ¹H-NMR, ¹³C-NMR, AFM, SEM, TEM, EDX, TGA, and XRD examinations, they proved the fullerenol C₆₀ structure and demonstrated the remarkable change in fullerene C₆₀ topography from un-uniform particles to shape like spherical with high aggregation.

Keywords: Fullerene C₆₀, fullerenol, functionalization.

Introduction

Carbon is an extraordinary element. The electronic configuration of 1s² 2s² 2p² allows carbon atoms to form three different types of bonding, i.e., single, double, and triple bonds. This versatility of carbon to bond with other atoms is based on the ability of carbon to hybridize its 2s and 2p atomic orbital's into three different manners: sp³ (for single bonding, tetrahedral), sp² (for double bonding, trigonal planar), and sp (for triple bonding, linear).

The carbon family is traditionally covered graphite, diamond, and amorphous carbons. Recently, fullerenes and carbon nanotubes [1]. Fullerenes led to various breakthroughs in science and nanoscience. Fullerenes have important electronic properties, such as photo induced electron transfers,

photodynamic therapy agents, and components of photovoltaic cells which make them highly applicable [2]. C₆₀ is the most important member of the family [3]. The fullerene C₆₀ is considered the simplest and stable member of fullerene family that consists of 20 hexagons fused with 12 pentagons, C₆₀ is a pure molecule and found in a single isomer [4, 5]. The interesting physical, photophysical, and electrophysical properties of fullerenes have brought a lot of interest from the scientists.

These properties have been comprehensively studied. Fullerene C₆₀ and other members of the family are insoluble or sparing in the most organic solvent, therefore, they are difficult to be handled. Accordingly, exohedral chemical functionalization became

necessary to synthesis fullerene C_{60} derivatives, to increase solubility feature and maintain the electrochemical and photochemical properties.

This work aimed on converting the fullerene C_{60} to highly soluble hydroxyl functionalized fullerene C_{60} (Fullerenol).

Materials and Methods

Fullerene C_{60} (50 mg, 99.95% SAS, USA) was dissolved in 20 mL of toluene (99% Sigma Aldrich, Germany) then stirred at room temperature for 30 min. until the transparent solvent totally turned into

purple. Hydrogen peroxide (30 %, PanReac AppliChem, Spain) 1.9 mL was added, and followed by (0.5 mL) of trimethylamine (99%, BHD, UK). Two layers were formed after 15 min. of stirring, one was transparent and the second was yellow aqueous layer settled down at the flask.

Layers were separated using separation funnel, cold ethanol (5-10 mL) was added to the yellow aqueous layer and a milky white precipitate was collected by Millipore filtration, washed with cold diethyl ether (10 mL), and dried in the oven at 50 °C for 2 hrs. To obtain pure product .Fig. 1 shows the reaction flask and the obtained product.



Fig.1: The reaction flask and the obtained product

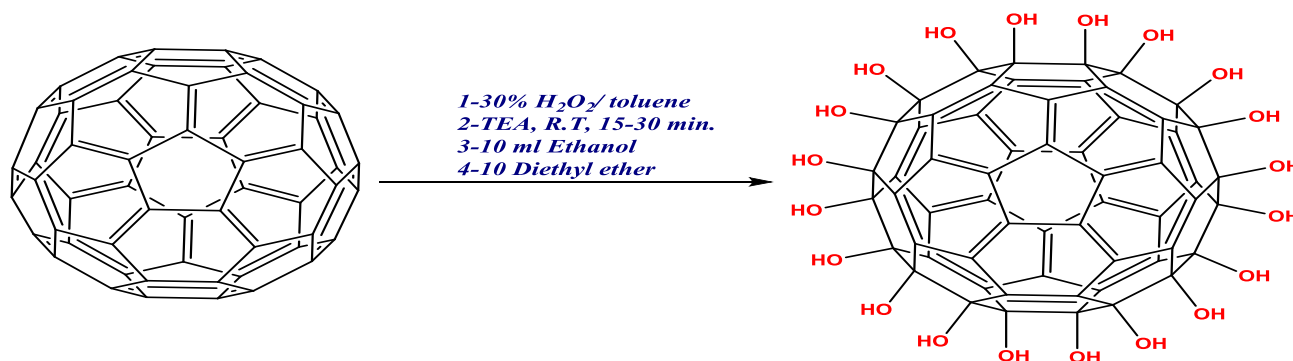


Fig. 2 Schematic diagram of synthesis of fullereneol in presence trimethylamine

Results and Discussion

Physical Properties

The yield of the prepared fullereneol was

about 82% and was pale yellow in color as shown in Fig. 3; the melting point was higher than 160°C.



Fig. 3: Fullereneol color appearance

FT-IR Analysis of Fullerenol

FT-IR (8400s, SHIMADZU Co., Japan) (KBr) spectrum of fullerenol is depicted in Fig. 4, showed a band at 3400 cm^{-1} within range of $3650\text{--}3200\text{ cm}^{-1}$, indicated the hydroxyl groups and confirmed a successful functionalization onto C_{60} cage. Three characteristic peaks of fullerenol centered at 1625 , 1363 , and 1087 cm^{-1} were assigned to

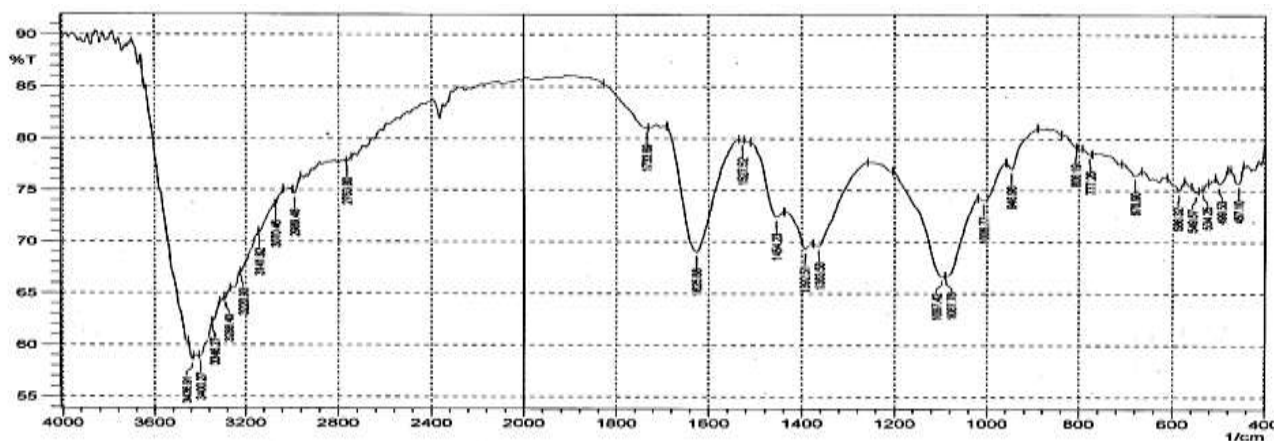


Fig. 4: FT-IR spectrum of the produced Fullerenol

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of Fullerenol:

Fig. 5 show (Bruker, Ultrasheild 300 MHz) $^1\text{H-NMR}$ spectrum of hydroxylated fullerene carried out on 300 MHz using D_2O as a solvent. A well-defined peak at 3.36 ppm due to the proton of hydroxylated fullerene. This peak is considered a diagnostic signal of fullerenol in a range of $0.5\text{--}5\text{ ppm}$, which depending on concentration, temperature,

and solvent. Remarkable peaks appeared at $3.07\text{--}3.14\text{ ppm}$ (q, $J=7.3\text{ Hz}$, 6H) was corresponded to $(-\text{CH}_2, 2^\circ)$ protons of triethylhydroxylammonium, while peaks at a range of $1.18\text{--}1.23\text{ ppm}$ (t, $J=7.2\text{ Hz}$, 9H) was assigned to methyl groups, a weak signal at 2.13 ppm may be attributed to proton of hydroxyl attached to triethylhydroxylammonium salt.

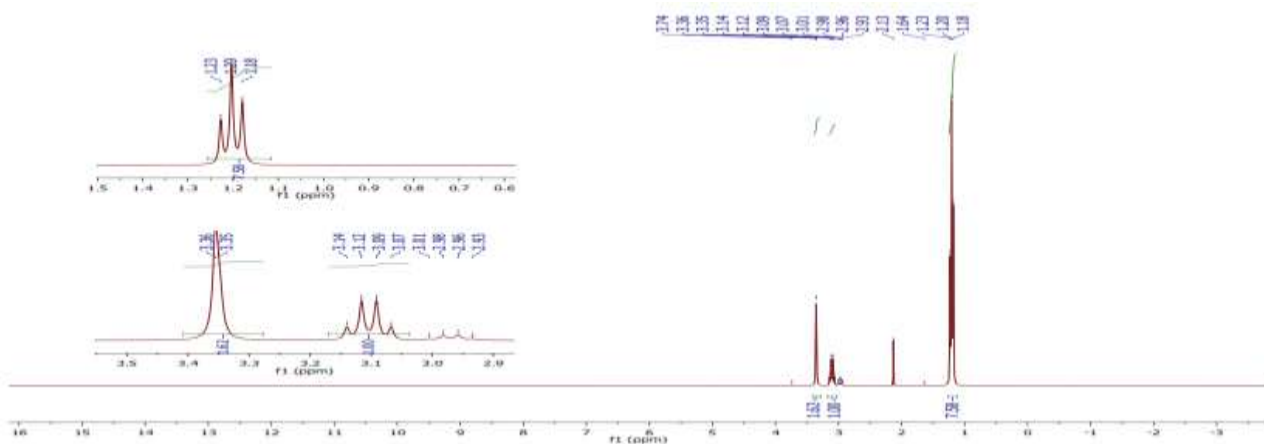


Fig. 5: $^1\text{H-NMR}$ spectrum of $\text{C}_{60}(\text{OH})_{40.6}\text{H}_2\text{O}$

The $^{13}\text{C-NMR}$ spectrum as represented in Fig. 6, showed a characteristic strong signal centered at a chemical shift 58.71 ppm . This peak assigned to the carbon atoms attached to hydroxyl groups of fullerenol, thus, introducing of hydroxyl groups on fullerene cage has achieved [15, 16]. A small signal observed at 99.98 ppm was as consequence of

hemiketal carbon [8]. A peak appeared at 46.64 ppm was attributed to secondary aliphatic carbon atoms linked with nitrogen atom of triethylhydroxylammonium (TEHA). A strong peak at 7.27 ppm belonged to primary carbon atoms, which confirmed the presence of TEHA with fullerene structure as a salt or secondary bounded molecule.

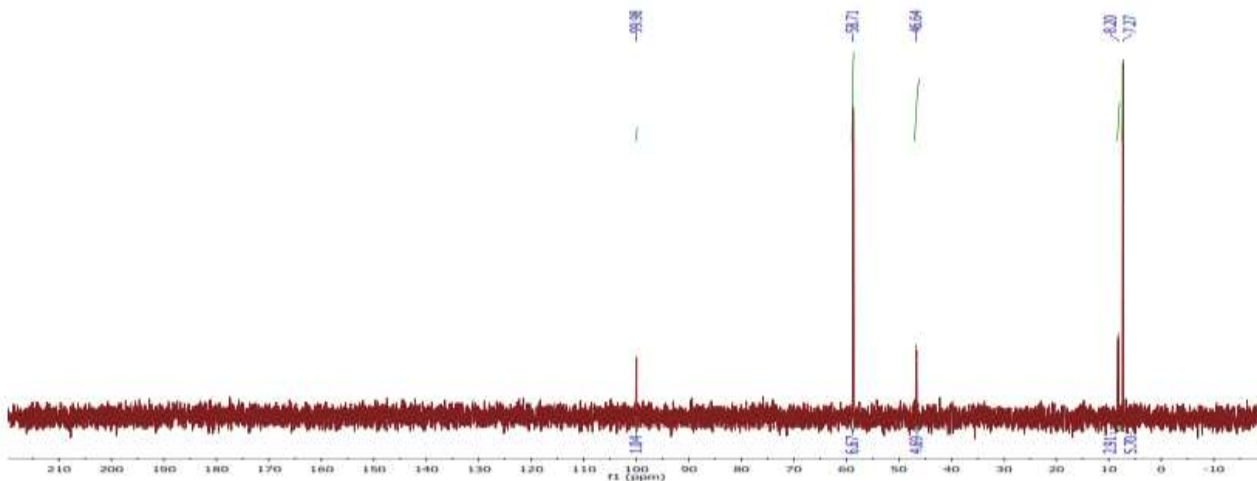


Fig. 6 ¹³C-NMR spectrum of fulleranol

Determination the Number of Hydroxyl Groups of Fulleranol:

To estimate the number of hydroxyl groups attached to the fullerene C₆₀ cage and the average structure of C₆₀ (OH) *n*. *m*H₂O as a hydrated formula, elemental analysis along with TG analysis were used. TG analysis employed to determine the water content as a secondary bounded molecule with high hydroxylated fulleranol. Weight loss by TG analysis observed when the sample was

heated from room temperature to 816 °C as depicted in Fig. 7. The thermograph showed three stages of decomposition at different temperature ranges. First weight loss (6.8 wt. %) between 32 to 100 °C, which attributed to secondary bounded water [9]. The second weight loss (33 wt. %) in the range of 100-250 °C was assigned to dehydration of hydroxyl groups and can be interpreted to Pinacol rearrangement [11]. Above 250 °C, the weight loss of fullerene cage was (27.51%).

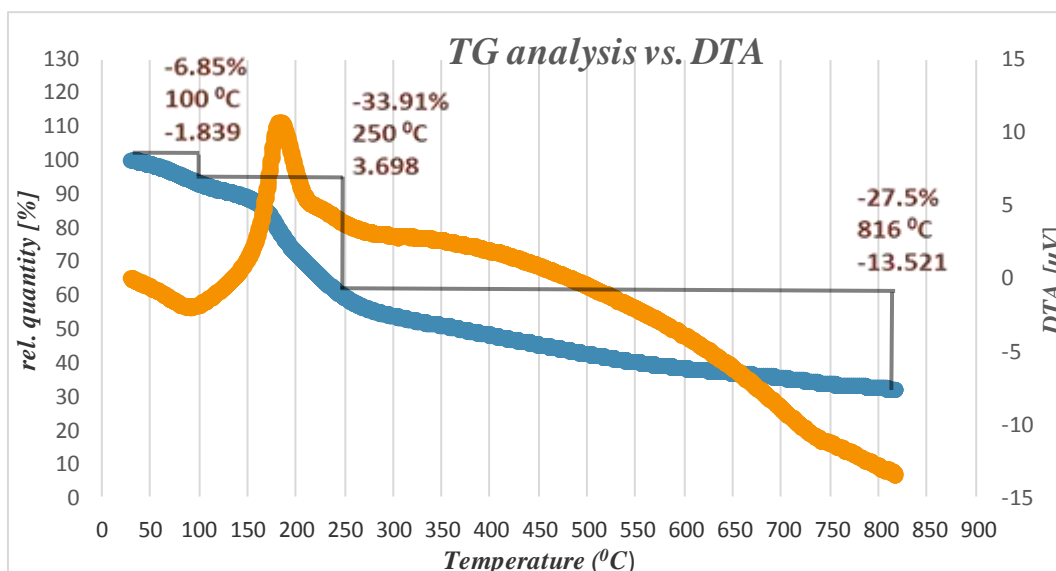


Fig. 7: TG analysis (Blue line) and differential thermogravimetric analysis (yellow line) curves of C₆₀(OH)₄₀.6H₂O

Elemental analysis showed that the composition of fulleranol was consisted of C (47.79%), H (4.53%), and O (47.67%), which was similar to the theoretical calculations as shown in Table 1. Therefore, the deduced

chemical formula without TGA was C₆₀(OH)₄₆ (C:47.95, H:3.09, O: 48.97). Water content was determined depending on the weight loss in TG analysis and compared with estimated structure.

Table 1: Predicted formula of C₆₀ (OH) *n*. *m*H₂O with elemental analysis and water content which calculated theoretically

No.	Estimated structural formula	Elemental analysis (T)	H ₂ O (Wt %) T
1	C ₆₀ (OH) ₄₀ .5H ₂ O	C:48.33, H:3.38, O:48.29	6.0
2	C ₆₀ (OH) ₄₀ .6H ₂ O	C:47.76, H:3.47, O:48.77	7.1
3	C ₆₀ (OH) ₄₀ .7H ₂ O	C:47.19, H:3.56, O:49.24	8.2

T, refer to water content calculated theoretically. The differ between experimental and calculated should be ± 1%

The weight loss (6.8%) of water obtained from the results of TG analysis which referred to the loss of the secondary bounded water attached together with fullereneol, thus this value is compatible with water content determined theoretically as illustrated in Table 1. our conclusion the water content is congruent with the estimated formula is C₆₀(OH)_{40.6}H₂O, according to TG and elemental analysis.

AFM, SEM and TEM Study of Fullereneol

The AFM (SPM-AA3000 Angstrom Advanced Inc., USA) images was employed to study the surface morphology of synthesized fullereneol particles with two and three-dimension view as depicted in Fig. (8). Images demonstrated the dense aggregation of spherical particles with the average diameter was within a range of 20-44 nm.

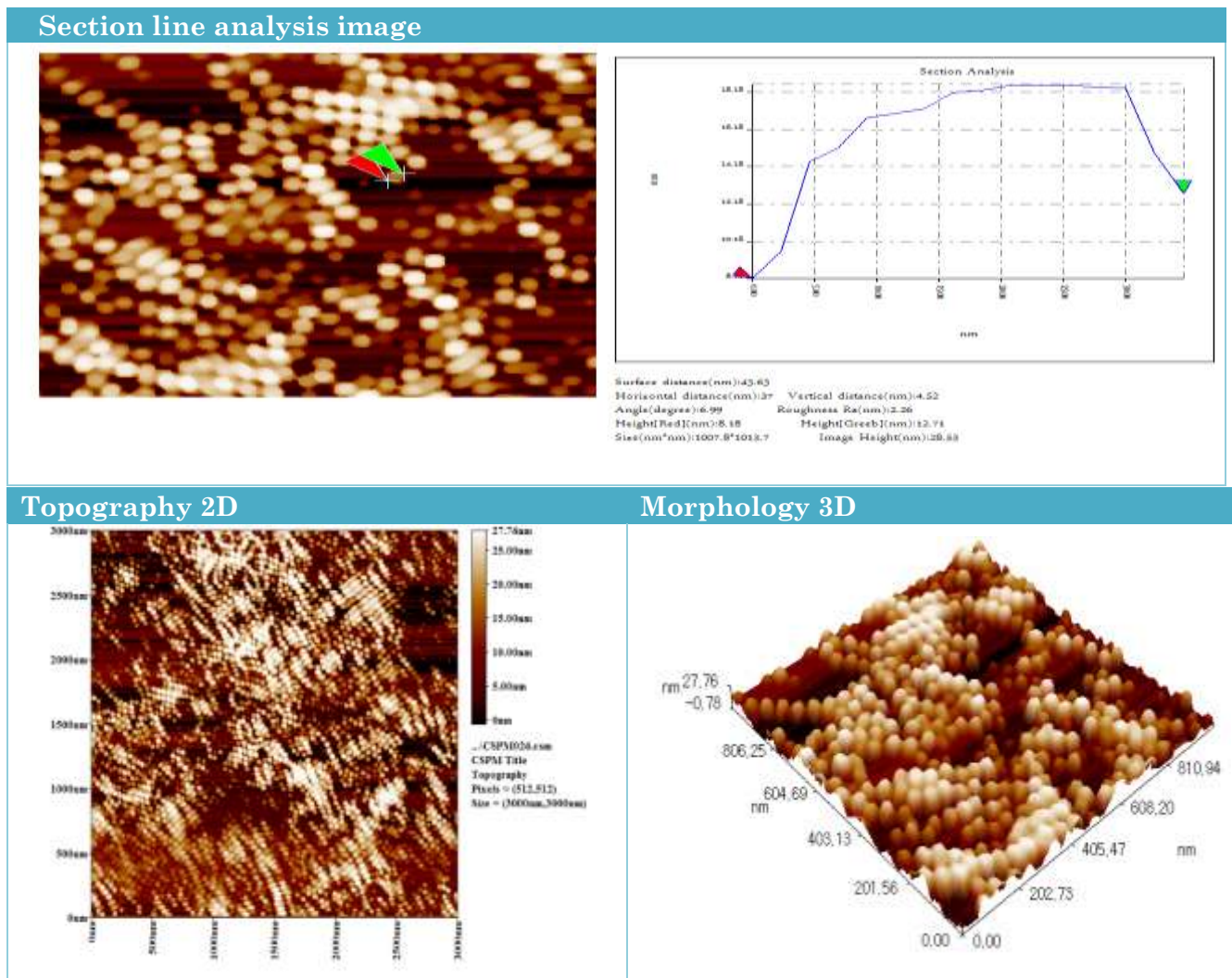


Fig. 8: Section line analysis, topography 2D, and morphology 3D AFM images of C₆₀ (OH)_{40.6}H₂O

The particle size distribution also deduced from

AFM analysis report as shown in Fig. 9.

Avg. Diameter:29.34 nm		
Diameter (nm)	Volume (%)	Accumulation (%)
20.00	3.14	3.14
22.00	8.94	12.08
24.00	10.63	22.71
26.00	11.84	34.54
28.00	11.59	46.14
30.00	9.18	55.31
32.00	9.66	64.98
34.00	9.66	74.64
36.00	8.21	82.85
38.00	7.25	90.10
40.00	5.31	95.41
42.00	4.11	99.52
44.00	0.48	100.00

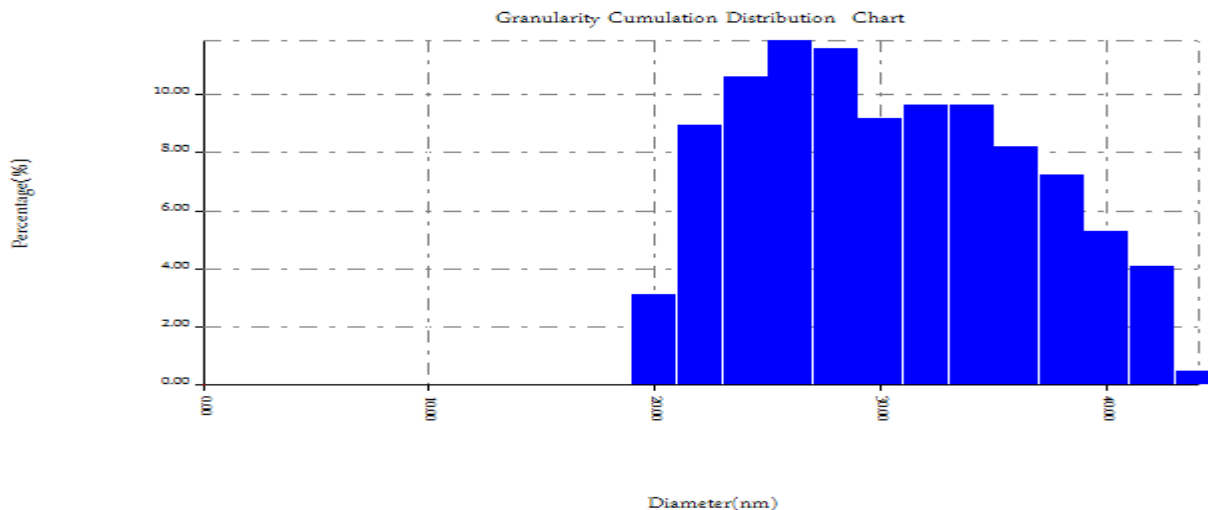


Fig. 9 AFM Particles size distribution analysis of C₆₀ (OH)40.6H₂O

The depth imaging of SEM (SIGMA VP-ZEISS) was to study surface morphological of fulleranol as shown in Fig. 10, Particles were highly aggregated as ball-structures with an average diameter between 50-98 nm.

The SEM results showed an increase in the average size as a compared with AFM due to combining two or more of spherical particles to form a larger particle with an average diameter of more than 50 nm.

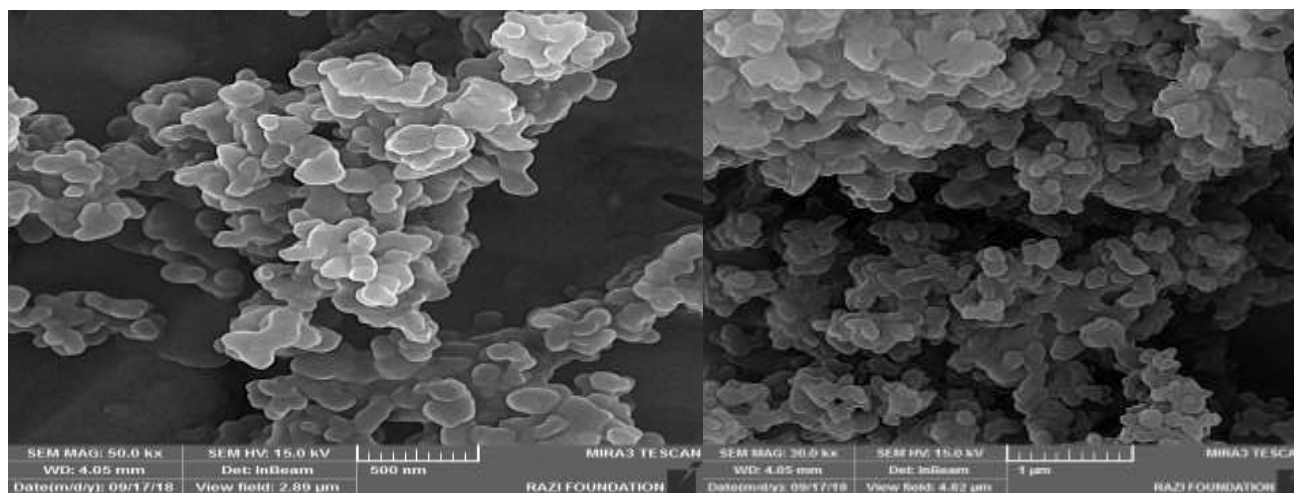


Fig. 10: SEM images of C₆₀ (OH) 40.6H₂O

ED's analysis, Fig. 11, proved the synthesized fulleranol, is composed of carbon and oxygen with a percentage of 62.72%, 36.88%, respectively. Therefore, the presence of oxygen in the fulleranol composition this

confirmed that hydroxyl groups was introduced on fullerene C₆₀, while the pure fullerene C₆₀ totally composed of (100%) carbon only.

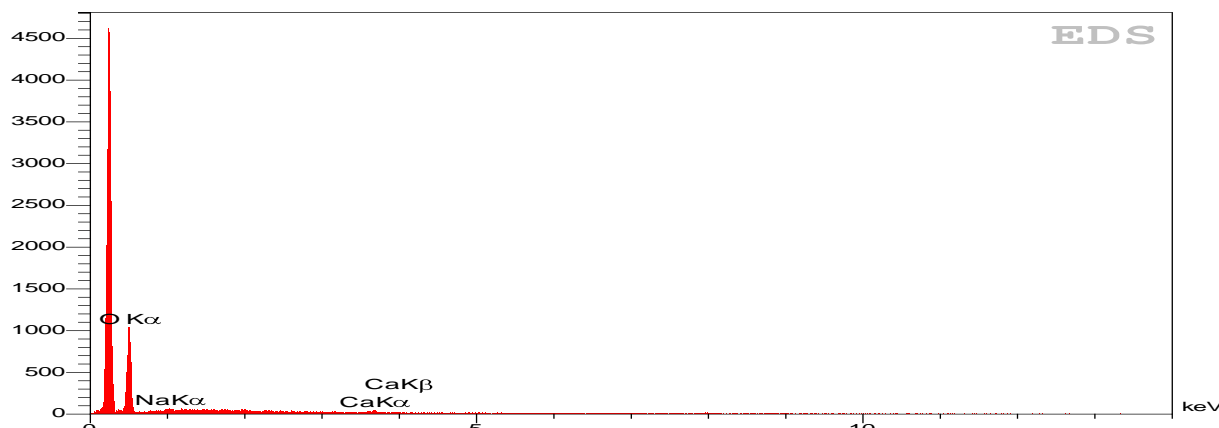


Fig. 11: EDS analysis of C₆₀ (OH) 40.6H₂O

Spherical shapes clearly demonstrated with TEM technique (Carl Zeiss-EM10C-100 KV, Germany) as illustrated in the Fig. 12.

TEM images appeared combination two or more than particle, thus resulted in high aggregation and increasing in sizes.

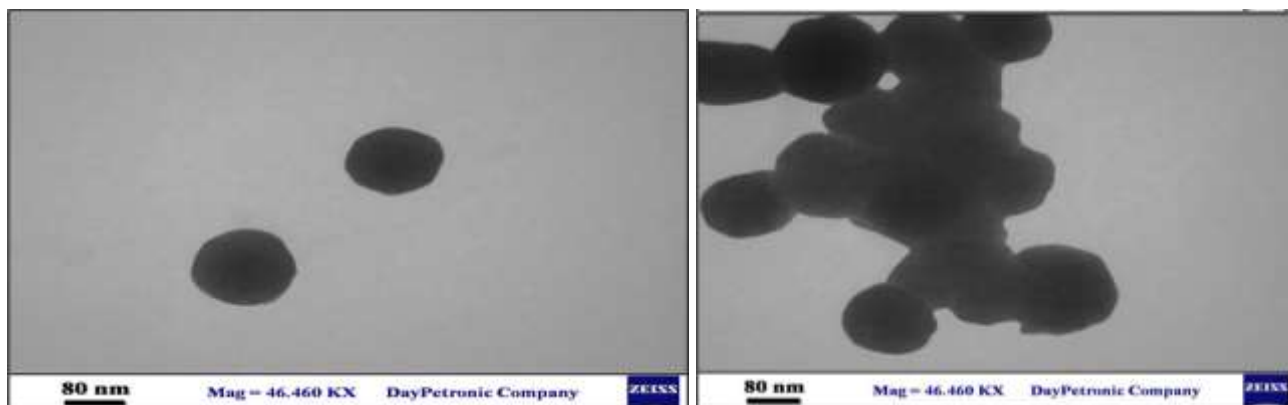


Fig. 12: TEM images of synthesized Fullerene

XRD Analysis of Fullerene

The Diffractogram (PANalytical XPert Pro XRD device, Philips, Netherlands, Cu-K α radiation target ($\lambda = 1.54180$)) of the synthesized fullerene as depicted in Fig. 13 was accomplished in a range of 10-80 $^{\circ}$, which showed a broad peak (A) at 16.65 $^{\circ}$ corresponding to d-spacing of 0.532 nm as shown in Fig. 13. That implies that synthesized particles were amorphous. A medium to weak diffraction peak (B)

appeared at 29.56 $^{\circ}$ with an inter-planar spacing of 0.302 nm. The particle sizes were calculated for both peaks based on the **Debye-Scherrer** equation and found to be 10.07 and 68.68 nm for (A) and (B) peaks, respectively. The particle sizes determined by XRD are approximately compatible with data obtained using AFM and SEM. We can infer that the particle sizes which determined by XRD technique are approximately compatible with those obtained from AFM and SEM.

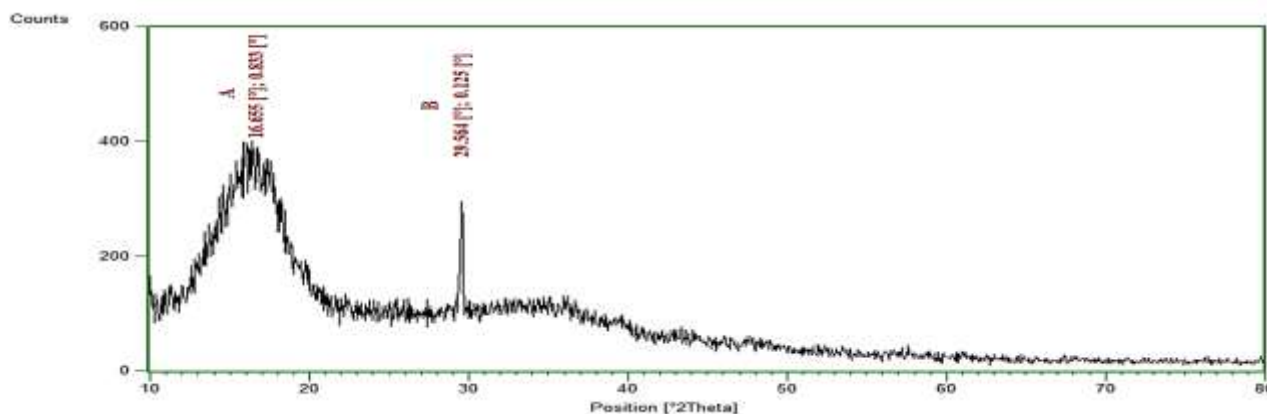


Fig. 13: Diffractogram of C₆₀ (OH) 40.6H₂O nanoparticles

Mechanism of Fullerene Formation

The predicted mechanism of fullerene synthesis is shown in Fig 14. The mechanism included some subsequent steps; First step, formation of triethylamine oxide (R₃N-O) [17] by a reaction of hydrogen peroxide (pK_a=11.6) with triethylamine (pK_a= 11.01). The nitrogen atom of amine behaved as a nucleophile and attacked on oxygen atom of hydrogen peroxide to generate triethylhydroxylammonium (TEHA) as an intermediate step. Therefore, deprotonation of hydroxyl group connected with TEHA by

hydroxide ion (OH) and resulted in formation of triethylamine oxide, this step was exothermic [18]. TEAO reacted with another molecule of H₂O₂ to produce hydroperoxide ion (-OOH), which attacked the double bond of fullerene C₆₀ and formed fullerene epoxide (C₆₀O). A second nucleophilic attack by hydroxide ion (-OH) was for opening epoxide ring and produce hydroxylated fullerene epoxide [19]. This mechanism is followed the Bingel reaction [20]. Where the final step included proton addition to hydroxylated fullerene epoxide and produce polyhydroxylated fullerene [21, 15].

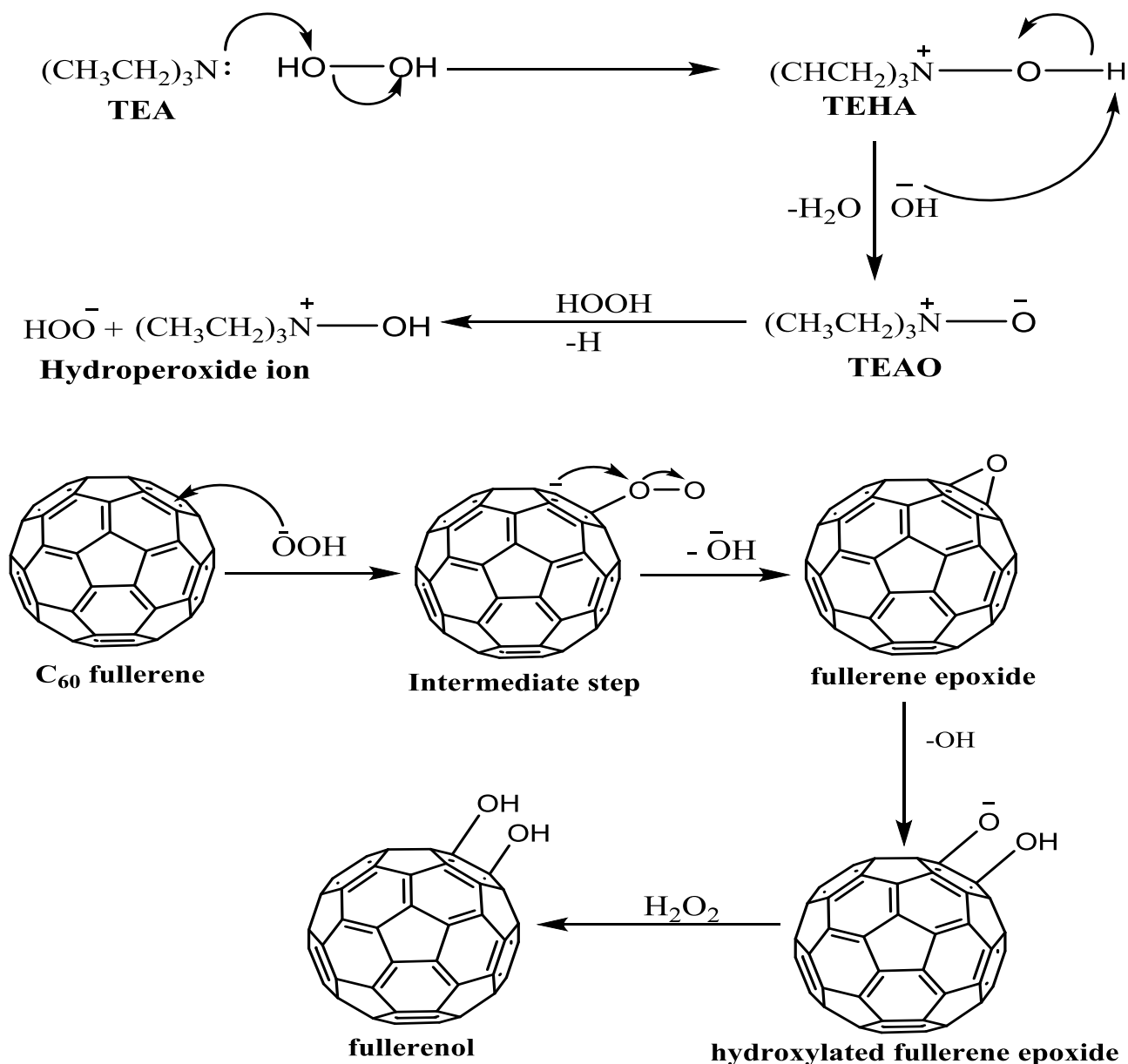


Fig. 14 Predicted mechanism of fullereneol synthesis

Conclusions

Fullerene C_{60} was successfully converted to high soluble fullereneol C_{60} by simple efficient method using toluene as solvent for fullerene

C_{60} , hydrogen peroxide as oxidant and trimethylamine for hydroxylation. The structure and surface profile were approved by extensive analysis using AFM, SEM, TEM, XRD, NMR, EDS, and TGA.

Abbreviations

AFM	Atomic force microscopy
^{13}C -NMR	Carbon nuclear magnetic resonance
D_2O	Deuterium oxide
PTC	Phase transfer catalyst
ppm	Part per million
^1H -NMR	Proton nuclear magnetic resonance
q	Quartet
TEA	Triethylamine
SEM	Scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy
FT-IR	Fourier transform infrared spectroscopy
TGA	Thermogravimetric analysis
C_{60}	Fullerene
XRD	X-ray diffractometer
TEAO	Triethylamine oxide
TBAH	Tetra- <i>n</i> -butylammonium hydroxide
TEHA	<i>N,N,N</i> -Triethylhydroxylammonium
J	Coupling constant

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