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Inkjet Printing of Palladium Decorated-Carbon Nano Onion-based Aqueous Inks

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Herein, we designed a novel ink formulation with high stability and printability using onion-like carbon nanoparticles (CNO) decorated with sulfonate (-SO_3H) groups and Palladium (Pd) nanoparticles. The modification of hydrophilic -SO_3H groups enabled us to achieve high print quality. We also demonstrated that Pd nanoparticle decoration did not yield a detrimental effect on the printability of the CNOs. The surface tension of Pd-decorated SO_3H/CNO was measured to be 70.3 mN/m, and using sodium dodecyl sulfate (SDS) surfactant with 0.5 mg/ml concentration, the printability of the ink was enhanced. The stability of the inks was experimentally studied by zeta potential measurements. The printed layers were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) methods, and the results indicated highly homogeneous printed layers. The effect of the printing pass number was evaluated by measuring the print resistance, and the lowest resistance was achieved at 65 printing passes.

1. Introduction

Flexible and wearable electrodes pose great advantages in various applications ranging from wearable energy storage devices and wearable sensors [1, 2]. In addition, flexible electrodes find a vast range of applications in flexible circuits, sensors, screens, and antennas [3-6]. The fabrication of highly conductive and robust flexible sensors is of great importance for the commercialization of flexible electrodes. Furthermore, the cost and efficiency of the fabrication method play a key role in a wide range of practical applications. While various sophisticated methods have been applied for the fabrication of flexible electrodes, including photolithography, screen printing, and chemical vapor deposition techniques, the use of high-cost equipment and the requirement of experienced persons in the fabrication process make it essential to discover new methods with low-cost and high production efficiency [7]. Inkjet printing (IJP) is a versatile and low-cost method that renders it a potential alternative to the aforementioned fabrication techniques [1, 7, 8]. In the IJP method, conductive inks are deposited/printed on various substrates in a non-contact manner using a low-cost widely available personal printer [9, 10].

Besides the advantages of the IJP method, there are some challenges to be alleviated to achieve an efficient printing process and obtain highly conductive printed patterns. Ink formulation has a profound importance on the ultimate properties of the flexible electrodes. Carbon and carbon-based nanomaterials have been widely exploited as functional materials in the inks [9, 11]. The hydrophobic surface of carbons, however, the preparation of highly stable and concentrated inks is challenging [12]. To enhance the dispersibility of the carbon surfaces in aqueous media, some surface modification methods have been applied, which included surface modification of carbon surfaces with carboxyl and hydroxyl groups, the use of oxidized carbon surfaces (graphene oxide), and the use of surface-active agents [13-15]. On the other hand, those methods show detrimental effects on the conductivity of the carbon nanoparticles, which in turn results in printed electrodes with high resistivity and low conductivity.

The multilayered structure of carbon nano onions (also known as onion-like carbon, CNOs), their nanoscale diameter (5-10 nm), and their high electrical conductivity enable their utilization in electrochemical systems [16, 17]. Studies demonstrate the successful use of these materials in lubricants, fuel cells, heterogeneous catalysts, as

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well as gas and energy storage applications. However, the inkjet printing of CNO-based aqueous inks is in the infant stage. While CNO-based materials have been the focus of research in electrochemical applications due to their unique properties, their electrochemical activities are insufficient, which makes the modification of their surfaces with electroactive nanoparticles essential. Metal and metal oxide nanoparticles have been widely exploited for the enhancement of electrocatalytic activity of carbon-based materials owing to their high electrocatalytic activity [18-20]. Those nanoparticles encompass palladium, gold, platinum, iridium, copper, silver, and their corresponding oxide forms [19, 21, 22]. Herein, we prepared highly soluble CNOs with covalent surface modification and studied the printability of the inks on flexible substrates to construct flexible electrodes which have a great potential for electrochemical sensor applications. Within this context, we modified the surface of CNOs using a facile surface modification process by forming hydrophilic -SO_3H groups, which enabled us to prepare concentrated inks. Furthermore, Pd nanoparticles were anchored on -SO_3H/CNO surfaces to achieve high electrocatalytic activity.

2. Results and Discussion

The characterization of Pd-SO_3H/CNO was reported in a previous study reported by Ipekci et al. [24]. The TEM images of CNOs recorded at different magnifications are displayed in Figure 1a-d. As observed, carbon-based structures were obtained after the synthesis procedure. The TEM images indicated the presence of CNO structure, showing the successful synthesis procedure [16]. The nature of the fringes observed in the images at high magnifications (Figure 1c-d) confirmed the formation of the CNO nanoparticles. The distribution of the Pd nanoparticles on the SO_3H-modified CNO surface is displayed in Figure 1e-f. It may be alleged that the -SO_3H groups anchored on the surface yielded highly distributed Pd nanoparticles on the carbon surface with a particle size of less than 10 nm [13, 14]. The TEM image given in Figure 1e showed that no significant Pd agglomeration was obtained on the CNO surface. The XRD results of CNO are displayed in Figure 1g. The broad XRD reflection located at $2\theta < 20°$ is associated with the PMMA-based sample holder [25]. Two broad XRD reflections were observed in the XRD results, located at ca. 30° and 43° which correspond to the (002) plane in hexagonal graphitic carbon and and irregular CNO structures [17, 26, 27]. Besides the characteristic CNO and PMMA reflection, the XRD results showed the presence of sharp XRD peaks which are ascribed to the residual metal phases originating from the precursors used in the synthesis process. The bonding properties and the defect concentration of CNO were elucidated using Raman Spectroscopy and the results are displayed in Figure 1h. The typical D and G reflections were obtained from the Raman results. The peaks obtained at the wavenumbers of 1360 (D band) and 1580 cm^{-1} (G band) originate from sp^3 and sp^2 structural carbon bonds [28]. The XRD reflection of Pd-SO_3H/CNO is displayed in Figure 1i. The characteristic Pd peaks located at ca. 40.11°, 46.96°, 69.16°, and 82.68° are ascribed to the face-centered cubic (111), (200), (220), and (311) planes, respectively (JCPDS # 05-0681), confirming the successful immobilization of Pd nanoparticles on the CNO surface.

The surface chemical composition of the samples was studied using X-ray photoelectron spectroscopy method and the general XPS survey collected from Pd-SO_3H/CNO is given in Figure 2a. The sample contained C, O, Pd, and S elements with atomic ratios of 47.6, 34.7, 4.98, and 1.78, respectively. It should be highlighted that the O concentration was higher than regular carbon structures. These results may be attributed to the oxygenated surface anchored CNO and the presence of O-containing SO_3H groups. The S content detected in the XPS survey confirmed the success of the surface modification with -SO_3H groups [7]. To unravel the oxidation states of the elements, partial and high-resolution XPS analyses were conducted, and the obtained XPS peaks were deconvoluted. The deconvoluted C1s peak is displayed in Figure 2b. The deconvoluted S2p and Pd3d peaks confirmed the presence of S and Pd atoms on the CNO surface.

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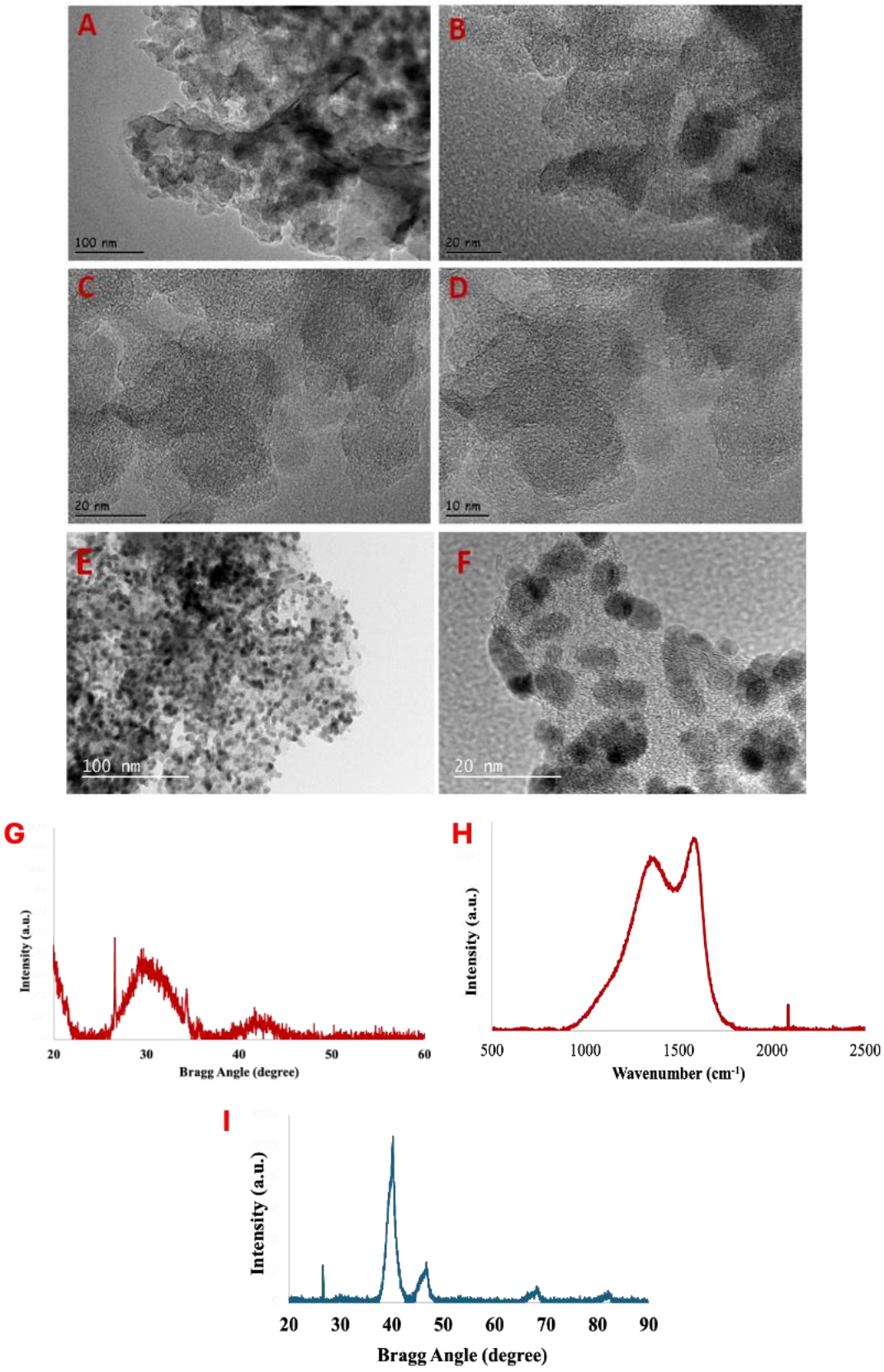

Figure 1. Physical characterizations of CNO: a-d) TEM images of CNO, e-f) TEM images of Pd-SO_3H/CNO, g) XRD and h) Raman spectrum of CNO, and i) XRD pattern of Pd-SO_3H/CNO.

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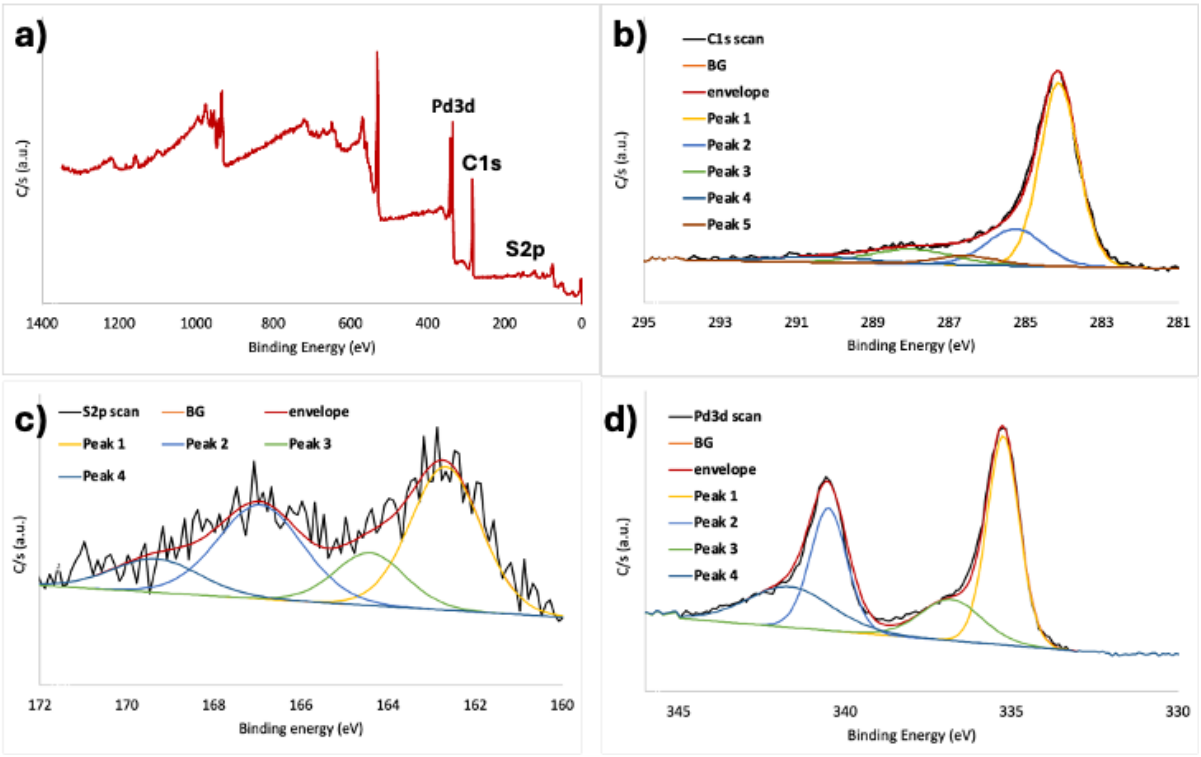

Figure 2. XPS Results of Pd-SO_3H/CNO; a) general XPS survey, b) C1s, c) S2p, and d) Pd3d peaks.

Pd-SO_3H/CNO was then used to prepare the inks for the inkjet printing process. Before the printing process, the surface wetting properties of polyethylene tetraflate (PET)--based flexible substrates were assessed using an optical goniometer. To enhance the wetting property and reduce the contact angle, the surface of PET was cleaned using a plasma cleaner. The images taken during contact angle measurements are given in Figure 3. While a high contact angle value of 79.85 ± 0.2° (Figure 4a) was obtained from untreated PET surface, after the plasma cleaning process, the contact angle was measured as 33.72 ± 0.46° (Figure 4b). Therefore, it was concluded that the plasma-cleaned surface will be more suitable to achieve printed layers with high quality and homogeneity. The inks were prepared by dispersing Pd-SO_3H/CNO in DI (10 mg/ml) water using ultrasonic treatments. The zeta potential of the ink was measured to be -18.81 mV, which suggested that the stability of the inks should be further enhanced. The optimum printing pass number was determined by measuring the resistance of the printed layer, and the printing process was repeated until obtaining the lowest sheet resistance. The lowest printing resistance was measured as 5.25 MΩ at 65 printing passes. The effect of the printing pass number on the resistance is shown in Figure 4c. The digital images of the printed layer are displayed in Figure 4d-e.

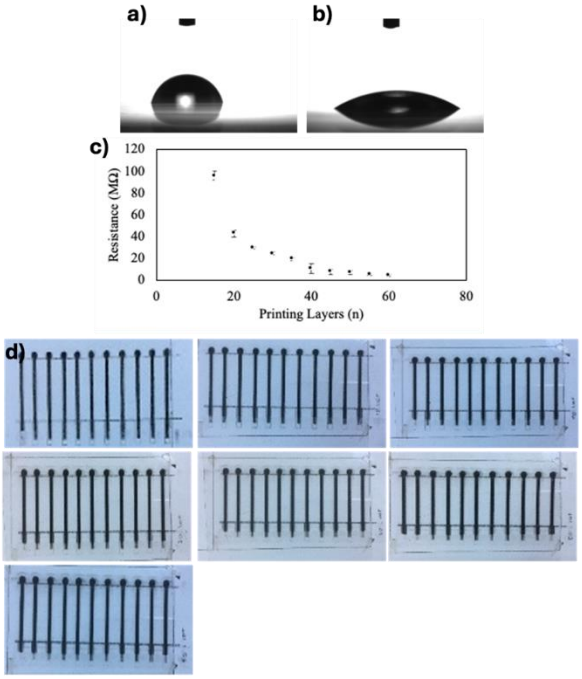

Figure 3. Contact angle measurement results obtained from a) untreated PET and b) plasma-cleaned PET, c) the effect of the number of printing passes on the resistance of the prints, and d) digital images of the prints taken at different printing passes.

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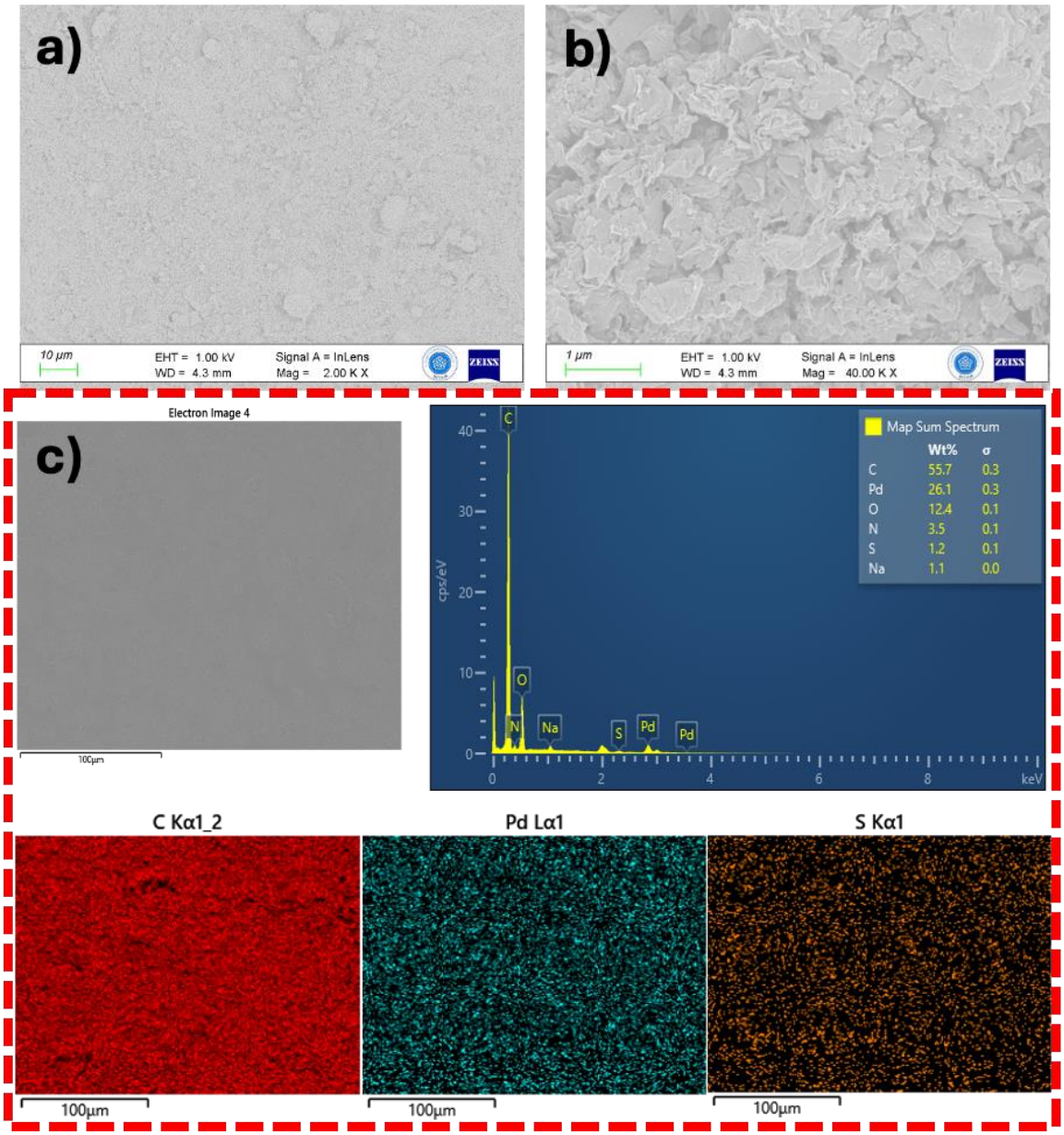

Figure 4. a-b) SEM images of the printed electrodes at different magnifications, c) EDS mapping results.

The quality and the homogeneity of the printed layers were assessed using SEM and EDS methods. The SEM images taken at different magnifications are given in Figure 4a-b. The image taken at low magnification indicated the homogeneous distribution of the functional material in the prints. The image given in Figure 4b shows the presence of carbon-based materials with three-dimensional surface topography. The EDS method was also applied to confirm the homogeneity of prints. As shown in Figure 4c, the distribution of C, S, and Pd elements was randomly and homogeneously distributed over the surface, confirming that high-quality printed layers were achieved.

3. Conclusion

This work demonstrates the development of highly concentrated onion-like carbon-based aqueous inks and their printability using an inkjet printing method. The characteristic CNO structures were observed in the TEM images, which was proven by the XRD results. The TEM images also demonstrated the even distribution of small Pd nanoparticles on SO3H-modified CNO surfaces. The successful modification of the CNO surface with -SO_3H and Pd was proven using TEM and XPS results. The aqueous Pd-SO_3H/CNO-based inks were printed on PET surfaces which were cleaned by a

plasma-assisted cleaning method. The optimum printing pass number was determined by measuring the resistance of the prints, and the lowest resistance was achieved after 65 printing passes. The SEM and EDS results suggested the homogeneous printing process. On the other hand, the stability of the inks needs to be enhanced more according to the zeta potential results.

Method

Synthesis of CNOs: In the synthesis process; 10 grams (0.059 mol) of $CuCl_2 \bullet 2H_2O$ (Merck, 99%) and 3.2 grams (0.05 mol) of CaC_2 (Merck) were placed into a 30 ml Teflon autoclave. Subsequently, the lid of the autoclave was tightly closed and subjected to heat treatment at 600°C for 10 hours without any atmosphere control. After 10 hours, the oven cooled down naturally, and the obtained products were removed from the oven and washed using $NH_3 \bullet H_2O$ (Sigma-Aldrich, 28-30%) and chloroform to remove the copper phase.

Surface modification: Carbon/deionized water suspensions with a concentration of 10 mg/ml were prepared. 1 gram of sulfonic acid (Sigma-Aldrich, 99%) was dissolved in a solution containing 2% NaOH by weight (Carlo Erba, 97%). Then, 0.4 grams of sodium nitrate (Sigma Aldrich, 99%) were added to this solution. This solution was slowly added to 10 ml of ultra-pure water at an ice-cold temperature (0°C) and stirred for 30 minutes. After this period, the solution was slowly added to 30 ml of carbon/water suspension previously prepared in an ice bath and stirred for an additional 5 hours in the ice bath. The surface-modified nanostructures were separated from the liquid phase by centrifugation, washed, and dried in a vacuum oven at 50°C. Pd nanoparticles were deposited onto modified carbon forms as previously conducted in a study (Bozkurt et al., 2017). In brief, 30 mg of the -SO_3H functionalized CNO was taken and dispersed in ultra-pure water containing K_2PdCl_4 at 55°C for 12 hours. Then, freshly prepared $NaBH_4$ (Sigma Aldrich, 96%) was slowly added dropwise to the solution, allowing the deposition of Pd nanoparticles onto the nanocarbon surface. The resulting suspension was separated from the liquid phase by centrifugation and dried.

Characterization of the nanoparticles: The average size and distribution of Pd nanoparticles deposited on SO_3H/CNOs were determined using transmission electron microscopy (TEM, FEI @ 200kV). The morphologies and surface properties of the samples were observed using scanning electron microscopy (Zeiss GeminiSEM 500, SEM), and elemental analysis was conducted using energy-dispersive spectroscopy (EDS). The crystal structure and average particle sizes of the prepared nanocomposites were determined using X-ray diffraction (XRD, Rigaku Ultima-IV), with Cu Kα (λ=0.15406 nm) radiation source used in the XRD method. The bond vibrations were determined, and the bond structures of the materials were examined using Raman spectroscopy (Renishaw inVia Reflex) for the prepared carbon-based materials. Additionally, X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) was used to determine the bond structures and oxidation states of the prepared nanostructures. The obtained data were processed using CasaXPS software and XPS peaks were deconvoluted into sub-peaks.

Preparation of the inks and the characterization of the inks and the printed layers: The inks were prepared by dispersing Pd-SO_3H/CNO in ultra-pure water at different concentrations. The suspension was homogenized for 2 hours using an ultrasonic bath and then further homogenized using an ultrasonic probe. A certain amount of polystyrene-block-polyisoprene-block-polystyrene (PS-PI-PS) solution was added to impart elastic properties to the ink [23]. The Zeta potential measurements were performed using Micromeritics Nanoplus 3. The printing process was conducted using a Canon E414 personnel inkjet printer. The surface properties and the elemental analysis of the prints were evaluated using SEM equipped with an EDS unit. The number of printing passes required to reach the saturation point in the resistance was determined.

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Authors' contributions:

M. D.: performed the experiments. H. I.: performed the experiments. A. U.: corresponding author, conceived of the presented idea, funding acquisition, writing the manuscript.

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