

# SYNTHESIS OF CARBON NANOTUBES VIA CATALYTIC CHEMICAL VAPOR DEPOSITION METHOD AND THEIR MODIFICATION WITH PREYSSLER ANION, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$

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Multiwalled carbon nanotubes (MWCNTs) were synthesized by catalytic chemical vapor deposition method using Fe/Co catalyst over  $\text{CaCO}_3$  support and acetylene gas as a carbon precursor in the temperature range of 650–800°C, and were modified with Preyssler anion nanostructures via impregnation method. The existence of nanoheteropolyacid  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  inside the MWCNTs was confirmed by infrared spectroscopy and transmission electron microscopy.

*Keywords:* Preyssler anion; multiwalled carbon nanotubes; nanostructure; impregnation; modification.

## 1. Introduction

Nanosystems, with characteristic lengths between 1–100 nm, have been attracting much attention in many fields, including physics, material science, chemistry, and biology. Along this line, polyoxometalates (POMs) are attracting much attention as building blocks for functional composite materials because of their interesting nanosized structures.<sup>1</sup> They are ideal models for the construction of hybrid systems, so they are regarded as the potential candidates to be transformed into nanometer-sized materials. Thus, in recent years,

considerable effort has been devoted to the design and controlled fabrication of nanostructured POMs. Recently, carbon nanotubes (CNTs) have been the focus of intense research.<sup>2</sup> They have triggered intensive research for their unique properties, including high surface area, specific electrical conductivity, exceptional physicochemical stability, and significant mechanical strength. They have wide applications in material science, sensor technology, catalysis, and biomedical fields.<sup>3</sup> However, the low chemical reactivity of raw CNTs leads to some limitations in their applications.<sup>4</sup> Enhancing

the activity and extending the applications of CNTs depends strongly on the development of methods for functionalizing these nanotubes. Therefore, modifying CNTs with POMs will make CNTs more attractive in various fields. Also, the electrochemical properties of POMs may be fully maintained when they are introduced to CNTs.<sup>5</sup> However, in spite of extensive investigations on modifying CNTs by Keggin and Dawson type POMs,<sup>6–20</sup> modification of CNTs with sodium 30-tungstophosphate, the so-called Preyssler anion, has been largely overlooked. Preyssler anion has exclusive properties and excellent stability.

According to the principles proposed for green chemistry, Preyssler anion is a promising candidate as a green catalyst. This catalyst is green with respect to corrosiveness, safety, quantity of waste, and separability. It is also unique due to its stability and functionality in the wide pH range of 0–12.<sup>21–27</sup>

This heteropolyanion with 14 acidic protons is an efficient “super acid” solid catalyst, which can be used both in the homogeneous and heterogeneous phases.<sup>21–27</sup> Other important features of this polyanion are:

- (1) The anion is thermally stable, rendering high temperature reactions practical.
- (2) Both pure and supported form can be easily recovered and recycled without degradation and loss of activity.

Encouraged by our recent results with polyoxometallate of Preyssler,<sup>21–27</sup> we tried to develop our research in the field of nanotechnology.<sup>28–33</sup>

In addition, due to the existence of repulsive forces between anionic cluster of Preyssler anion,  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ , this polyanion can act as an inorganic surfactant capable of stabilizing and protecting nanostructures from agglomeration. In the present work, we used MWCNTs materials as nanostructured porous supports for immobilization of Preyssler anion. CNTs provide large surface areas and can also facilitate electron transfers to reactive sites, and such properties make them attractive materials for applications in both sensors and electrocatalysis. On the other hand, due to the recyclability of Preyssler anion during oxidation/reduction process, and its good catalytic properties, the combination of Preyssler anion with CNTs may provide enhanced catalytic activities. In this paper, the chemical modification of MWCNTs by Preyssler anion nanoparticles was successfully

achieved. Based on the novel properties of both Preyssler anion and CNTs, such structures may find wide applications, especially in electrocatalysis.

Also, our work provides novel nanohybrid of Preyssler anion/CNT with several benefits. So, the significance and novelty of the current study is three fold: first, the whole synthesis process can be performed under room temperature, without adding any more agents, such as template, surfactant, nanometals, polymers, etc. Second, the preparation process is atom economic, with all the reactant going to the final product with special functions. Third, the Preyssler anion can play a key role in improving electrocatalytic activities in electrocatalytic reactions.

## 2. Experimental Procedure

### 2.1. Chemicals and instruments

All of the chemicals were obtained from Merck Company and used as received. Preyssler acid was prepared by passage of a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50 W × 8 in the H<sup>+</sup> form and evaporation of the elute to dryness under vacuum. The particle size and shape of nanostructures were observed by TEM (LEO 912 AB). FT-IR spectra were recorded with a Bruker scientific spectrometer (solid sample, KBr pellets).

### 2.2. Synthesis of MWCNTs by catalytic chemical vapor deposition method

MWCNTs were synthesized by catalytic decomposition of acetylene in the temperature range of 650–800°C over bimetallic catalyst supported on CaCO<sub>3</sub>. As catalyst, the bimetallic combination of Fe(III) and Co(II) was used. For being precise, a calculated amount of metal salts Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O was mixed with a few drops of distilled water and subsequently CaCO<sub>3</sub> powder was added to the mixture. After mixing well, the resulting powder was dried in an oven at 120°C overnight and then collected as dry powder. The total concentration of catalysts was about 5 wt.%. The decomposition of acetylene was carried out in a horizontal reactor at different temperatures (Fig. 1). Approximately 500 mg of the prepared supported catalysts (Fe(III),Co/CaCO<sub>3</sub>) was placed in a quartz boat, which was inserted in a ceramic tube under nitrogen flow. A continuous nitrogen flow was kept until

the final temperature was reached and then acetylene was let through with a gas flow of 100 ml/min for 20 min to 40 min. After rinsing the system with nitrogen, the reaction product was collected from the boat. Our reactor was a ceramic tube of 85-mm diameter with the heated length of 200 mm.

For purification, raw MWCNT samples were sonicated (30 W) in diluted nitric acid (30% HNO<sub>3</sub>) for 30 min at room temperature, filtered, washed several times with distilled water, and finally dried at 120°C overnight.

### 2.3. Impregnation method

Purified MWCNT was used as support materials. Prior to impregnation, the CNTs were treated with 30 wt.% HNO<sub>3</sub> at 100°C overnight, washed with distilled water, and dried at 120°C for 6 h. All modified samples were prepared with incipient wetness impregnation of Preyssler anion solution on treated MWCNT. Using sequential impregnation method, modified samples were prepared with Preyssler anion loadings of 30 wt.%. After impregnation step, the sample was dried at 120°C and calcined at 350°C for 3 h with a heating rate of 10°C/min under argon flow.

## 3. Results and Discussion

To date, Muller *et al.* have ingeniously synthesized many giant clusters of POMs within the nanometer-scale, including novel kinds of large rings and wheel-shaped systems.<sup>34,35</sup> Whereas a wide variety of these “magic” clusters have been reported to date,<sup>36</sup> there are only three anions, [NaSb<sub>9</sub>W<sub>21</sub>O<sub>86</sub>]<sup>-</sup>,<sup>37</sup> [NaAs<sub>4</sub>W<sub>40</sub>O<sub>140</sub>]<sup>25-</sup>,<sup>38</sup> and [NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>]<sup>14-</sup> that have been reported to encapsulate rare-earth ions. The latter, [NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>]<sup>14-</sup> so-called Preyssler anion, Na<sup>+</sup> is encrypted inside a central cavity formed by five PW<sub>6</sub>O<sub>22</sub> units arranged in a crown.<sup>39</sup> This polyanion consists of a cyclic assembly of five PW<sub>6</sub>O<sub>22</sub> units, each derived from the Keggin anion, [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>, by the removal of two sets of three-corner-shared WO<sub>6</sub> octahedral. In the recent study, the modified CNTs with Preyssler anion nanostructures were obtained through an impregnation method. Although the procedure has been reported previously, this method has never been reported for the synthesis of the modified CNTs with Preyssler anion nanostructures. MWCNTs were synthesized via chemical vapor deposition (CVD) method.

In principle, CVD is the catalytic decomposition of hydrocarbon or carbon monoxide feedstock with the aid of supported transition metal catalysts. The CVD method is believed to be the most suitable carbon nanotube synthesis method in terms of product purity and large scale production.<sup>40</sup>

Most of carbon nanotube synthesis techniques require the introduction of catalyst in the form of gas particulates or as a solid support. The selection of a metallic catalyst may affect the growth and morphology of the nanotubes. In this work, bimetallic combination of Fe and Co was used. Esconjauregui and his coworkers have shown that Ni, Co, and Fe display the highest catalytic activity in CNT synthesis process.<sup>41</sup> The catalytic activity of these metals strongly depends on their electronic structure. We have checked the catalyst/support ratio. When both Fe and Co were present in the catalyst/support ratio between 1.5–3% abundant double-walled carbon nanotubes could be synthesized. When the catalyst/support ratio was 5% most of the products were MWNTs. We suggest that Fe plays a major role in the catalytic CVD process and Co might play co-catalyst role in this process. Catalyst support has a profound effect on the quality and efficiency of CNTs. Although support with higher surface area demonstrates higher reactivity, the experimental results with porous catalysts such as zeolites and silicagels indicate higher production of amorphous carbon. Application of CaCO<sub>3</sub> support shows high density and purity of CNT products.<sup>41</sup> The second advantage of CaCO<sub>3</sub> is its easy removal in the purification stage.<sup>42</sup>

Reaction time and temperature, and gas flow rates of carbon source and inert gas are also important factors to optimize the carbon nanotube synthesis conditions and product quality. These parameters are adjusted so that the experimental conditions are optimized. A schematic diagram is shown in Fig. 1.

The synthesis process was carried out in two steps:

- In the first step, bimetallic catalyst was deposited on the CaCO<sub>3</sub> substrate.
- Then, acetylene gas as a carbon source was introduced in the reaction chamber. In this stage, metal carbides are formed and then these materials are converted to carbon atoms by using energy source. These carbons will get diffused towards substrate, which is coated with catalyst and nanotubes grow over the metal catalyst.

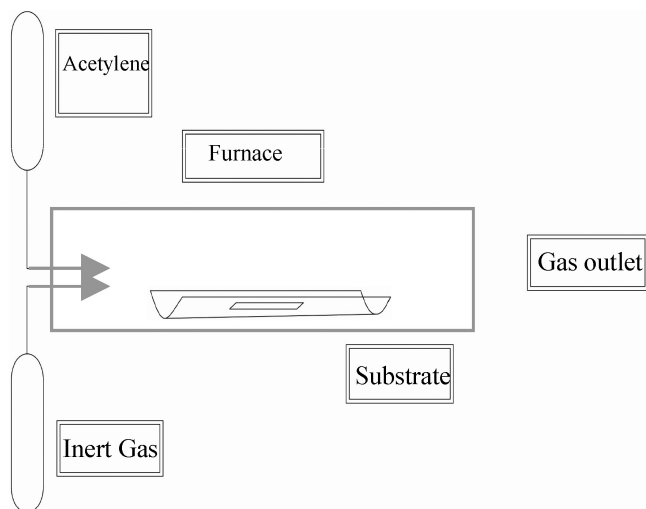


Fig. 1. Schematic diagram for CVD synthesis.

Figure 2 shows TEM images of the carbon nanotubes grown on Co-Fe particles deposited on  $\text{CaCO}_3$  substrate at  $650\text{--}800^\circ\text{C}$ . This figure shows a view of carbon nanotube, revealing the bamboo-like structure. The inner and outer diameters are about 20 nm and 35 nm, respectively.

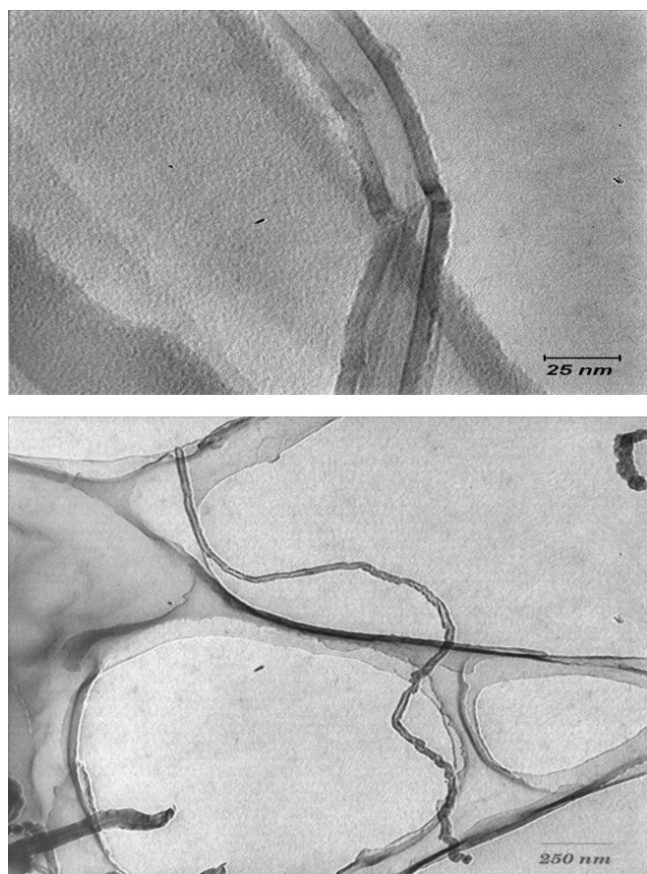


Fig. 2. TEM images of the CNTs.

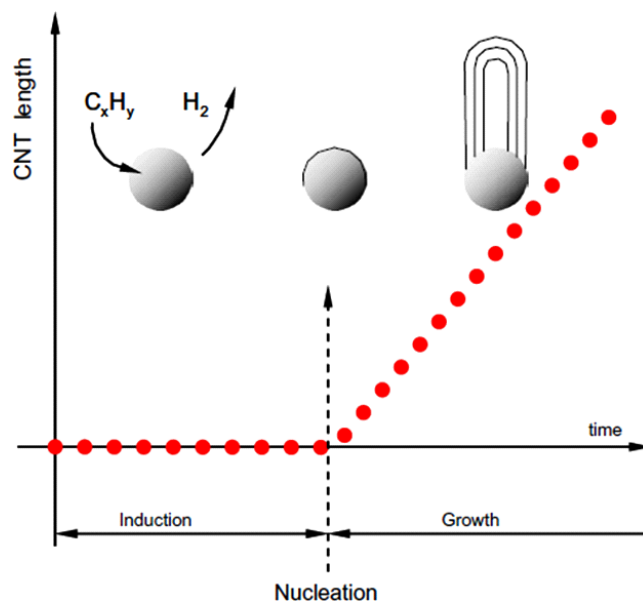


Fig. 3. Schematic diagram of CNT preparation mechanism.<sup>41</sup>

Saito and Yoshikawa reported the bamboo-like structure of CNTs grown by using arc-discharge method.<sup>43</sup> Recently, Wang and his coworkers have shown the bamboo shaped CNTs synthesized using pyrolysis method.<sup>44</sup> The bamboo-like structure is also found in the CNTs grown using microwave plasma enhanced CVD.<sup>45</sup> Li *et al.* have reported the bamboo-shaped CNTs grown by thermal CVD using alloy catalyst.<sup>46</sup>

Esconjauregui *et al.* presented a induction, nucleation and growth mechanism in CNT preparation using metallic nanoparticles (Fig. 3). Therefore, the formation of bamboo-like structure under a base growth mechanism seems to be possible in the most CNT preparation techniques.

For a systematic comparison, we compared the TEM images of MWCNTs, Preyssler anion, and modified CNTs with Preyssler anion. Figure 4 shows TEM images of the Preyssler anion alone. Interestingly, the TEM images show the spherical and tubular structures, which have a diameter in the range of 5–15 nm.

Figure 5 presents typical TEM images of the modified CNTs with Preyssler anion. In the Preyssler anion/CNT composite, Preyssler anion nanoparticles are not aggregated. It is suggested that the existence of electrostatic repulsive interactions between the negatively charged Preyssler anion on the outer walls of the CNTs could effectively prevent the agglomeration of Preyssler anion nanoparticles and CNTs. The arrow (a) in Fig. 5



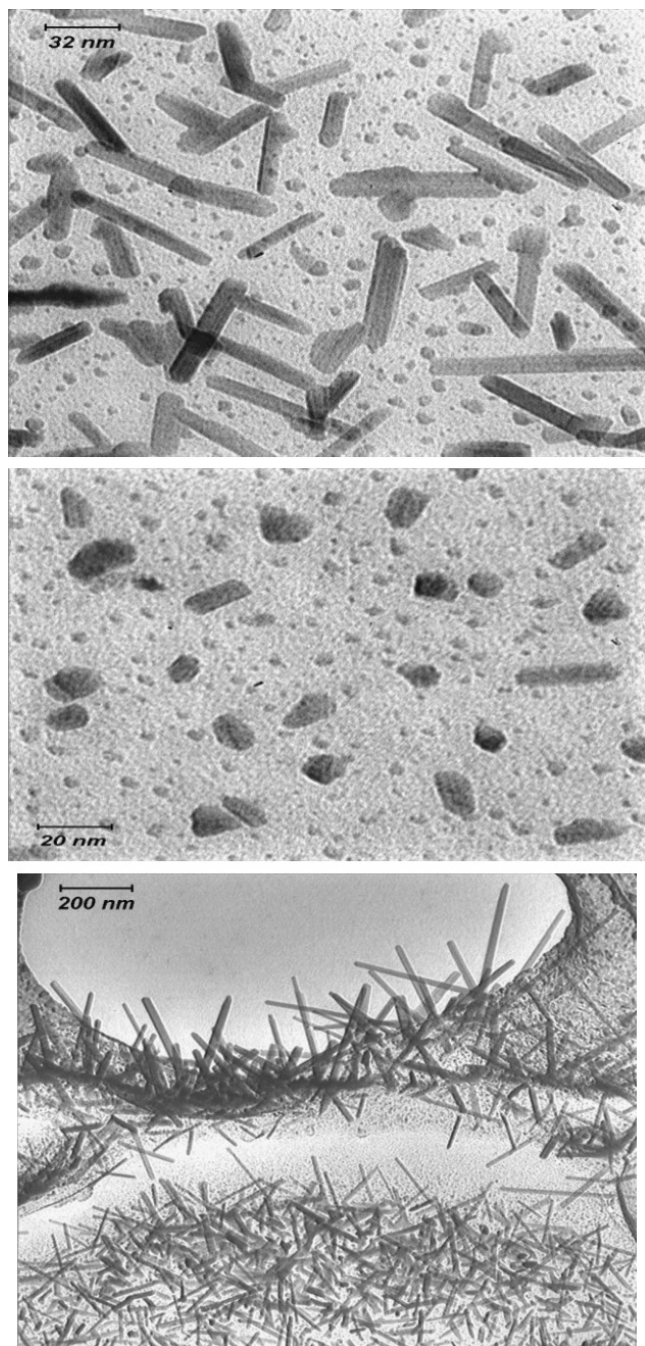


Fig. 4. TEM images of the Preyssler anion nanostructures.

indicates Preyssler anion nanoparticles inside the MWCNTs. It also reveals the bamboo-like structure in which the tube is consisted of hollow compartments (b). There are a few spherical particles around the CNTs, indicated by (c) and the nanorod structures are indicated by (d). Supporting Preyssler anion nanoparticles on CNTs is due to the chemical adsorption between carboxylic acid groups on CNTs and Preyssler anion nanoparticles, in which Preyssler anion nanoparticles tend to be

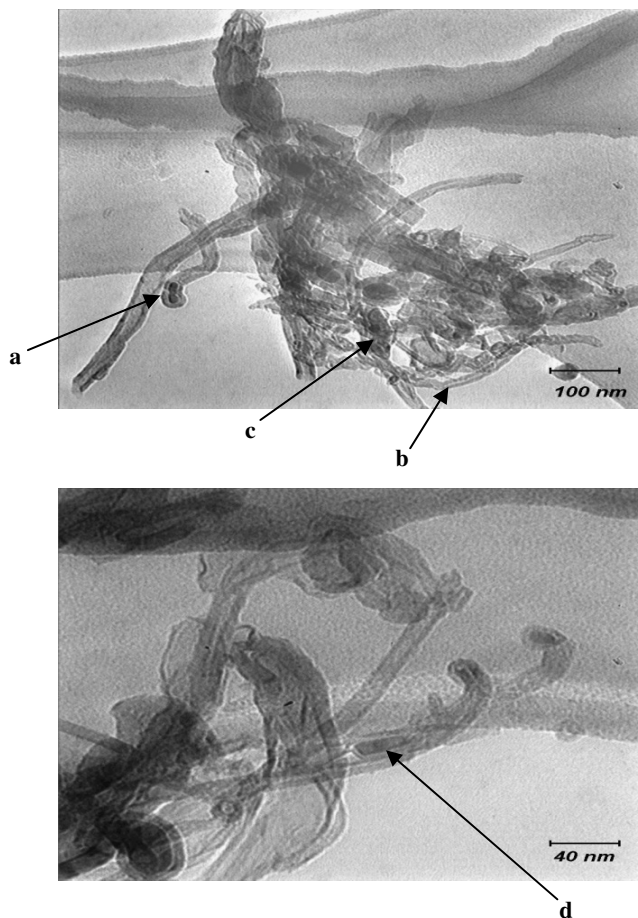


Fig. 5. TEM images of the modified CNTs with Preyssler anion.

preferably attached to the ends, the curves, and the connection points of CNTs.

The existence of heteropolyacid  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  in the MWCNTs was also confirmed by infrared spectroscopy. The asymmetric stretching frequency of the terminal oxygen was observed at  $960\text{ cm}^{-1}$  and the P-O asymmetric stretching frequency was noted at  $1080\text{ cm}^{-1}$  and  $1165\text{ cm}^{-1}$ . The prominent P-O bands at  $960$ ,  $1080$ , and  $1165\text{ cm}^{-1}$  were consistent with a  $\text{C}_{5V}$  symmetry anion. Also, IR spectra showed a peak at about  $1578\text{ cm}^{-1}$ , corresponding to the IR active phonon mode of CNTs.<sup>47</sup> The IR spectra indicated that the structure of the Preyssler anion retain upon impregnation.

#### 4. Conclusions

In conclusion, the modified CNTs with Preyssler anion nanoparticles have been prepared via the impregnation method at room temperature. This method can be used to exploit the properties of this POM-CNTs nanostructures and their application in

nanoelectronic devices, catalysis, electrocatalysis, electronic, pharmacology, and magnetic materials.

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