

Synthesis and characterisation of modified carbon nanotubes with potassium salts of the monosubstituted Keggin polyoxometalates

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A novel hybrid of potassium salts of the monosubstituted Keggin polyoxometalates/carbon nanotube nanocomposite is synthesised. Multiwalled carbon nanotubes (MWCNTs) were synthesised by the catalytic chemical vapour deposition method. The characterisation of the materials by Fourier transform infrared spectroscopy, and transmission electron microscopy, shows that the functionalisation of MWCNTs by potassium salts of the monosubstituted Keggin polyoxometalates was successfully achieved via the impregnation method in both endohedral and exohedral forms. Theoretical studies for the covalent conjugation of Keggin polyoxometalates to carbon nanotubes, showed that the functionalisation of MWCNTs by some groups such as COOH and OH is required.

1. Introduction: Since the innovation of carbon nanotubes (CNTs) in 1991, scientists have been interested in their exceptional structure and physical properties. This interest has been ongoing, and research into the practical application of CNTs has recently become very popular [1–6]. They have attracted much interest in the fields of material science, sensor technology, catalysis and biomedical science [7]. However, the low chemical reactivity of raw CNTs causes some limitations and drawbacks for their applications [8]. For usefulness, nanotubes need functionalisation, such as altering some of the graphite properties, supporting or attaching different various groups, especially inorganic particles for further applications of modified nanotubes.

Heteropolyacids (HPAs) are a large and diverse class of inorganic oxides which have attracted much attention in both academic research and applied chemistry relating to the chemical industry due to their unique properties, such as being strong Bronsted acids, structure alterability, high proton mobility, redox behaviour as well as being environmentally benign [9, 10]. Therefore, modification and alteration of CNTs with HPAs will convert CNTs to be more attractive in various fields. The electrochemical properties of HPAs may also be fully kept when they are introduced to CNTs [11].

Recently, HPAs have been introduced for the modification of CNTs. Pan *et al.* [11] reported the modification of CNTs using phosphomolybdic acid (HPMo) via chemisorption and mentioned that catalysts supported on modified CNTs presents a higher performance for methanol oxidation as compared with catalysts supported on CNTs. Seo *et al.* [12] deposited HPMo on Pt/CNTs and the HPMo-Pt/CNTs catalysts showed 50% higher catalytic mass activity along with improved stability for the electrooxidation of methanol than Pt/CNTs. Kim *et al.* [13] also reported that HPMo can facilitate the electrooxidation of intermediate species such as CO and a decrease in the amount into the catalysts being poisoned.

In spite of extensive investigations of the modification of CNTs by various HPAs, modification of CNTs with potassium salts of the monosubstituted Keggin polyoxometalates, has been largely overlooked. It is an ideal model for the construction of hybrid systems, and therefore it is considered as a potential candidate to be transformed into nanometre-sized materials. Very recently, we

have focused on the design and controlled fabrication of nanostructured HPAs [14].

Encouraged by our recent results with HPAs [15–21], in the present work, we used multiwalled carbon nanotubes (MWCNTs) materials as nanostructured porous supports for the immobilisation of potassium salts of the monosubstituted Keggin polyoxometalates. In our previous work, we investigated the performance and capability of sodium-30-tungstopentaphosphate for the modifying of MWCNTs [22]. To make a new contribution to the field of nanotechnology, it is of great interest to know what occurs if the potassium salts of the monosubstituted Keggin polyoxometalates are used in the chemical modification of MWCNTs. Interestingly, we have found that the potassium salts of the monosubstituted Keggin polyoxometalates not only functionalises MWCNTs as endohedral but also in exohedral form, and fill MWCNTs more effectively than sodium-30-tungstopentaphosphate anion.

CNTs provide large surface areas and can also facilitate electron transfers to reactive sites. Such properties are decided by finding out Lewis and Bronsted acidities and make them attractive materials for being applied in both sensors and electrocatalysis.

2. Results and discussion: MWCNTs were synthesised via the chemical vapour deposition (CVD) method. In this work, the bimetallic combination of Fe and Co was taken to consideration. The catalytic activity of these metals strongly depends on their electronic structure. We have examined the catalyst/support ratio. When both Fe and Co were present in 5 wt%, most of the products were MWNTs. We believe that Fe plays a major role in the catalytic CVD process and Co acts as a co-catalyst in this process. Calcium carbonate was used as a support catalyst. The application of CaCO₃ support gave rise to a high density and purity of CNT products.

CaCO₃ has been found to be a support material which actively influences the growth of CNTs by the CO₂ produced by its thermal decomposition at 650–800°C. The interaction between C₂H₂ and CO₂ significantly promotes CNT growth and allows the growth of CNTs on unfavourable substrate materials, as well as at much lower temperatures, rather than via traditional decomposition

of C_2H_2 (1)



Fig. 1 shows transmission electron microscope (TEM) images of the CNTs. This Figure demonstrates a bamboo-like structure. The inner and outer diameters were about 20 and 35 nm, respectively.

At the other stage, the functionalisation of MWCNTs by potassium salts of the monosubstituted Keggin polyoxometalates was successfully obtained via the impregnation method. All functionalisation methods of CNTs can be divided into two major classes [23, 24]: (i) functionalisation from inside (endohedral) meaning that nanotubes are functionalised by filling them with different particles; and (ii) chemical functionalisation from outside (exohedral) by attachment of different groups or compounds to the sidewall of the nanotubes.

Fig. 2 presents typical TEM images of the modified CNTs with potassium salts of the monosubstituted Keggin polyoxometalates. Our results revealed that the chemical modification of MWCNTs by potassium salts of the monosubstituted Keggin polyoxometalates was successfully achieved in both endohedral and exohedral forms.

The first is based on filling nanotubes with HPAs to obtain particles inside the tube. The second is achieved by the attachment of HPAs to the nanotube sidewalls.

Based on the novel properties of both Keggin and CNTs, such structures may find extensive usages, especially in electrocatalysis.

The existence of HPA in the MWCNTs was also confirmed by infrared spectroscopy. The asymmetric stretching frequency of the different oxygen particles was observed and was consistent with a Keggin structure. The IR spectra also showed a peak at about 1578 cm^{-1} , corresponding to the IR active phonon mode of the CNTs [25].

For the first time, for the investigation and confirmation of the interaction of Keggin polyoxometalates with CNTs, the quantum mechanical method was used. All of the present calculations have been performed with the PM6 semi-empirical level using the GAUSSIAN 03 package [26]. First, the structures of Keggin and (11, 11) CNT were optimised. Then, Keggin was put inside and outside of (11, 11) CNT and optimised structures were obtained. Figs. 3 and 4 show the optimised structures of Keggin- inside and outside of (11, 11) CNT, respectively. The interaction energy (ΔE) was calculated from the following equation

$$\Delta E = E_{\text{CNT-Keggin}} - E_{\text{CNT}} - E_{\text{Keggin}} \quad (2)$$

ΔE s obtained from outside and inside of (11, 11) CNT are equal to +0.254 and +0.329 Hartree, respectively, showing that interactions in relation to separate types are undesirable. Therefore, as mentioned in the following Experimental Section, for covalent

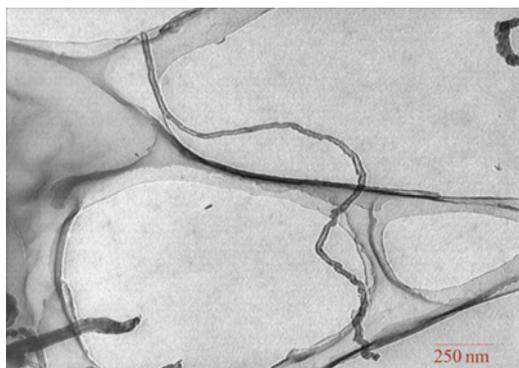


Figure 1 TEM images of the CNTs

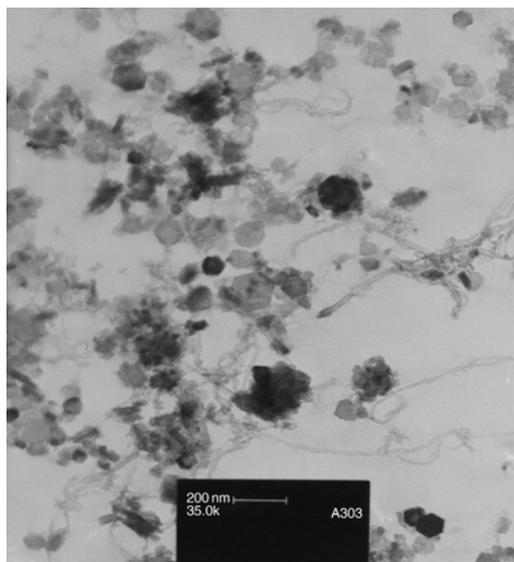


Figure 2 TEM images of the modified CNTs with Keggin

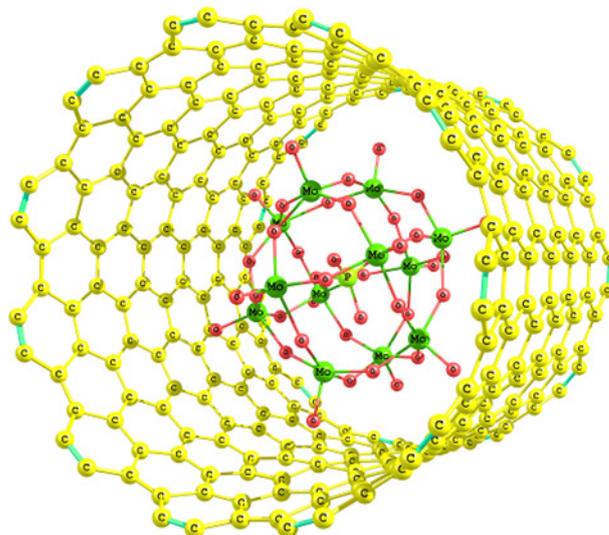


Figure 3 Optimised structure of Keggin⁻ inside of (11, 11) CNT

conjugation of Keggin polyoxometalates to CNTs, functionalisation of MWCNTs by groups such as COOH and OH is required.

3. Experimental

3.1. Instruments: A PHILIPS CM-120 TEM was used to examine the synthesised nanostructures. The IR spectra (KBr pellet; $4000\text{--}400\text{ cm}^{-1}$) were recorded on a Bruker scientific spectrometer. For the electron microscopy study, the powder was dispersed in absolute alcohol with an ultrasonic vibrator for 15 min, and then deposited on a grid covered with a perforated carbon film.

3.2. Synthesis of MWCNTs by catalytic chemical vapour deposition method: MWCNTs were synthesised by catalytic decomposition of acetylene in the temperature range of $650\text{--}800^\circ\text{C}$ over a bimetallic catalyst supported on CaCO_3 . As catalyst, the bimetallic combination of Fe(III) and Co(II) was used. For being precise, a calculated amount of metal salts $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was mixed with a few drops of distilled water and subsequently CaCO_3 powder was added to the mixture. After mixing well, the resulting powder was dried in an oven at 120°C

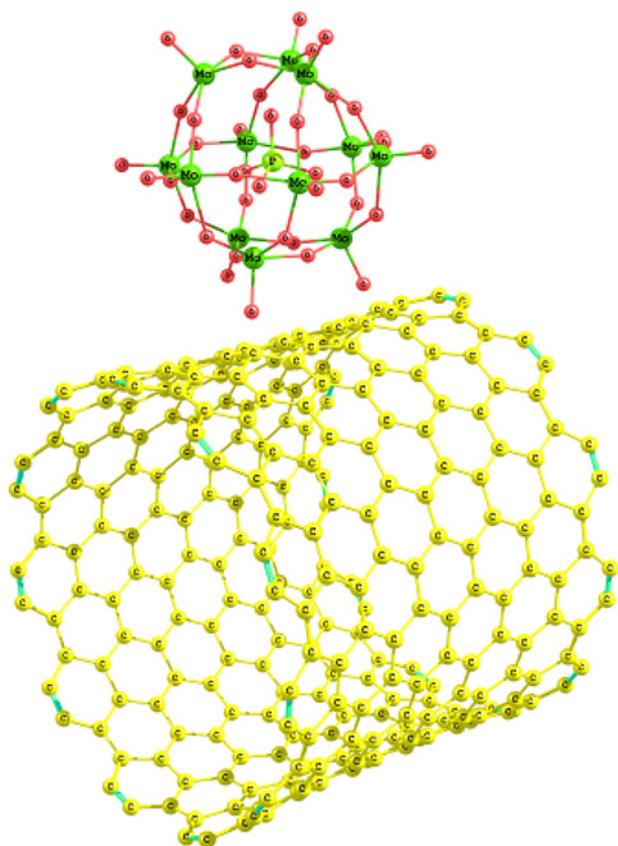


Figure 4 Optimised structure of Keggin outside of (11, 11) CNT

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. Approximately 500 mg of the prepared supported catalysts (Fe (III),Co/CaCO₃) was placed in a quartz boat, which was inserted in a ceramic tube under nitrogen flow. A continuous nitrogen flow was maintained until the final temperature was reached and then acetylene was introduced with a gas flow of 100 ml/min for 20–40 min. After rinsing the system with nitrogen, the reaction product was collected from the boat. The synthesis was carried out in two steps: in the first step, bimetallic catalyst was deposited on the CaCO₃ 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 transformed to carbon atoms by using an energy source. These carbons will get diffused towards substrate, which is coated with catalyst and nanotubes grown over the metal catalyst.

For purification, raw MWCNT samples were sonicated (30 W) in diluted nitric acid (30 wt% HNO₃) for 30 min at room temperature, filtered, washed several times with distilled water, and finally dried at 120°C overnight.

3.3. Impregnation method: Purified MWCNTs were used as support materials. Prior to impregnation, the CNTs were treated with 30 wt% HNO₃ 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 potassium salts of the monosubstituted Keggin solution on treated MWCNTs [27]. After the impregnation stage, the samples were dried at 120°C and calcined at 350°C for 3 h with a heating rate of 10°C/min under an inert atmosphere of argon flow.

3.4. Synthesis of K₇[PW₁₁O₃₉].14H₂O: To a solution of 181.5 g of Na₂WO₄.2H₂O in 300 mL of H₂O was slowly added 50 mL of 1M

H₃PO₄ and 88 mL of glacial acetic acid. This solution was refluxed for 1 h and then brought to room temperature. Addition of 60 g of solid KCl leads to white precipitate which was collected after 10 min and air dried. Monosubstituted Keggin polyoxometalate was prepared by adding an aqueous solution of Co(NO₃)₂ to the above powder. The solid product was characterised using Fourier transform infrared spectroscopy and by comparison with that of reported sample.

4. Conclusion: In this reported work, an organic–inorganic nanostructure containing nanosized inorganic building blocks in organic material has been obtained by the impregnation method and theoretical studies for covalent conjugation of Keggin polyoxometalates to CNTs showed that the functionalisation of MWCNTs by some groups such as COOH and OH is required.

5 References

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