Two-electron oxygen reduction on fullerene C$_{60}$-carbon nanotubes covalent hybrid as a metal-free electrocatalyst

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Nanocarbon materials are considered to be active for electrochemical oxygen reduction reaction (ORR) for hydrogen peroxide (H$_2$O$_2$) synthesis. In the present work, a new type of fullerene 60 (C$_{60}$)-carbon nanotubes (CNTs) hybrid with covalently attached C$_{60}$ onto outer surface of CNTs was synthesized. The structure of C$_{60}$-CNT hybrid was confirmed by physical and chemical characterizations and its conformation is proposed featuring the covalent incorporation of CNTs and C$_{60}$ derivative. C$_{60}$-CNT hybrid showed high efficiencies on electro-generating H$_2$O$_2$, owing to huge surface area and intermolecular electron-transfer in the hybrid structure. A high H$_2$O$_2$ production rate of 4834.57 mg L$^{-1}$ h$^{-1}$ (426.58 mmol L$^{-1}$) was achieved at $-0.2$ V vs saturated calomel electrode (SCE).

Hydrogen peroxide (H$_2$O$_2$) is an eco-friendly and essential chemical that is widely used as an oxidizer, antiseptic and bleaching agent for a huge range of industrial processes$^1$. The well-developed anthraquinone-based H$_2$O$_2$ production is the current method that has taken in multistep reactions and separations, energy-intensive and along with the production of organic wastes$^{2,3}$. Furthermore, the use of noble-metal based catalysts (Pt, Pd, Au, and Ag) and hydrogenation step under high-pressure H$_2$ have a negative effect on the production costs$^4$. These major disadvantages have triggered the interests in the development of more facile and green method for H$_2$O$_2$ generation. As a substitute route, H$_2$O$_2$ production through the reaction of O$_2$ and H$_2$ have a direct catalytic process has been proposed$^5$. However, the use of toxic and expensive catalysts based on precious metals and the possible explosion of the O$_2$ and H$_2$ mixture made this approach unattractive for industrial applications$^2,4$. By contrast, electrochemical H$_2$O$_2$ generation through the two-electron oxygen reduction reaction (ORR) is an appealing procedure that allows green, safe route, low-cost, and in-situ generation of H$_2$O$_2$.$^6-8$. However, H$_2$O$_2$ production from the ORR competes with the O$_2$ reduction to H$_2$O through a four-electron transfer, and thus, the main challenge lies in the development of efficient electrocatalysts that can selectively prefer the two-electron reduction pathway.$^1,9$

Noble-metal-based catalysts with engineered reactive sites by means of various strategies, such as coating of their surfaces with amorphous carbon, supporting with single-atom catalysts, and alloying by inactive elements, have shown outstanding catalytic activity and selectivity for H$_2$O$_2$ generation.$^{6,10}$ Unlike these materials, metal-free carbon materials have found remarkable research attention as low-cost and conducitive electrocatalysts. Furthermore, most of the carbon-based catalysts present a rather low overpotential for the two-electron oxygen reduction pathway$^{11}$. In fact, dissociation of the potent O=O bond occurs in the four-electron pathway, whereas the O–O bond remains during the two-electron pathway$^1$.

Applications of nanocarbon materials (e.g., graphene, carbon nanotubes (CNTs), and fullerenes) in numerous areas have received considerable attention due to their unique physicochemical properties$^{12}$. Moreover, the incorporation of nanocarbons can develop the existing features or benefit from their excellent properties. Therefore, in recent years, efforts have been being made to develop various carbon nanomaterral hybrids with each other so as to extend their applications$^{13}$. Nanocarbon hybrids such as graphene-CNT$^{14-17}$ and C$_{60}$-graphene$^{18}$ are the
promising electrocatalysts for the ORR because of their higher performance compared to that of their individual forms. The hybridizations of CNTs and C₆₀ fullerene (or a fullerene derivative), which have been shown as the excellent electron acceptor, can be prepared through either non-covalent or covalent procedures²⁸⁻²¹. However, covalent functionalization of C₆₀ and its derivatives to the outer surface of the CNTs is more potent than the van der Waals interaction between them and thus can impose more remarkable changes on their hand and electronic structures. Additionally, the covalent nature renders powerful intermolecular interactions between CNTs and C₆₀ structures. A main challenge in this context is to develop the effective and convenient approaches for the synthesis of C₆₀–CNT covalent hybrids. Here, a new type of C₆₀–CNT covalent hybrid was prepared by Birch reduction²² reaction between multi-walled CNTs and 4-chlorobenzoic acid functionalized-fullerene (CB–C₆₀) via Friedel–Crafts acylation.

Herein, the formation of a new C₆₀–CNT hybrid based on the direct covalent linkage of C₆₀ derivative molecules on the sidewalls of CNTs was explored, and the structural properties of the as-prepared hybrid were studied by means of microscopic and spectroscopic approaches. Subsequently, the selectivity and electrochemical activity of the C₆₀–CNT hybrid were studied toward the two-electron ORR for H₂O₂ generation. Physical and chemical characterization tools were associated with obtained results from electrochemical analyses to clarify the distinctive features of as-prepared nanocarbon hybrid that contribute to the H₂O₂ electro-generation activity.

Experimental Section

Chemicals and materials. Hydrochloric acid (37%, Sigma-Aldrich®), lithium granular (98%, Sigma-Aldrich®), sulfuric acid (>95–97%, Merck, Germany), C₆₀ (purity: >98%, Sigma-Aldrich®), 4-chlorobenzoic acid (CB) (>99%, Sigma-Aldrich®), multi-walled CNTs (~90% purity on carbon basis, size 8–15 nm outer diameter and 3–5 nm inner diameter, Cheap Tubes, USA) and phosphorous pentoxide (>98%, Merck, Germany) were used without further purification to prepare different solutions in Milli-Q water (resistivity ≥18.2 MΩ·cm at 25°C).

Functionalization of C₆₀ with 4-chlorobenzoic acid. 4-Chlorobenzoic acid (0.25 mmol), C₆₀ (0.45 mmol), and polyphosphoric acid (PPA, 83% assay, 20 g) were added in a 250-mL resin flask containing a mechanical stirrer under nitrogen atmosphere. After being stirred at 130°C for 3 h, 5 g of phosphorous pentoxide (P₂O₅) was added into the reaction medium in one portion. The dark mixture turned into lighter brown. The resulting solution was further stirred at 130°C for 48 h. Afterwards, the mixture was cooled down to reach the room temperature and it was slowly poured into deionized water to dissolve the PPA and P₂O₅. The precipitate was gathered by suction filtration and washed with NH₄OH. Residual PPA and unreacted CB were eliminated by Soxhlet extraction with deionized water and methanol for four days, respectively. Finally, the sample was vacuum-dried at 60°C for 12 h, as a result, the gray powder was obtained.

Preparation of C₆₀–CNT hybrid and mixture. The preparation procedures using Birch reduction²² were as follows: 0.2 g of multi-walled CNTs were added into a dry 150-mL three-neck round-bottom vessel under argon atmosphere. Then, 60 mL of NH₂ was condensed into the reaction medium, which was cooled down to −77°C in a liquid nitrogen-butyl acetate bath. Subsequently, 1.2 g of lithium metal was gradually added to the reaction vessel while being stirred. 40 min after the lithium addition, 1.4 g of as-prepared CB–C₆₀ sample was slowly added and the reaction mixture was endlessly stirred at −33°C during 24 h. In order to quench the reaction, absolute ethanol was added followed by the addition of deionized water. The resulting suspension was acidified by adding 1.0 mol L⁻¹ HCl and washed with absolute ethanol by centrifuging several times and finally dried at 80°C for 8 h under vacuum (See Fig. 1).

Fabrication of gas diffusion electrode. 0.2 g of carbon nanomaterials (CB–C₆₀, CNTs and C₆₀–CNT hybrid), 0.42 g of PTFE, 3% V/V of n-butanol were thoroughly blended and dispersed in 30 mL of N-methyl-2-pyrrolidone (NMP) for 1 h to prepare the gas diffusion electrode (GDE) electrodes. The as-prepared mixture underwent heat treatment at 80°C until a paste-like ink was obtained and pressed by a stainless steel mesh current collector at 10 MPa for 5 min. The prepared electrodes were sintered under N₂ atmosphere at 350°C for 30 min, followed by cutting to diameter of 15 mm. The obtained electrodes were put at the bottom of a polypropylene cylindrical holder for manufacturing the GDEs. A graphite disk, which is in contact with a copper wire as the electrical connector, is located in the cylindrical holder.

Physical and chemical characterization methods. TESCAN (Mira3, Czech Republic) and JEOL (JEM-2200FS, Japan) microscopes were used to record the scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM) micrographs, respectively. X-ray diffraction (XRD) analysis was done by Siemens D5000 X-ray diffractometer (Germany) using Cu Kα exciting source (λ = 1.54056 Å). Raman spectra were acquired by a WiTech confocal Raman microscope equipped with a 532 nm NdYAG laser. A Tensor 27 IR-spectrometer (Bruker, Germany) on the KBr pellets over the range of 400–4000 cm⁻¹ was utilized for taking the Fourier transform infrared spectroscopy (FT-IR) spectra. Brunauer, Emmett and Teller (BET) method was performed using nitrogen adsorption/desorption at 77 K with a Belsorp mini II device (Bel, Japan). Atomic force microscopy (AFM) was applied to study the surface topography of the coated electrodes, which was performed by a Nanosurf Mobile S microscope (Nanosurf, Switzerland). The elemental composition was studied by X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versaprobe, Al Kα source). The water contact angles of the prepared electrodes were determined using a standard goniometer (200, Rame-Hart, USA). For this aim, 5 μL water droplet were deposited onto surface of prepared electrodes at ambient temperature. For each sample, at least five contact angle measurements were averaged on different areas of electrode surface.
Electrochemical characterization. The electrochemical measurements were done by means of a computer-controlled potentiostat (PARSTAT 2273). For the rotating disk electrode (RRDE) measurements, a three-electrode system was assembled with a standard three-electrode configuration. The as-prepared catalyst ink, consisting of nanocatalyst powder, water, isopropanol and Nafion solution (5 wt%), was carefully dropped on the RRDE electrode (the electrode area is 0.2475 cm²) with a catalyst loading of 0.1 mg cm⁻² as working electrode. Graphite rod and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. For the accurate and reproducible measurement of H₂O₂ selectivity, it is very important to clean the RRDE thoroughly prior to each experiment. Cyclic voltammetry (CV) was performed between −1.2 and 0.3 V (vs. SCE) in N₂-saturated 0.5 mol L⁻¹ H₂SO₄ at a scan rate of 5–10 mV s⁻¹, in which a steady CV response was obtained. O₂ gas was purged into the electrolyte for 5 min (caution: if the time interval between the Pt ring cleaning and ORR measurement is long, the H₂O₂ selectivity can be underestimated due to the surface passivation of the Pt ring). The electrochemical impedance spectroscopy (EIS) was conducted at −0.2 V (vs. SCE) from 100,000 to 1 Hz to determine the uncompensated resistance (Rₘ) in a high-frequency range for iR-correction. The H₂O₂ production activity was assessed by linear sweep voltammetry (LSV) in O₂-saturated 0.1 mol L⁻¹ H₂SO₄ at a scan rate of 5 mV s⁻¹ and a rotation speed of 1600 rpm. The ring electrode was set at a constant potential of 0.5 V vs. SCE to detect the generated H₂O₂. The electron transfer numbers (n) and H₂O₂ selectivity were calculated using the following relations:

\[ n = \frac{4I_d}{NI_d + I_r} \]  

(1)

\[ H_2O_2 \text{ %} = \frac{200I_r}{NI_d + I_r} \]  

(2)

where \( I_r \) and \( I_d \) denote the ring current and disk current, respectively. The N was the collection efficiency of Pt ring, which was determined to be 0.3 with [Fe(CN)₆]⁴⁻/³⁻ redox probe.

The Koutecky-Levich (K-L) plots (\( J^{-1} \) versus \( \omega^{-1/2} \)) represents the relation between the measured current, electron transfer number, and rotation speed as follows:

\[ \frac{1}{J} = \frac{1}{I_K} + \frac{1}{B\omega^{1/2}} \]  

(3)

\[ B = 0.62 nF_v^{-1/6} C_{O_2} D_{O_2}^{3/2} \]  

(4)

where \( J, I_K, \omega, n, F, v, C_{O_2}, \) and \( D_{O_2} \) indicate the determined current, kinetic current densities (mA cm⁻²), rotation rate (rad s⁻¹), number of transferred electrons for ORR, Faraday constant (96485.34 C mol⁻¹), viscosity of electrolyte (0.01 cm²/s), oxygen concentration in the electrolyte (1.26 × 10⁻⁸ mol cm⁻³), and oxygen diffusion coefficient in electrolyte (1.93 × 10⁻⁵ cm² s).
The stability of as-prepared C_{60}-CNT hybrid was evaluated using the chronoamperometric method performed at a constant potential of $-0.2 \text{ V vs. SCE}$. The $\text{H}_2\text{O}_2$ faradaic efficiency was determined from the $\text{H}_2\text{O}_2$ yield against the quantity of charge passed:

$$\text{H}_2\text{O}_2 \text{ faradaic efficiency (\%)} = \frac{2\text{CVF}}{Q}$$

where $C$ is the $\text{H}_2\text{O}_2$ concentration (mol L$^{-1}$), $V$ is the volume of electrolyte (L), $F$ is the Faraday constant (96485.3 C mol$^{-1}$), and $Q$ is the passed charge amount (C).

To appraise the number of electrochemically active centers on the surface of as-prepared hybrid electrodes, CV analysis in a solution containing potassium hexacyanoferrate-III (1 mmol L$^{-1}$) and potassium chloride (1 mmol L$^{-1}$) was fulfilled. The Randles-Sevcik equation$^{25}$ (Eq. 6) was applied to calculate electrochemically active surface area (ECSA) of the mentioned electrodes.

$$I_p = 2.65 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2}$$

where $I_p$ is the peak current (A), $n$ (=1) is the number of electrons transferred, $A$ is the effective area of the electrode(cm$^2$), $D$ is the diffusion coefficient of potassium hexacyanoferrate-III (taken to be $7.60 \times 10^{-6}$ cm$^2$ s$^{-1}$ at 25$^\circ$C$^{26}$), $C$ is the concentration (mol cm$^{-3}$), $v$ is the scan rate (V s$^{-1}$).

Nafion 117 membrane was applied as a separator in $\text{H}_2\text{O}_2$ electro-generation experiments which were carried out in a cell with two portions. The cathodes were chosen in the form of pure carbon paper, improved cathode electrodes with 100% Pt content (10 cm$^2$). The cathode was steadily provided in a cell with two portions. The cathodes were chosen in the form of pure carbon paper, improved cathode electrodes with 100% Pt content (10 cm$^2$). For electro-generation of $\text{H}_2\text{O}_2$, the diffusion cathode was steadily provided with pure O$_2$ gas. 100 mL of Na$_2$SO$_4$ solution with specific concentrations was magnetically stirred (at 300 rpm) and produced as a supporting electrolyte for all tests. The pH ($\text{Ohaus}$, Switzerland) was set by H$_2$SO$_4$ and NaOH solutions (0.1 mol L$^{-1}$). The pH 4.00 was maintained throughout the experiment. The pH was set to 4.00 by addition of H$_2$SO$_4$ and NaOH solutions (0.1 mol L$^{-1}$). The concentration of electro-generated $\text{H}_2\text{O}_2$ was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE. The H$_2$O$_2$ faradaic efficiency was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE. The H$_2$O$_2$ faradaic efficiency was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE. The H$_2$O$_2$ faradaic efficiency was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE. The H$_2$O$_2$ faradaic efficiency was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE. The H$_2$O$_2$ faradaic efficiency was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE. The H$_2$O$_2$ faradaic efficiency was determined from the H$_2$O$_2$ yield at a constant potential of 0.2 V vs. SCE.
D and G bands at 1350 and 1582 cm\(^{-1}\), respectively, a peak located at 1458 cm\(^{-1}\) was clearly detected, which can be ascribed to the A\(_2\)(2) mode of the C\(_{60}\) framework\(^{33}\). However, the up-shift of the D and G peak positions and down-shift of the A\(_2\)(2) mode in the C\(_{60}\)-CNT hybrid spectrum compared to the individual materials showed that the charge-transfer from CNTs to C\(_{60}\) may happen as a result of strong electron-withdrawing ability of C\(_{60}\)\(^{34}\), which was in agreement with the reported results\(^{19,20}\). On the other hand, the intensity ratio of these bands (I\(_D\)/I\(_G\)) was proportional to the disorder degree on the carbon matrix and applied as a probe to identify the covalent attachment of the CNTs surface. The I\(_D\)/I\(_G\) value of the C\(_{60}\)-CNT hybrid (0.96) was greater than that of the CNTs (0.43), indicating that the CB-C\(_{60}\) covalently bonded onto the CNTs surface\(^{33}\). These results readily concur with those obtained from FT-IR analysis (see ESI Fig. S2).

XRD diffractograms of C\(_{60}\), CB-C\(_{60}\), CNTs and C\(_{60}\)-CNT hybrid are revealed in Fig. 2b. For bare C\(_{60}\), the localized peaks at 2\(\theta\) = 10.8°, 17.7°, 20.8°, 21.7°, 27.5°, 28.2°, 30.8° and 32.7° that referred to plane reflections of (111), (220), (311), (222), (331), (420), (422) and (511), respectively, associated with face centered cubic (fcc) crystalline phase of C\(_{60}\) with lattice constant a = 14.17 Ångstrom (JCPDS 44-0558)\(^{35,36}\). As for CB-C\(_{60}\), the detected peaks at 2\(\theta\) = 10.2°, 17.1°, 20.2°, and 21.5° became slightly broader with decreased intensity compared to those of the unfunctionalized C\(_{60}\), indicating that functionalization of C\(_{60}\) did not completely change the lattice structure of C\(_{60}\). As can be observed in Fig. 2b, the pure CNTs\(^{37}\) displayed two broad peaks at 2\(\theta\) = 25.74° and 42.87° which can be ascribed to the hexagonal graphite crystal planes (002) and (001), respectively, with an interlayer distance (d) of 0.34 nm. XRD diffractogram of C\(_{60}\)-CNT hybrid demonstrates a superposition of the peaks of the CB-C\(_{60}\) and CNTs, evidencing the hybrid structure of these two nanocarbons. The intensity of the (002) diffraction peak at 26.12° remarkably decreased in comparison to the pure CNTs with negligible shift. However, the weaker peak at 42.87° (001) of CNTs pattern almost disappeared in the C\(_{60}\)-CNT hybrid illustrating that the lattice structure of CNTs was relatively changed upon the linkage of the CB-C\(_{60}\) moiety. On the other hand, in comparison to the XRD analysis of CB-C\(_{60}\), the diffraction peaks of C\(_{60}\)-CNT hybrid centered at 10.5°, 18.1° and 20.9° appeared which asserted the formation of C\(_{60}\)-CNT hybrid. For further investigation, the XRD pattern for the mixture of CNTs and bare C\(_{60}\) (C\(_{60}\)-CNT mixture) was taken, which indicated a poorly crystalline or amorphous feature to that of CNTs and peaks of C\(_{60}\) that were hardly detected (see ESI Fig. S3). It was confirmed that physical mixing of C\(_{60}\) with CNTs slightly influenced the properties of CNTs compared to covalent hybrid structure. In fact, in the mixture, C\(_{60}\) molecules were attached to the CNTs surface by van der Waals forces\(^{38,39}\).
The SEM micrographs of synthesized C₆₀-CNT hybrid (Fig. 3a) demonstrate the growth in wall width of C₆₀-CNT hybrid in comparison with unmodified CNTs (SEM and TEM images are shown in Fig. S4) which can be attributed to the addition CB-C₆₀ on the CNTs surface. In addition, as observed by the HR-TEM image of C₆₀-CNT hybrid in Fig. 3b,c, the spherical CB-C₆₀ molecules are covalently conjugated on the CNTs sidewall. The diameter of the individual CB-C₆₀ sphere was determined to be around 1 nm (Fig. 3c, inset), while TEM micrographs of spherical particles of C₆₀ (Fig. S5a) and CB-C₆₀ (Fig. S5b) display the facile agglomeration of their molecules resulted from the potent van der Waals attractions and profound π-π forces between them. It should be noted that for removing the unreacted and physically adsorbed CB-C₆₀ particles, the synthesized samples were washed via ultrasonication in CS₂ solvent several times.

XPS analysis was fulfilled to clarify the bonding configurations and the chemical composition in synthesized C₆₀-CNT hybrid. The C 1s scan of the pristine CNTs (Fig. 4a) indicated the C–C bonds (sp² carbon) at 284.4 eV, together with different peaks located at 284.9, 286.1, and 288.0 eV could be connected to the C–H, C–O, and C=O bonds, respectively, because of native surface groups and structural defects present in the raw CNTs sample. A minor peak at 290.9 eV can be ascribed to the π–π* changes in sp² carbon structures. The XPS spectrum of C₁s

Figure 4. Deconvoluted XPS plots: C 1s core level of (a) pristine CNTs; (b) C₆₀; (c) CB-C₆₀; (d) Cl2p region of the structure in (c); and (e) C 1s core level of C₆₀-CNT hybrid.
of C60 shows the located peaks at 284.6 eV (C–C), 286.1 eV (C–O), and two π–π* shake-up peaks around 290 eV (Fig. 4b). As it can be observed in Cls region of CB-C60 (Fig. 4c), three new peaks appear at 287.1, 285.3, and 288.0 assigned to aromatic C–Cl, C–OH, and C=O bonds, respectively. XPS spectrum of Cl2p (Fig. 4d) indicates two major peaks centered at 200.5 eV (Cl2p1/2) and 202.1 eV (Cl2p3/2). The results can confirm the successful functionalization of C60 within the CB. In case of C60-CNT hybrid (Fig. 3e), the peaks at 288.0 and 285.3 eV assigned to C=O and C–OH groups, respectively18, indicating a higher relative intensity than those of the pristine CB-C60 and CNTs. It is suggesting that more C=O and C–OH bonds have been introduced to the hybrid structure. These results readily concur with those obtained from the characterizations discussed above.

Physical characterization of fabricated GDE cathodes. SEM micrographs of prepared electrodes by CB-C60 (Fig. 5a), CNTs (Fig. 5b), and C60-CNT hybrid (Fig. 5c) indicate the mesoporous morphology of CNTs and the slightly smooth plate surface of CB-C60, while C60-CNT hybrid electrode possesses a rough surface and heterogeneous porous structure. These results were further confirmed by means of BET analysis (Fig. 5d), wherein C60-CNT hybrid presented a higher surface area (422.52 m² g⁻¹) compared to that of the CNTs (185.28 m² g⁻¹), C60-CNT mixture (258.5 m² g⁻¹), and CB-C60 (98.2 m² g⁻¹), respectively.

The hydrophilic feature of the fabricated nanocarbon based electrodes was investigated by water contact angle (Fig. 5a–c, inset). The average contact angles of CB-C60, CNTs, and C60-CNT hybrid were found to be 76.5°, 64.8°, and 37.2°, respectively. As can be seen, the decrease in contact angle value means the increase hydrophilicity of the samples, which could be caused by the presence of carboxyl and hydroxyl groups in the fabricated C60-CNT hybrid electrode, as verified in the Raman and XPS data.
Figure 6. 3D AFM images of the fabricated electrodes with (a) CB-C_{60}; (b) CNTs; (c) C_{60}-CNT hybrid, and (d) Cyclic voltammograms of CB-C_{60}, CNTs, C_{60}-CNT mixture, C_{60}-CNT hybrid electrodes in O_{2} saturated solutions and C_{60}-CNT hybrid in N_{2} saturated solution. Experimental conditions for CV: room temperature, [Na_{2}SO_{4}] = 0.05 mol L^{-1}, pH = 4, and scan rate = 10 mV s^{-1}.

Figure 7. (a) EIS data with a frequency range between 100 kHz and 0.1 Hz, and (b) Cyclic voltammograms of Fe(CN)_{6}^{3−/4−} and 1 mol L^{-1} KCl solution at scan rate of 10 mV s^{-1}, for CB-C_{60}, CNTs, C_{60}-CNTs mixture, and C_{60}-CNT hybrid electrodes.

The surface morphology of the CB-C_{60} (Fig. 6a), CNTs (Fig. 6b), and C_{60}-CNT hybrid (Fig. 6c) electrodes were examined using AFM analysis, and the 3D images in the scale of 8 × 8 μm² are displayed. In these graphs, dark areas show the pores or valleys, while bright areas show the highest point of the fabricated electrodes surface. The
parameters of roughness were measured by the AFM images. The observed increase in the average roughness of the fabricated electrode with C60-CNT hybrid could be attributed to the increased surface porosity as shown in the SEM images and BET analysis.

Electrochemical activity of oxygen reduction. In the first step, the electrochemical activities of the fabricated hybrid as the GDE materials towards ORR were evaluated by CV method in N2- or O2-saturated acidic media. As can be seen from Fig. 6d, there were no obvious reduction peaks in the N2-saturated solution using C60-CNT hybrid electrode, while there were well-known oxygen reduction peaks for all nanocarbon based materials in the O2-saturated solution, suggesting their distinct electrocatalytic activity toward ORR. Furthermore, the synthesized C60-CNT hybrid demonstrated the highest reduction current density of 2.2 mA cm\(^{-2}\), followed by CB-C60 (0.56 mA cm\(^{-2}\)), CNTs (0.85 mA cm\(^{-2}\)), and C60-CNT mixture (1.2 mA cm\(^{-2}\)).

The onset potential for CB-C60, CNTs, C60-CNT mixture, and C60-CNT hybrid was –0.32, –0.28, –0.21 and –0.11 (V vs. SCE), respectively. These results suggest that the fabricated C60-CNT hybrid cathode had the best
ORR activity amongst all the as-prepared nanocarbon catalysts. Besides, the EIS of all the samples was carried out in O₂-saturated 0.5 mol L⁻¹ Na₂SO₄ electrolyte solution (Fig. 7a). Evidently, the C₆₀-CNT hybrid indicated a lower resistance for mass- and charge-transfer than those of CB-C₆₀, CNTs, C₆₀-CNT mixture samples, showing a more promising reactant diffusion and electron transfer for ORR. These observations confirmed that the covalent integration of CB-C₆₀ molecules into CNTs structure could reduce the resistance of charge transfer because of charge-transfer from CNTs to CB-C₆₀, which was effective for improving catalytic activity toward ORR.

**Figure 9.** Schematic illustration of the H₂O₂ production by the C₆₀-CNT hybrid electrode.

**Figure 10.** (a) Cyclic voltammetry of C₆₀-CNT hybrid electrode for various cycles ([Na₂SO₄] = 0.05 mol L⁻¹, pH = 3, and scan rate = 10 mV s⁻¹); (b) chronoamperometric (current-time) response of C₆₀-CNT hybrid in O₂ saturated; and (c) H₂O₂ electrogeneration on C₆₀-CNTs hybrid electrode for 15 repeated runs; [Na₂SO₄] = 0.05 mol L⁻¹, pH = 3 and V = −0.2 V (vs SCE).
To appraise the number of electrochemically active centers on the surface of the fabricated nanocarbon based electrodes, CV analysis in a solution containing potassium ferrocyanide was performed. The obtained voltammograms (Fig. 7b) demonstrate the high electrochemical performance of the C$_{60}$-CNT hybrid electrode compared to others, where the electrochemical active surface area of C$_{60}$-CNT hybrid was 27.78 ± 0.45 cm$^2$ (Fig. 6).

**Selectivity of hydrogen peroxide generation.** The selectivity of the fabricated nanocarbon electrocatalysts toward ORR to H$_2$O$_2$ was evaluated by the RRDE method, using LSV at 1600 rpm rotating speed. As shown in Fig. 8a, among the material, C$_{60}$-CNT hybrid presented the highest overall electrocatalytic activity for ORR with disk current density ($j_{disk}$) about −5.3 mA cm$^{-2}$, and the main hydroperoxyl productivity under ring current density ($j_{ring}$) around 0.91 mA cm$^{-2}$ at −0.4 V (vs. SCE). Furthermore, C$_{60}$-CNT hybrid exhibited the most positive onset potential around −0.12 V (vs. SCE). Figure 8b,c indicate the number of electrons transferred and the H$_2$O$_2$ selectivity trends resulting from the RRDE voltammograms, respectively. In the potential range of −0.3 to −0.8 V (vs. SCE), the mean number of transferred electrons was determined to be close to two (Fig. 8b), suggesting that ORR predominated by two-electron reduction pathway. The H$_2$O$_2$ selectivity within the studied applied potential range followed the order of C$_{60}$-CNT hybrid > C$_{60}$-CNT mixture > CNTs > CB-C$_{60}$.

RDE analyses were further used to prove the ORR kinetics of C$_{60}$-CNT hybrid. As shown in Fig. 8d, higher current densities were obtained by increasing the rotation rate for the reduction of oxygen due to the decrease in the diffusion layer. The K-L plot (Fig. 8e) with a good linearity at different potentials proved first-order reaction kinetics of the ORR process. In case of the fabricated C$_{60}$-CNT hybrid, the mean number of transferred electrons per O$_2$ was measured to be ~2.2 (−0.3 to −0.7 V) based on the obtained slope of K-L plots.

For further evaluation of electrocatalytic performance, H$_2$O$_2$ generation rate of the fabricated nanocarbon based electrodes was investigated in O$_2$-saturated acidic solution under the obtained optimal conditions (pH = 3 at −0.2 V vs SCE). As showed in Fig. 8f, the H$_2$O$_2$ concentration increased versus reaction times for all as-prepared nanocarbons. Notably, the C$_{60}$-CNT hybrid electrocatalysts produced 426.58 mmol L$^{-1}$ of H$_2$O$_2$ within 3 h and displayed a remarkably high H$_2$O$_2$ electrogeneration rate of 4834.57 mg L$^{-1}$ h$^{-1}$. This amount was greater than those of C$_{60}$-CNT mixture (307.79 mmol L$^{-1}$, 3488.28 mg L$^{-1}$ h$^{-1}$), CNTs (244.60 mmol L$^{-1}$, 2772.13 mg L$^{-1}$ h$^{-1}$) and CB-C$_{60}$ (97.72 mmol L$^{-1}$, 1107.49 mg L$^{-1}$ h$^{-1}$).

It is noticeable that the faradaic efficiency for H$_2$O$_2$ production on C$_{60}$-CNT hybrid electrode could reach 82.6% in the investigated applied potential, which is greater than those of previous studies of electrocatalysts under the same experimental conditions (Table S1). The observations show that the C$_{60}$-CNT hybrid was a promising cathode material for H$_2$O$_2$ electrogeneration.

The higher ORR activity of the C$_{60}$-CNT hybrid can be ascribed to the following reasons: (a) The carbon nanostructured morphology could provide higher active centers on the surface of electrode; (b) CB-C$_{60}$ structures, as the electron acceptor, facilitate the electron transportation inside the hybrid and (c) the covalent attachment of CB-C$_{60}$ into CNTs framework facilitates the oxygen adsorption and OOH desorption pathways. The schematic of H$_2$O$_2$ production by C$_{60}$-CNT hybrid electrode is represented in Fig. 9.

The stability of as-prepared electrodes is one of the most noteworthy parameters to evaluate their performance toward two-electron ORR. The stability of C$_{60}$-CNT hybrid electrode was studied by sequential scanning of potential for 100 cycles (Fig. 10a), the chronoamperometric method for 10 h (Fig. 10b), and H$_2$O$_2$ generation rate over 15 repeated runs (Fig. 10c). As can be observed, C$_{60}$-CNT hybrid even shows well two-electron ORR efficiency in the 100th cycle compared to the 1st cycle. Moreover, the peak current in the chronoamperometric curve, after a prolonged operation, about 98% of the initial current is retained and the rate of H$_2$O$_2$ generation after 15 runs (382.85 mmol L$^{-1}$) was close to 426.58 mmol L$^{-1}$. These obtained results proved high stability of the C$_{60}$-CNT hybrid electrode for two-electron ORR.

**Conclusion**

In summary, we demonstrated a method to synthesize the covalent C$_{60}$-CNT hybrid as a novel electrocatalyst for H$_2$O$_2$ production. The C$_{60}$-CNT hybrid exhibited high content of large surface area, intermolecular electron transitions, fast mass transport, and defect sp$^3$-C bonds. It was demonstrated here the high performance of C$_{60}$-CNT hybrid, as a cathode electrode, for electrogeneration of H$_2$O$_2$ (112.6–792.6 mmol h$^{-1}$ g$^{-1}$). In addition, the C$_{60}$-CNT hybrid showed high stability and reusability in ORR. This study may provide a new insight into the design of metal-free and efficient nanoporous-based electrocatalysts for production of H$_2$O$_2$.

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Acknowledgements
The authors thank the University of Tabriz for all the support provided (Project No: 825, 97.3.5). Authors would like to thank Prof. Aziz Shahrisa and Dr. Zarrin Ghasemi for their valuable help on hybrid synthesis.

Author Contributions
A.H. designed, performed and analyzed experiments and wrote the manuscript. A.R.K. funded the field project, supervised, and revised the manuscript. M.Z. and Y.Z. contributed reagents/materials/analysis tools. All authors discussed the results and commented on the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-019-50155-7.

Competing Interests: The authors declare no competing interests.

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