Section A-Research paper

Hydrothermal Synthesis and Characterization of Zirconia Di-Oxide Coated Multi walled Carbon Nanotubes

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Abstract:

In this study, an effort has been made to achieve a homogeneous coating of ZrO_2 on multi-walled carbon nanotubes (MWCNTs). The hydrothermal method, known for its cost-effectiveness, has been employed to synthesize composites of ZrO_2-coated MWCNTs. The initial step involved the functionalization of MWCNTs through acid treatment. Subsequently, the acid-treated MWCNTs were subjected to hydrothermal treatment with an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ at a temperature of 180°C for a duration of 16 hours. The resulting nano composites were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy.

The SEM analysis confirmed the formation of ZrO_2 nanoparticles on the surface of the functionalized MWCNTs, with a uniform distribution observed. XRD analysis indicated the formation of monoclinic ZrO_2 (m-ZrO_2). Raman spectroscopy ensures the presence of specific bands such as D-bands and G-bands, and the determination of carbon defects through the ID/IG ratio. By adjusting the reaction time, it was possible to control the thickness and achieve uniform coating, thereby enhancing the physical, mechanical, and thermal properties of the nanocomposite. This nanocomposite exhibits great potential for application as a reinforcing material in the fabrication of other composites.

Keywords: Multi-walled carbon nanotubes; ZrO_2; Nano composites; Hydrothermal synthesis; Acid Treatment.

1. Introduction

In the present decade, Carbon Nanotubes (CNTs) have emerged as an exceptionally appealing material in the domain of nanotechnology. The primary advantage of CNTs lies in their ease of blending with diverse materials such as metals, polymers, and ceramics. Consequently, they are extensively employed as reinforcing agents, augmenting the properties of other materials. Among them, interest are ceramic composites reinforced with Multi-Walled Carbon Nanotubes (MWCNTs), which have gained significant traction and are now commercially competitive with traditional materials. As a result, numerous researchers are currently focusing on enhancing the properties of various ceramic materials—such as alumina, silicon carbide, aluminium nitride, silicon nitride, and ZrO_2—by reinforcing them with MWCNTs to amplify their characteristics. Among these ceramic materials, ZrO_2 stands out as the strongest, thereby motivating extensive efforts to further enhance its properties and explore diverse applications.

The pioneering work of CNR Rao et al. in 1997 involved successfully coating ZrO_2 onto MWCNTs. Their achievement was confirmed through Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses [1]. F. Lupo et al. prepared ZrO_2 and MWCNT nanocomposites using the hydrothermal method, highlighting that the ZrO_2 coating on MWCNTs remained undamaged during the process. SEM and TEM observations revealed a uniformly coated ZrO_2 layer on the MWCNTs. However, they also observed the growth of ZrO_2 clusters due to the precipitation of ZrO_2 from its hydroxide solution [2]. The impact of reaction time and pH on the structure of ZrO_2-coated MWCNTs was elucidated by Yan Shan et al. They too, utilized the hydrothermal method for composite preparation. Subsequently, the composites underwent characterization via Infrared (IR) analysis, X-ray Photoelectron Spectroscopy (XPS), TEM, and X-ray Diffraction (XRD). Their findings indicated that longer reaction times led to better crystallization of ZrO_2 nanoparticles. Moreover, in weak alkaline mediums, the majority of MWCNTs were not coated, and ZrO_2 agglomerated and adhered to the MWCNT side walls. Conversely, in strong alkaline mediums, almost no coating was observed. However, in acidic mediums, a homogeneous ZrO_2-coated MWCNT structure was observed [3]. J. Lu et al. presented a novel, simple method for coating ZrO_2 onto MWCNTs using isothermal hydrolyzing techniques. They demonstrated that increasing the reaction time also increased the thickness of the coating, with reaction time serving as a pivotal input parameter influencing the coating process [4]. N. Garmendia et al. discussed the enhanced wettability and the synthesis of desired biomaterial coatings composed of nano ZrO_2 via hydrothermal synthesis on MWCNTs and Single-Walled Carbon Nanotubes (SWCNTs) [5]. Further research has focused on enhancing electron and proton conductivity, as well as catalytic activity. For instance, Pt catalysts have been synthesized on ZrO_2-coated MWCNTs, demonstrating a growing interest in this area [6], [7]. ZrO_2 nanostructures possessing wide-band gaps and emitting short-wavelength luminescence have been shown to have potential in photonic applications [8]. Additionally, a hetero-coagulation processing approach has been employed to obtain uniform dispersion and enhance fracture toughness and hardness, with carbon nanotubes acting as strengthening agents for ZrO_2-based materials [6].

Different techniques have been explained in the various literatures to obtain the ZrO_2-coated MWCNT such as, Solgel method [9], fast spark plasma sintering [10]–[12] isothermal hydrolyzing, chemical precipitation method [13], [14]. immersion-precipitation approach [15], inverse precipitation method [16], Electrospinning technique [17] and atomic layer deposition [18].Recently, ZrO_2-coated MWCNT has found many applications in the field of biosensors, electrodes, bone scaffolds [19]–[23]and also, used as a reinforcement for other materials.

2. Materials and method

2.1 Materials

The high purity (99%) MWCNT prepared by chemical vapor deposition (outer diameter~10-30nm, inner diameter~5-10nm, length~5nm,surface area~110-350m^2/g and density~0.04g/cm^3) was purchased from AD-Nano technologies pvt ltd. zirconium oxychloride octahydrate ZrOCl2·8H2O is purchased from Loba Chemie.

2.2 Acid-treatment of MWCNT

A reflux set-up was used to perform acid treatment of MWCNT, as shown in Figure 1. It helps in avoiding the acid loss during evaporation. Reflux set-up possess a condenser with water running continuously for cooling purpose. The evaporated acid gets cooled down in the condenser and returns to the reaction flask [24], [25]. 100ml of 6M HNO_3 solution prepared using deionized water, 1g of MWCNT weighed were added. The mixture was magnetically stirred for 1 hour to disperse MWCNT in the nitric acid solution and ultrasonicated for 1 hour before acid treatment in order to de-agglomerate the MWCNT and get better dispersion. The ultrasonic bath was maintained at room temperature ice cubes were added to reduce the increase in temperature. This is because is has been reported that the increase in temperature of the ultrasonic bath may thermally degrade and ruptures the tubes of MWCNT [26]. The excessive ultrasonication and stirring duration will make it structurally defected, such as curling, fracturing and shortening of the MWCNTs which in turn disrupt the bond structure. A reflux set-up is used for performing acid treatment. It consists of a round bottom flask, condenser and hot water bath for uniform distribution of heat. Round bottom flasks are used in refluxes because they are good for and allows more even heating.

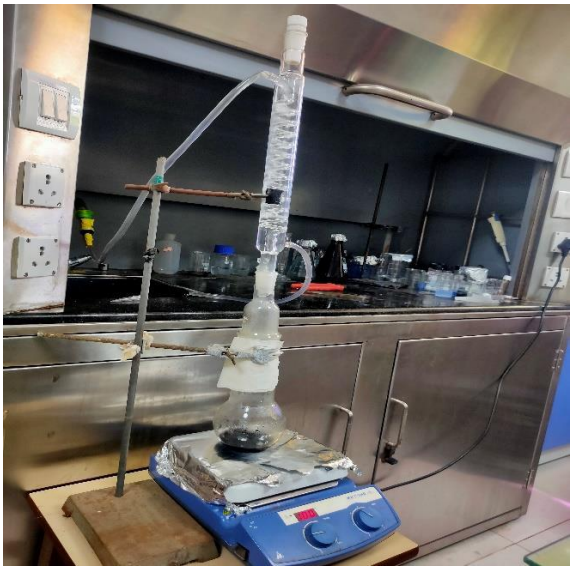

Figure 1: Acid Treatment using Reflux Set-up

The condenser should be long so that the vapours do not evaporate through the top of the condenser. The mixture was kept in the reflux setup for 3 hours at 60^0 C and magnetically stirred continuously. The temperature and duration of reflux are the main affecting parameters. Higher temperatures and longer duration of time result in the degradation of MWCNT, weight loss, ruptures the walls and shortens the MWCNTs. Once the reaction is completed, then the mixture is allowed to cool down to room temperature and frequently washed with deionized water 3-4 times recursively, until a neutral balanced pH is obtained. Later the diluted mixture was centrifuged for 30 minutes and then filtered using vacuum filter. It is then dried at 50^0C to remove the water content. The acid treatment generates the oxidation on the walls of the MWCNT which results in formation of -COOH and OH- groups.

2.3 Hydrothermal synthesis

To obtain the coating of ZrO_2 on MWCNT, the acid-treated samples were subjected to hydrothermal treatment. Initially, 0.2 M ZrOCl2·8H2O aqueous solution is prepared using distilled water and 100 mg of acid-treated MWCNT was weighed and mixed with the ZrO_2 solution. The mixture is vigorously magnetically stirred for 30 minutes at 500-700 rpm till the black solution is obtained. Then, the solution is subjected to ultra-sonication for 1 hour in order to get a better dispersion of MWCNT. Later the black solution is put into stainless steel Teflon-lined autoclave and subjected to hydrothermal treatment for 16-17 hours at 180^0C.

Figure 2: Hydrothermal Synthesis Reactor

The hydrothermal set-up is as shown in the figure 2. Finally, the obtained products were dried overnight until the water content in them completely gets evaporated and a powdered form of ZrO_2-coated MWCNT was obtained. The detailed fabrication procedure is shown in Figure 3.

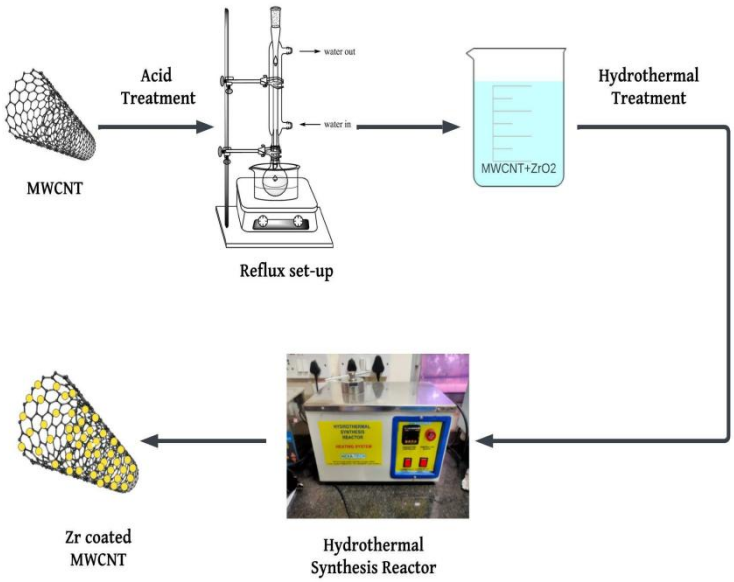

Figure 3: ZrO_2 coated MWCNT Fabrication Procedure

3. Results and Discussions

3.1 Fourier transform infrared spectroscopy (FTIR) of ZrO_2 coated MWCNT

FTIR is performed to identify the presence of functional groups in the outer surface of the ZrO_2 coated MWCNT. Figure 4 depicts the FTIR analysis of acid treated ZrO_2 coated MWCNT.

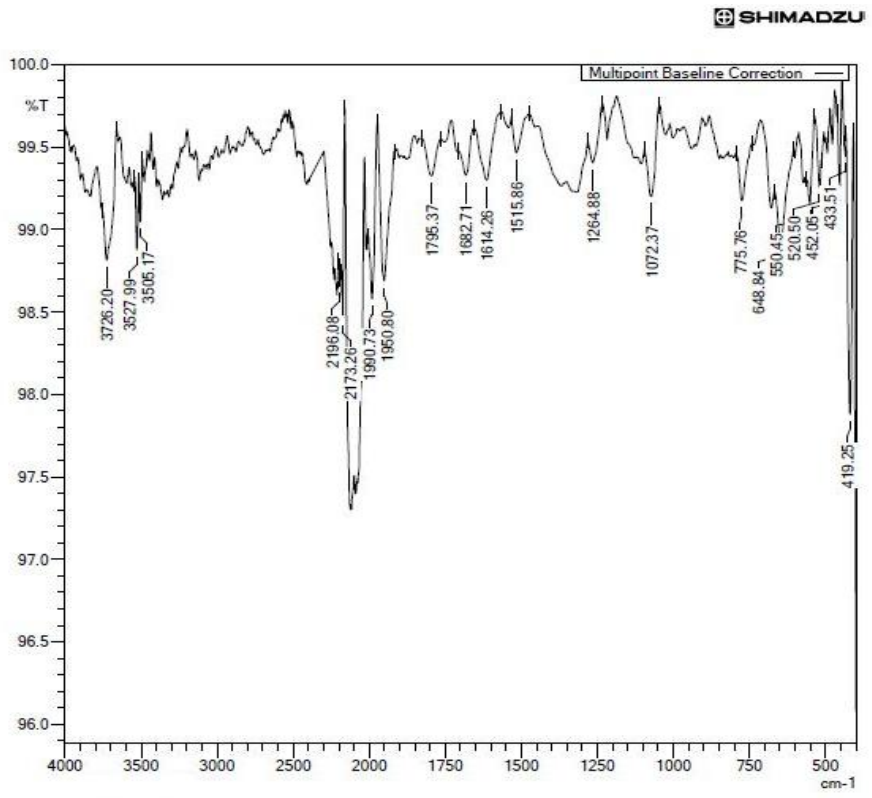

Figure 4: FTIR image of acid treated ZrO_2 coated MWCNT

The acid treatment of MWCNT ruptures the outer most walls and generates the -OH and -COOH carboxyl functional groups on the walls. These functional -OH and -COOH acts as acceptors sites for the ZrO_2 to deposit on the walls of the MWCNT. In figure 4 the intense peaks around 3700-3500cm-^{1} region represents the isolated surface of –OH substituents and –COOH of carboxyl groups. Along with that, absorbed water may be seen in the spectra. C=O groups can be ascribed to bands in the 1800–1500 cm-^{1} range, which can be noticed in the FTIR spectra. The strong and powerful stretching vibration link is visible in the infrared spectra of ZrO_2 nanoparticles at 750 cm-^{1} and 600 cm-^{1}. This depicts that presence of ZrO_2 on the surface of the MWCNT which is confirmed in EDX & XRD.

3.2 SEM imaging & EDX of ZrO_2 coated MWCNT

Scanning Electron Microscopy (SEM) was employed in this work, to study the presence and distribution of a ZrO_2 coating on Multi-Walled Carbon Nanotubes (MWCNTs) [27]. Figure 5 presents illustrative SEM images showcasing the ZrO2-coated MWCNTs, wherein the presence of open tubes and uniformly dispersed ZrO_2 particles of varying shapes is rendered with enhanced clarity.

The SEM images unveil the accumulation of slender MWCNT tubes, intricately intertwined and combined, thereby indicating a successful integration of ZrO_2 with the MWCNTs. Particularly notable is the denser ZrO_2 coating adorning the peripheries of the tubes, signifying a heightened concentration of ZrO2 in these regions. Additionally, certain tubes exhibit intricate clusters of ZrO_2 particles delicately positioned upon their surfaces, indicating not only adhesion but also a dispersed distribution pattern.

Collectively, the SEM analysis clearly verifies the efficacious application of the ZrO_2 coating onto the MWCNTs, ensuring a uniform dispersion of ZrO_2 particles throughout the sample. The pronounced coating density observed at the tube edges, coupled with the presence of dispersed ZrO_2 clusters on the tube surfaces, further reinforces the seamless amalgamation of ZrO_2 with the MWCNTs.

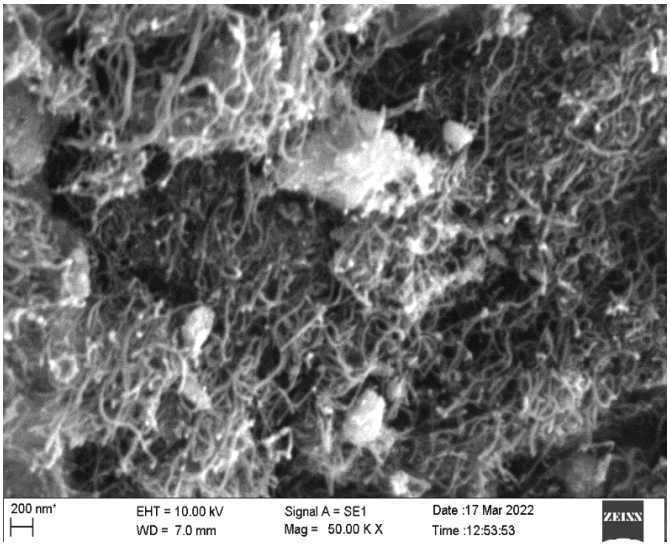

Figure 5: SEM image of ZRO_2 - coated MWCNT

EDX (Energy Dispersive X-ray Spectroscopy) was conducted to analyze the percentage compositions of the different elements in a ZrO_2 coated MWCNT sample. The results revealed an increase in the percentage of oxygen, OH- (hydroxyl groups), and COOH- (carboxyl groups) in the individual f-MWCNT samples after acid treatment. This increase facilitated the deposition of ZrO_2 on the walls of the MWCNT.

The analysis of the ZrO_2/MWCNT composite demonstrated the presence of Zr (zirconium), O (oxygen), and C (carbon) elements. The optimized parameters yielded an atomic ratio of 12.62% for Zr in the composite material. These findings indicate that the ZrO_2 coating on the walls of MWCNTs was thick and uniformly distributed. Figure 6 displays the EDX image associated with these results.

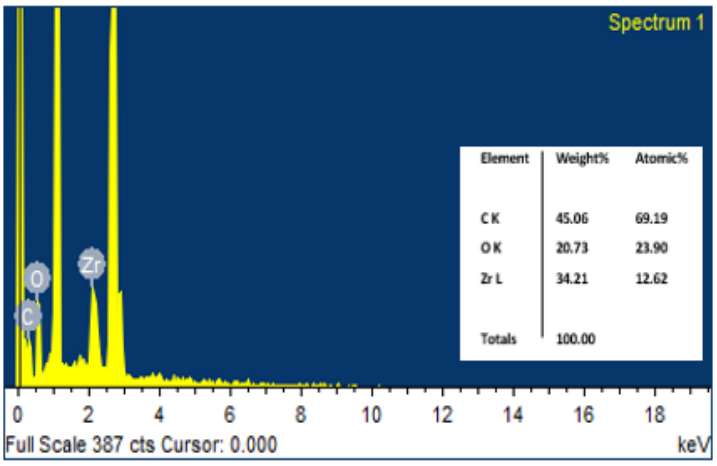

Fig 6: EDX image of ZRO_2-coated MWCNT

3.3 X-Ray Diffraction (XRD) of ZrO_2 coated MWCNT

XRD (X-ray diffraction) is used to analyse the crystalline phases present in ZrO_2 coated MWCNT to understand and gather the information about chemical composition. Figure 7 shows the XRD pattern of coated material with major diffraction peaks at 2θ =31.735 corresponds to ZrO_2. It is noted that the highest peak of (111), corresponding to monoclinic ZrO_2, is discernible. The XRD pattern exhibits a diffraction peak of ZrO_2, aligning with the established monoclinic XRD pattern (JCPDS - 96-210-7452). Likewise, the (002) peak corresponds to the MWCNT (multi-walled carbon nanotube), which undergoes a notable attenuation due to the ZrO_2 coating applied onto it.

Within the spectrum, it is observed that both m-ZrO_2 (monoclinic ZrO_2) and t-ZrO_2 (tetragonal ZrO_2) coexist, with m-ZrO_2 prevailing. The m-ZrO_2 on MWCNT is acquired through the hydrothermal synthesis of $ZrOCl_2 \cdot 8H_2O$ under acidic conditions. Similarly, the growth of t-ZrO_2 on MWCNT is facilitated by the abundant presence of -OH and -COOH groups, owing to the hydroxyl effect.

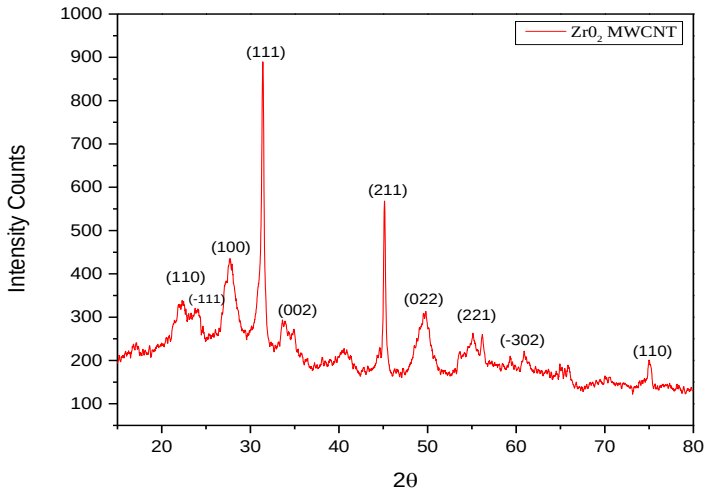

Figure 7: XRD image of ZrO_2-coated MWCNT

3.4 Raman Spectroscopy

Raman spectroscopy is a non-destructive analytical technique that provides valuable insights into various aspects of a material, including its chemical structure, phase, crystallinity, and molecular interactions. By studying Raman spectra, one can gather information about the degree of disorder within a material.

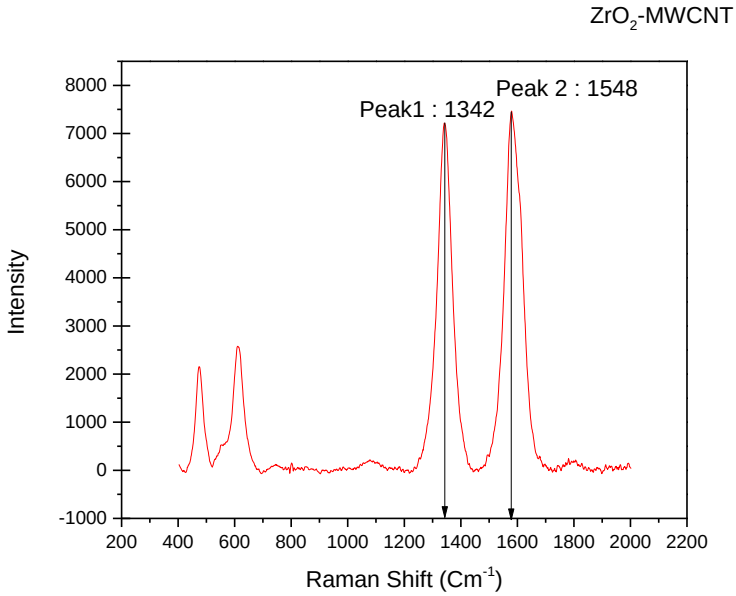

Figure 8: Raman image of ZrO_2-coated MWCNT

In Raman spectroscopy for the analysis of ZrO_2 coated MWCNTs, specific bands in the spectra are of particular interest. The disorder induced D-bands are observed around 1342 cm^{-1}, indicating the presence of disorder within the material. These D-bands are associated with the defects introduced during the coating process or due to the intrinsic characteristics of the MWCNTs.

On the other hand, the g-bands, which appear around 1548 cm^{-1}, correspond to the vibration of SP_2 carbon atoms in tangential modes. The presence of these g-bands in the Raman spectra further confirms the successful coating of ZrO_2 on the MWCNTs.One crucial aspect to consider is the carbon defects within the MWCNTs, which are indicated by the ID/IG ratio. Surprisingly, the ID/IG ratio is found to be similar to that of pristine MWCNTs, suggesting that the structural defects observed after the ZrO_2 coating process are not significantly different from those present in the original MWCNTs.

4. Conclusion

ZrO2 (ZrO_2) coated MWCNT composites were prepared using the hydrothermal method, ensuring the selection of optimal experimental parameters to achieve a remarkably thick and uniformly distributed ZrO2 coating. The effectiveness of this coating was validated through Fourier Transform Infrared Spectroscopy (FTIR), which clearly demonstrated the formation of -OH and -COOH functional groups as a result of the acid treatment. These functional groups played a pivotal role in facilitating the strong bonding of ZrO_2 onto the surface of MWCNT.The comprehensive analysis carried out using Scanning Electron Microscopy (SEM) and

Energy-Dispersive X-ray Spectroscopy (EDX) further substantiated the exceptional quality of the ZrO_2 coating. The SEM images unveiled the uniform and homogeneous distribution of ZrO_2 across the entire surface of the MWCNTs. Meanwhile, the EDX analysis provided a significantly high atomic percentage of ZrO_2, precisely measured at an impressive 12.42%. This observation highlights the substantial thickness of the ZrO_2 coating achieved in this experimental process. X-ray Diffraction (XRD) analysis, not only confirmed the presence of ZrO_2 in the composites but also identified the predominant presence of the stable monoclinic ZrO_2 phase. The XRD pattern prominently exhibited the characteristic diffraction peaks corresponding to the (111) plane, signifying the successful coating of this particular plane with ZrO_2. This result underscores the exceptional adherence and coverage of the ZrO_2 on the walls of the MWCNTs. Raman spectroscopy enables the characterization of ZrO_2 coated MWCNTs by providing information on disorder, the presence of specific bands such as D-bands and G-bands, and the determination of carbon defects through the ID/IG ratio. This technique allows researchers to assess the structural changes and quality of the MWCNTs after the ZrO_2 coating process.

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