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Adding Tungsten to Synthesize Multi-metal Catalysts and Growing High-quality Carbon Nanotube

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Abstract

Recently, the need for sustainable development of a large population and the uneven distribution of resources have compelled people to make new breakthroughs in the energy revolution. The field of energy technology has been rapidly advancing, and researchers are increasingly focusing on energy materials. Single-walled carbon nanotubes (SWCNTs) play a vital role in this area. However, the initial challenge of producing SWCNTs in large batches hampers their widespread application. This study successfully synthesized a catalyst consisting of Fe-Co-W using an impregnation-calcination technique and achieved high-yield production of SWCNTs. The results indicate that the addition of W enables the formation of stable $FeWO_4$ and $CoWO_4$ phases from Fe and Co, significantly enhancing the system's stability. Subsequent growth of SWCNTs demonstrates that the catalyst performs exceptionally well, achieving a yield of 241% at a temperature of 900°C. This research contributes to the industrial-scale production of single-walled carbon nanotubes and the advancement of new energy materials.

Keywords

New Energy Materials, SWCNTs, Catalysts, CVD.

1. Introduction

As the industry evolves and people's lifestyle demands change, the overuse of energy resources, particularly fossil fuels, leads to the exhaustion of these resources and various environmental challenges, making energy advancement increasingly important.[1] Currently, innovations in energy technology are at the forefront of energy progress. Among these, new energy materials are specifically developed and created for the acquisition and storage of energy, with lithium-ion batteries (LIBs) being a key focus.[2-7] Additionally, carbon nanoscale materials serve as additives in composite electrodes and provide physical support due to their electronic characteristics, which can significantly boost rate capability and enhance cycle performance.[8-10]

Carbon nanotubes (CNTs) can be considered unique one-dimensional carbon structures. The diameter of carbon nanotubes typically varies from several nanometers to several hundred nanometers. In essence, they can be seen as formed by the curling of either a single layer or multiple layers of graphene. Depending on the number of layers, CNTs can be classified as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs).[11] Due to their remarkable properties such as a high specific surface area, excellent electrical conductivity, and nanoparticle effects, they represent a crucial type of carbon material that serves as fundamental tools in various fields like thermoelectric materials[12], battery electrodes,[8,10] and pharmaceutical ingredients.[13] Consequently, researchers are actively seeking improved methods to advance carbon nanotube technologies.

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Since CNTs were prepared for the first time by Japanese Ligima in 1991[14], the synthesis of CNTs has obtained complete development. The technologies include chemical vapor deposition (CVD)[15], laser ablation[16], arc discharge[17]. Varity of methods have their own unique technical characteristics. CVD is regarded as having the greatest potential for industrialization.[18]Lower reaction temperature (usually 650-1000°C), controllable operation procedures, uncomplex equipment and easy-to-adjust reaction conditions show its advantages. Catalyst plays a crucial role in the CNTs synthesis of CVD methods. The component, content, appearance and size of catalyst decide the yields and product quality of CNTs. In most studies, one or more than one transition metals element such as Fe, Co, Ni are used as the active components of catalyst. However, in the actual process the situation of carbon deposition and excessive temperature can lead to the coke growth and deactivation of catalyst.[19-20] Hence, on the one hand, researchers are working hard to find suitable growth conditions to improve the yield of CNTs products, on the other hand, they are trying to design and assemble the structures of catalysts to solve the problems and obtain the high quality of CNTs products.

This research initially involves the design and construction of a Fe-Co-W multi-metallic catalyst system, focusing on enhancing its stability at elevated temperatures. We analyze and discuss the dispersion and elemental distribution within the catalyst. Utilizing this catalyst with methane as the carbon source, we successfully produce high-quality carbon nanotubes and employ various techniques to assess its effectiveness. Additionally, we examine the growth mechanism and process of the CNTs. The findings indicate that this catalyst maintains a robust structure and effectively produces high-quality CNTs.

2. Organization of the Text

2.1. Materials and Methods

The synthesis of catalyst: according to reserved ratio, iron nitrate, cobalt nitrate, ammonium metatungstate are put into the container with pure water. Mixtures are stirred evenly for 1h until they are dissolved. Then magnesium oxide is added in it and mixed evenly for 3h. After standing still for 12h, catalyst precursor is dried with 80°C for 24h. the solid product is grinded carefully and calcinate in 600°C ~ 800°C muffle furnace for 3h ~ 4h. The raw material is grinded into uniform and fine powders and sift through 30-mesh sieve to stand by.

The growth of SWCNTs: After 0.1g catalyst is taken into tube furnace, we introduce 400sccm Ar gas to drive out free air and keep heating until the temperature is 900°C. Then the system introduces 300sccm CH_4 and 100sccm H_2, and continue to react for 30min. After reaction ends, the system stops introducing the CH_4, H_2 and heating. Ar gas is adjusted into 300sccm until it cools upon room temperature. Finally, we take the SWCNTs out from tube furnace.

Material characterization: the morphology of the materials is tested by scanning electron microscopy (SEM, ZEISS Gemini SEM 300,120 keV) to observe microstructure the surface. Element distribution information is obtained by the combined equipment energy dispersive X-ray (EDX, using a Cu target, the range is from 10 to 90 degrees). Transmission electron microscopy (TEM, JEOL JEM-2100 Plus) is used to obtain detail information including materials size, interface structure (dispersed on copper grids and ethanol as a dispersant). To determine the phase composition of catalyst, X-ray diffraction (XRD) is used on a miniFlex600-C (Cu-Kα, λ = 1.54, 40 kV, 40 mA). Raman spectroscopy (Thermo Scientific DXR2) is used to analyze the quality of SWCNTs(633nm).

2.2. Results and Discussion

The impregnation method is easy to implement and requires relatively low energy consumption. When compared to other techniques, it uses minimal chemical reagents and is environmentally friendly. This makes it a highly viable option for commercialization and large-

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scale production. Additionally, catalysts must undergo treatments such as ultrasound oscillation and hydrothermal processes to activate and stabilize their structures. Calcination is crucial for eliminating impurities and amorphous particles, facilitating a more uniform dispersion of composites, and leading to the formation of stable and complex crystal phases. Notably, the catalysts in this study are synthesized using the impregnation-calcination method. Specifically, iron, cobalt, and tungsten are integrated onto magnesium oxide and undergo calcination at temperatures ranging from 600°C to 800°C to establish a stable structure. We have employed various technical methods to analyze the product, and the findings are illustrated in Figure 1.

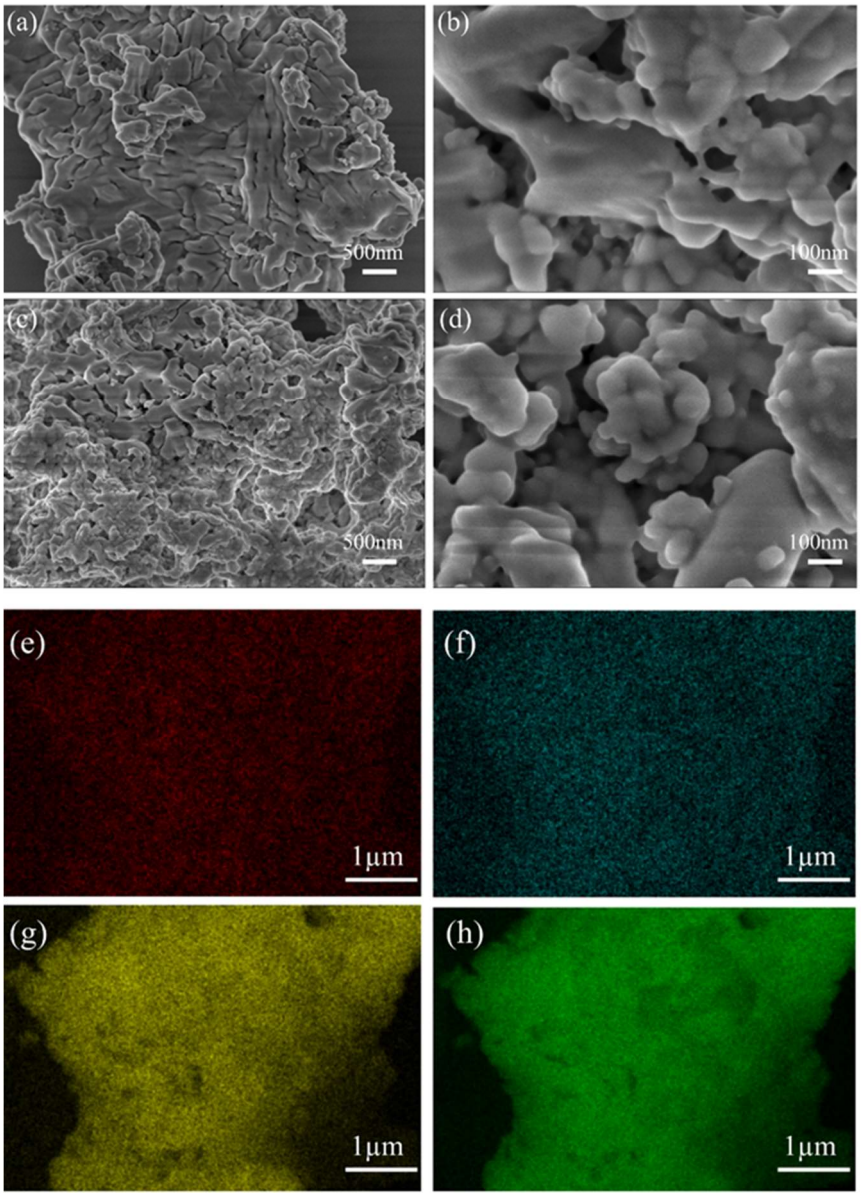

Figure 1. SEM images of catalysts (a, b-600°C; c, d-800°C) and the corresponding elemental mappings of metal elemental (e-Fe, f-Co, g-W, h-Mg).

In Figure 1, the catalyst composites after calcination exhibit a dense and uniform structure. All catalysts have a rough and uneven texture, with particles of different crystal phases clustered together. The surface of the catalyst is adorned with numerous raised dots. Notably, the catalyst treated at 800°C appears denser and features more dots compared to the one treated at 600°C.

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This indicates that the carbon source gas can diffuse more rapidly and adhere for extended periods on the catalysts.

Additionally, we utilized EDX analysis to uncover the distribution of metal elements within the catalyst (Figure 1e to 1h). Cobalt (Co), Iron (Fe), Tungsten (W), and Magnesium (Mg) are evenly distributed throughout. Co and Fe display similar distribution patterns, with a significant presence on the surface, while W and Mg are spread throughout the entire material. We postulate that a considerable amount of tungsten and magnesium oxides forms the foundation of the materials, while Fe and Co are interspersed within, contributing to the formation of stable crystalline phase compounds. This configuration enhances the catalyst's thermal stability at high temperatures. The raw materials undergo transformation during heating to achieve this stable structure, and the abundance of dots and structures creates an ideal environment for the growth of CNTs, regardless of whether conditions are high or low in temperature.

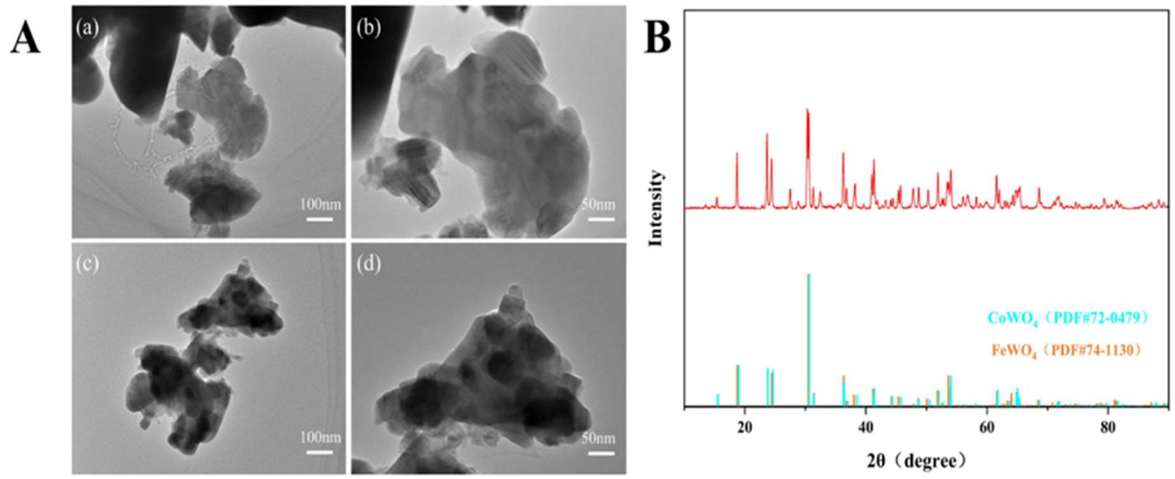

Figure 2. Microstructure of catalyst after high-temperature calcination. (A)SEM images of catalysts (a,b-600°C and c,d- 800°C) and (B)XRD patterns of catalysts.

Figure 2A presents the results from the transmission electron microscopy (TEM) analysis of the catalyst. It shows that the catalyst is composed of nanoparticles that have a uniform size, with iron (Fe) and cobalt (Co) located on the surface of the crystals. This observation aligns with previous research findings. Notably, the particles produced at 800°C are smaller and more uniform compared to those at 600°C. Smaller particles exhibit stronger interface energy, and we observe an increase in the number of active sites on the catalyst. This aggregation of effective and active sites suggests that carbon atom interactions will occur more rapidly.

To gain a deeper understanding of the phase composition of the catalyst, X-ray diffraction (XRD) analysis was performed. As illustrated in Figure 2B, the active catalytic components, Fe and Co, are present in the catalyst in the form of $FeWO_4$ and $CoWO_4$ phases. As noted in earlier research, magnesium (Mg) plays a fundamental role in the catalyst, and the addition of tungsten (W) leads to the formation of more stable $FeWO_4$ and $CoWO_4$ phases rather than the previously reported $MgFe_2O_4$ and $MgCo_2O_4$ phases. We believe that W inhibits the interaction between Fe, Co, and Mg. It is reasonable to predict that a more stable and heat-resistant crystal phase will enhance the catalyst's activity and broaden its application range, while also preventing sintering during the growth of carbon nanotubes.

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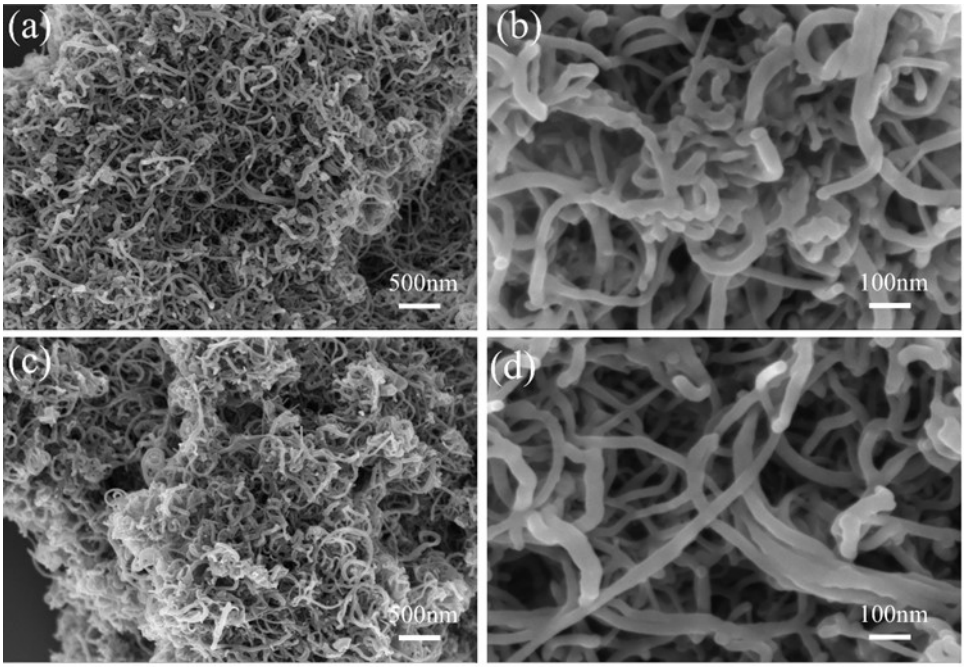

Figure 3. SEM images of the growing CNTs (a,b-800°C; c,d- 900°C).

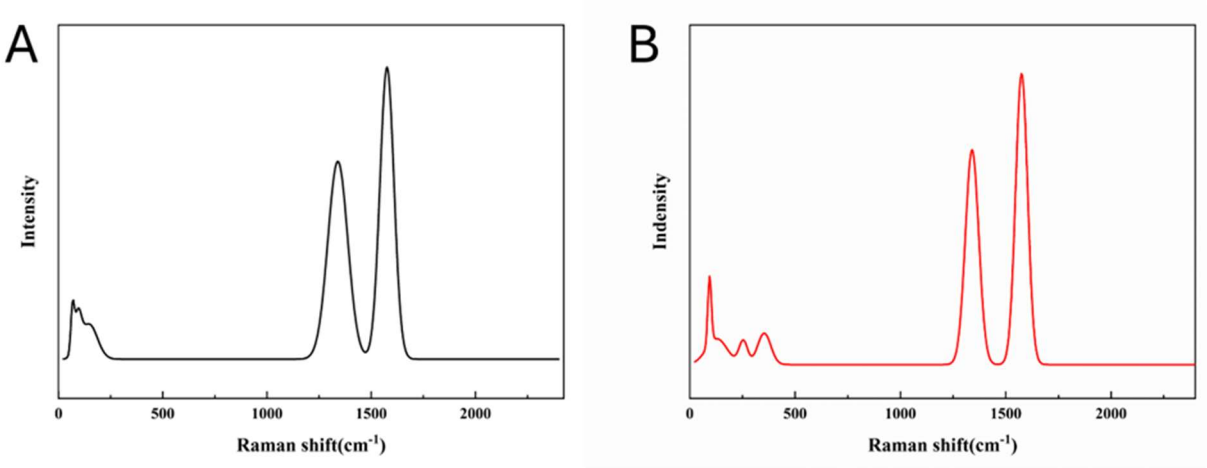

Figure 4. Raman spectra of CNTs in the different temperature. (A)800°C; (B)900°C.

Figures 3 and Figure 4 present the SEM and Raman spectroscopy findings of the carbon nanotubes products. The SEM images clearly illustrate the morphology of the carbon nanotubes, revealing that they intertwine and grow on the catalyst's surface. The Raman spectroscopy data shows a prominent D peak at approximately 1337.3 cm-1 and a G peak at 1575.1 cm^{-1}, with the I_D/I_G peak intensity ratios of 0.96 at 800°C and 0.98 at 900°C. Additionally, the RBM peaks, characteristic of single-walled carbon nanotubes, are observed between 70 cm^{-1} and 250 cm^{-1}. The position of the RBM peak is inversely related to the diameter of the SWCNTs; typically, a more leftward peak correlates with a smaller diameter. [21-22]Notably, the RBM peak at 900°C is situated further left than that at 800°C, indicating that higher temperatures enhance CNT growth on the catalyst. We hypothesize that elevated temperatures help to more rapidly reduce Fe and Co in the catalyst to atomic form, facilitating the formation of smaller particles and yielding these results. Overall, the findings suggest that our catalyst has significant potential for CNTs growth.

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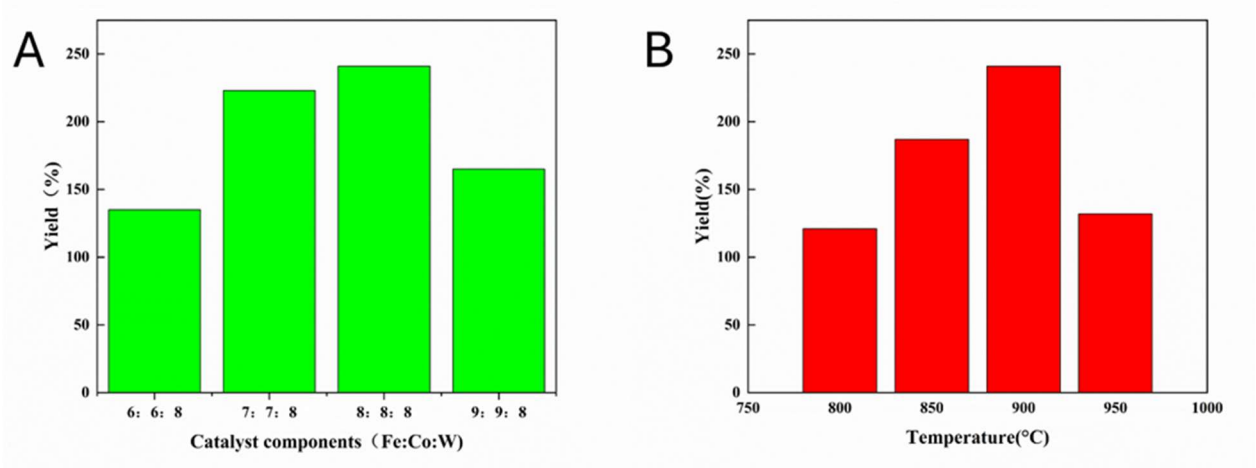

Figure 5. the yields of catalysts in different conditions. (A) the yields of CNTs using different catalysts; (B) the yields of CNTs at different temperature conditions.

Using varying doses and ratios of Fe and Co to synthesize the catalysts and promote the growth of CNTs, the yields are illustrated in Figure 5A. Here, yield refers to the ratio of the carbon nanotubes produced to the catalyst used. It is evident that within a specific range, increasing the amounts of Fe and Co leads to higher yields. Fe and Co serve as active catalytic components, which translates to having more active sites. However, when the total ratio exceeds 7%, the yield decreases. This decline could be attributed to the excessive amounts of Fe and Co, causing the catalysts to clump into larger particles. The size of the catalyst plays a crucial role in CNT growth. Larger particles are less effective in facilitating the diffusion of the carbon gas source, reducing the likelihood of carbon diffusing into the metal particles. Furthermore, larger particles exhibit lower catalytic activity, resulting in carbon atoms accumulating on the catalyst's surface and forming tubular structures, which can impede CNT growth. [23]

To determine the optimal growth temperature for the catalyst, we also investigated the yields of CNTs under different temperature conditions, as shown in Figure 5B. The results indicate a positive correlation between yield and temperature, with the catalyst achieving its peak yield at 900°C (241%). As the temperature rises, the rate of thermal decomposition of the carbon source gas also increases, which facilitates the growth of carbon nanotubes. However, at 950°C, there is a rapid decrease in yield, likely due to sintering of the catalyst particles at this higher temperature, which reduces catalytic activity. Additionally, elevated temperatures can accelerate the growth of unwanted carbon impurities, resulting in fewer active sites. This highlights the importance of finding an optimal temperature to achieve the best growth rate, ensuring the highest yield from the catalyst.

Numerous studies are currently underway to understand the growth mechanisms of carbon nanotubes (CNTs).[24-26] Our research contributes to this discussion. As illustrated in Figure 6, the results from the catalyst clearly demonstrate the growth outcomes of CNTs, indicating that most of them range in size from 3nm to 20nm. The TEM images showcase the growth process: initially, iron (Fe) and cobalt (Co) from the catalyst are reduced to nanoparticles at elevated temperatures. Methane adheres to the surface of these catalyst dots, decomposes, and the carbon atoms then diffuse into the Fe and Co particles, ultimately dissolving and forming carbon tubes. These catalyst dots become encased within the tubes and are continuously pushed and moved. Over time, the tubes wrap around each other, obscuring the catalyst dots. Additionally, the Van der Waals forces hinder the reaction, leading to the growth of amorphous carbon and a reduction in catalyst efficiency. Notably, we observe that the catalyst dots reside atop the CNTs, suggesting that the catalyst's growth mechanism follows a top-growth model. Furthermore, the diameters of the tubes that form on larger catalyst particles tend to exceed

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those on smaller ones, supporting previous research indicating a linear relationship between catalyst size and tube size within a specific range.

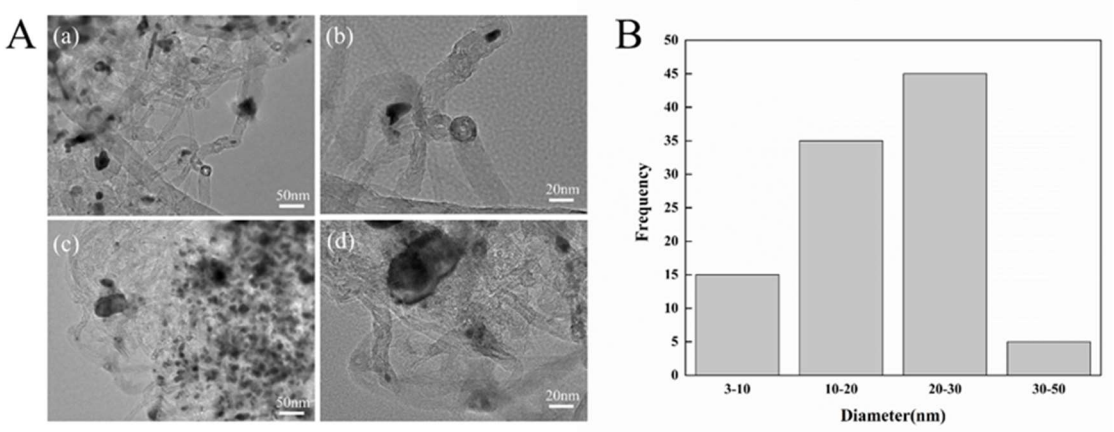

Figure 6. TEM characterization images of the growth of CNTs. (A) TEM images of CNTs and (B) diameter statistics situation of CNTs

Overall, new energy technologies are an important means for achieving sustainable development, providing clean and renewable energy guarantees for sustainable progress. The concept of sustainable development has prompted researchers to continuously explore more environmentally friendly and efficient new energy technologies. This research has developed an economical and efficient approach for producing higher yields of CNTs, including single-walled carbon nanotubes. The technology holds substantial practical value and shows promise for advancing industrialization. It is anticipated that this study could inform the production of other carbon materials through a more thorough investigation of precise control over growth conditions. Thus, this research offers a viable strategy to foster progress in new energy and carbon material sciences.

3. Conclusion

In summary, our research has developed an economical and effective method for producing new energy materials, specifically SWCNTs. We utilized an impregnation-calcination approach to synthesize the Fe-Co-W catalyst, which features an irregular and textured surface packed with numerous active sites made up of nano-sized particles. Our characterization results revealed that iron and cobalt are positioned as active sites on the catalyst's surface, while tungsten and magnesium are uniformly distributed throughout the catalyst, serving as a foundational element.

This catalyst was employed to promote the growth of CNTs using methane as the carbon source. The results demonstrated that it successfully produces SWCNTs with a significant yield. Further investigations showed that tungsten, iron, and cobalt could form stable crystal phases, namely $FeWO_4$ and $CoWO_4$, while inhibiting the formation of $MgFe_2O_4$ and $MgCo_2O_4$ phases. This stabilization contributes to a consistent dispersion and reactivity of iron and cobalt within the catalyst during the growth phase. Additionally, we examined the relationship between temperature conditions and catalyst yield in facilitating tube growth, concluding that both high and low temperatures can negatively impact catalytic activity, with optimal growth occurring at 900°C.

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