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Synthesis of Carbon Nanospheres From Vanadium β-Diketonate Catalyst

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Carbon nanospheres (CNS) were synthesized using bis(acaetylacetonato)oxovanadium(IV) as catalyst precursor in a traditional chemical vapor deposition (CVD) carbon nanotube synthetic reactor. The as-prepared products were characterized with Scanning electron microscope (SEM), Raman spectroscopy, High resolution transmission electron microscopy, (HR-TEM), Thermogravimetric analysis, (TGA), Powder X-ray diffraction, (PXRD) and Energy dispersive spectroscopy, (EDS). All indicate the presence of carbon nanospheres with uniform diameter, together with small amounts of carbon nanotubes and amorphous carbon.

Keywords: Carbon nanospheres, organometallic catalyst, bis(acaetylacetonato)oxovanadium(IV), raman, TGA, TEM, SEM, XRD

1. INTRODUCTION

The ability of carbon to hybridize into forming *sp*, sp^2 and sp^3 bonds [1] results in the formation of structures such as carbon nanotubes [2-6], fullerenes [7], nanofibers [8-11] and carbon nanospheres (CNS) among other structures [13-15]. Carbon nanospheres have a semi-crystalline structure which is a reflection of their unique properties of low density, high porosity, increased surface area and relatively high chemical and thermal stability [1].

Traditional methods employed in the fabrication of nanostructures have focused on a templating method with porous alumina, polystyrene spheres, silica spheres and micelles [16]. Chemical vapor deposition (CVD) method using porous silica, pyrolysis of hydrocarbon at high temperature in the presences of various catalysts has been employed [13].

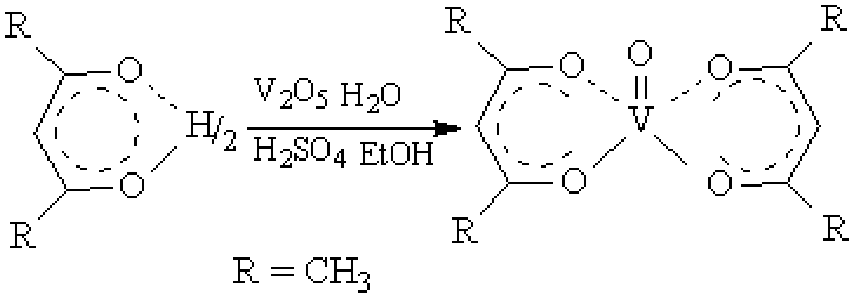
CNS and carbon nanotubes can be made by a variety of procedures and these include numerous variations of the arc-discharge, laser ablation and chemical vapor deposition processes with inorganic metals and in some instances organometallic complexes are used as catalysts in these methods. The catalysts are generally made from metals or their salts [5]. Hydrocarbons are by far the most widespread precursors among carbon sources employed in the production of carbon nanotubes and carbon nanospheres.

In our research, mixed transition metals such as nickel, iron, cobalt, zinc and aluminium have been used as catalyst particles [4,17]. In this study, we have utilized an organometallic compound, bis(acetylacetonato)oxovanadium(IV), [VO(acac)$_2$], as catalyst particle for carbon nanomaterial synthesis. Metal β-diketonate complexes such as nickel(II) acetylacetonate and copper(II) acetylacetonate have been utilized [18] as catalyst particles in the synthesis of carbon nanotubes. However, our survey of available literature indicate that bis(acetylacetonato)oxovanadium(IV) have not been used as catalyst precursor for the synthesis of carbon nanotubes and CNS. In this study and for the first time, we investigate what carbon nanomaterial are formed from acetylene and bis(acetylacetonato)oxovanadium(IV) in a traditional CVD process.

2. EXPERIMENTAL

2.1. Preparation of catalyst, vanadium β-diketonate complex.

Bis(acetylacetonato)oxovanadium(IV), [VO(acac)$_2$], (acac = acetylacetonate) was synthesized according to literature, Scheme 1, [19]. All reagents and solvents used were analytical grade and were purchased commercially and used without further purification.



Scheme 1.

Distilled water (6.0 ml), concentrated sulphuric acid (4.6 ml), 95% ethanol (12.6 ml) and 0.014 mol of vanadium pentoxide, V_2O_5 were mixed together. The mixture was heated to boil on a water bath with stirring. Reduced vanadium is filtered and collected in a beaker. 0.064 mol of acetylacetone was then added to the reduced vanadium. Then a solution of sodium carbonate in water was slowly added to the reaction mixture [17]. The product was filtered off and washed with water and dried overnight in a dessicator. The product was then recrystallized from chloroform. Reaction equation for the formation of the complex is according to scheme 2. Blue crystals were collected which were then dried, melting point, 257 – 259°C (yield: 94%). FTIR (cm^{-1}): 682 m, δ(ring); 788 – 797 sh γ(C-H); 991 s,sh ν(V=O); 1588 – 1516 s sh, $\nu(CO)_{(acac)}$; 1285 sh, $\nu(C{-}C{-}C)_s$; 1416 m,sh $\delta(CH_3)_{as}$.

$$V_2O_5 + 2H_2SO_4 + C_2H_5OH \longrightarrow 2VOSO_4 + CH_3CHO + 3H_2O$$

$$VOSO_4 + 2C_5H_8O \longrightarrow VO(C_5H_7O_2)_2 + H_2SO_4$$

Scheme 2.

2.2. Preparation of carbon nanomaterial

Experimental procedure employed in the synthesis has been reported [4]. The reaction to synthesize carbon nanomaterials were conducted in a horizontal tubular furnace at atmospheric pressure with acetylene gas as the carbon source. Pyrolysis of the hydrocarbon source was at 700°C. The reactor consisted of a 40 mm *o.d* x 70 cm long quartz tube heated by an electrical tube furnace with a temperature controller. Nitrogen gas flowing at 40 ml min^{-1} was passed through the reactor for approximately 70 min., and after stabilization for 10 min, the nitrogen gas flow was maintained at 240 mL min^{-1}. Acetylene gas with a flow rate of 90 mL min^{-1} was then passed through the reactor for 60 min. The catalyst placed on a quartz boat was placed in the centre of the furnace during the synthesis. The flow rate of the gases was controlled by a mass flow controller (MFC). At the completion of the reaction, the reactor was cooled to room temperature with nitrogen flowing at 40 mL min^{-1} for 3 to 4 hrs. In this process, a black material was formed after 60 minutes which we now call as-prepared nanomaterial. This as-prepared nanomaterial was then characterized as described below without further purification.

2.3. Characterization

The morphological features of nanomaterials were analyzed by Raman spectroscopy, FE-SEM, HR-TEM, EDS, TGA and XRD. The Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40 attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected by means of back scattering geometry with an acquisition time of 50 seconds. The surface morphology and EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope. The HR-TEM images of the sample were obtained by a CM 200 electron microscope operated at 100 kV. The thermal behavior of the carbon nanomaterials were investigated by TGA using a Q500 TGA instrument under an air environment. The prepared nanomaterial samples were heated in platinum crucibles with oxygen and nitrogen gases at a flow rate of 40 and 60 mL/min respectively. The dynamic measurement was made between ambient and 1000°C with a ramp rate of 10°C/min to 900°C. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper Kα1 radiation of wavelength (λ = 1.540598) and Kα2 radiation of wavelength (λ = 1.544426). Scan speed of 1 s/step and a step size of 0.03°. IR spectra were recorded using Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer in the range 400 – 4000 cm^{-1}. UV-vis spectra were recorded on a Perkin-Elmer lambda 9 UV-vis spectrometer.

3. RESULTS AND DISCUSSION

The UV-vis spectra of the complex (not included) show metal-to-ligand charge transfer transitions observed for the complex bis(acetylacetonato)oxovanadium(IV) [20]. Fourier transform infrared (FT-IR) spectra of liquid acetylacetone and bis(acetylacetonato)oxovanadium(IV), $VO(acac)_2$, are presented in figure 1. The peaks of primary interest from figure 1(a), the spectrum for acetylacetone, have already been reported and the agreement between our data and literature is satisfactory [21]. These data are presented in table 1.

Table 1: Selected FTIR bands of acetylacetone (Hacac) and bis(acetylacetonato)oxovanadium(IV) in wavenumbers (cm^{-1}).

Acetylacetone (Hacac)	Bis(acetylacetonato)oxovanadium(IV) **($VO(acac)_2$)**	**Assignment**
	3387 br	$\nu(C{-}H)$
1728 keto $\nu(C{=}O)$	2975 w	$\nu(CH_3)_{as}$
1708	2923 w	$\nu(CH_3)_s$
	1588 w	$\nu(C\overset{\cdots}{-}O)$
1604	1516 s, sh	$\nu(C\overset{\cdots}{-}O)$
1416	1416 w, sh	$\delta(CH_3)_{as}$
1359	1370, 1355 s, br	$\nu(C\overset{\cdots}{-}O)$
1301	1285 s, sh,	$\nu(C\overset{\cdots}{-}C\overset{\cdots}{-}C)_s$
1245		
1156	1112 br,	$\beta(C{-}H)$
999	1016 w, sh	$\alpha(CH_3)$
953	991 s, sh	$\nu(V{=}O)$
913	934 m	$\nu(C{-}CH_3)$
776	797, 788 s, sh	$\gamma(C{-}H)$
	682 m	δ(ring)
	657m-w	δ(ring)

ν stretching mode, *γ* out-of-plane bending mode, *δ* deformation mode, α rocking mode, β in-plane bending mode

The peaks of interest in the FT-IR spectra of the VO(acac)$_2$ complex, figure 1(b), are the intense band observed 1516 cm^{-1} having a shoulder at 1588 cm^{-1}, the band at 1370 cm^{-1} which are assigned as C−O stretching vibrations and the stretching vibrations of the V=O, vanadyl bond are observed at 991 cm^{-1}.

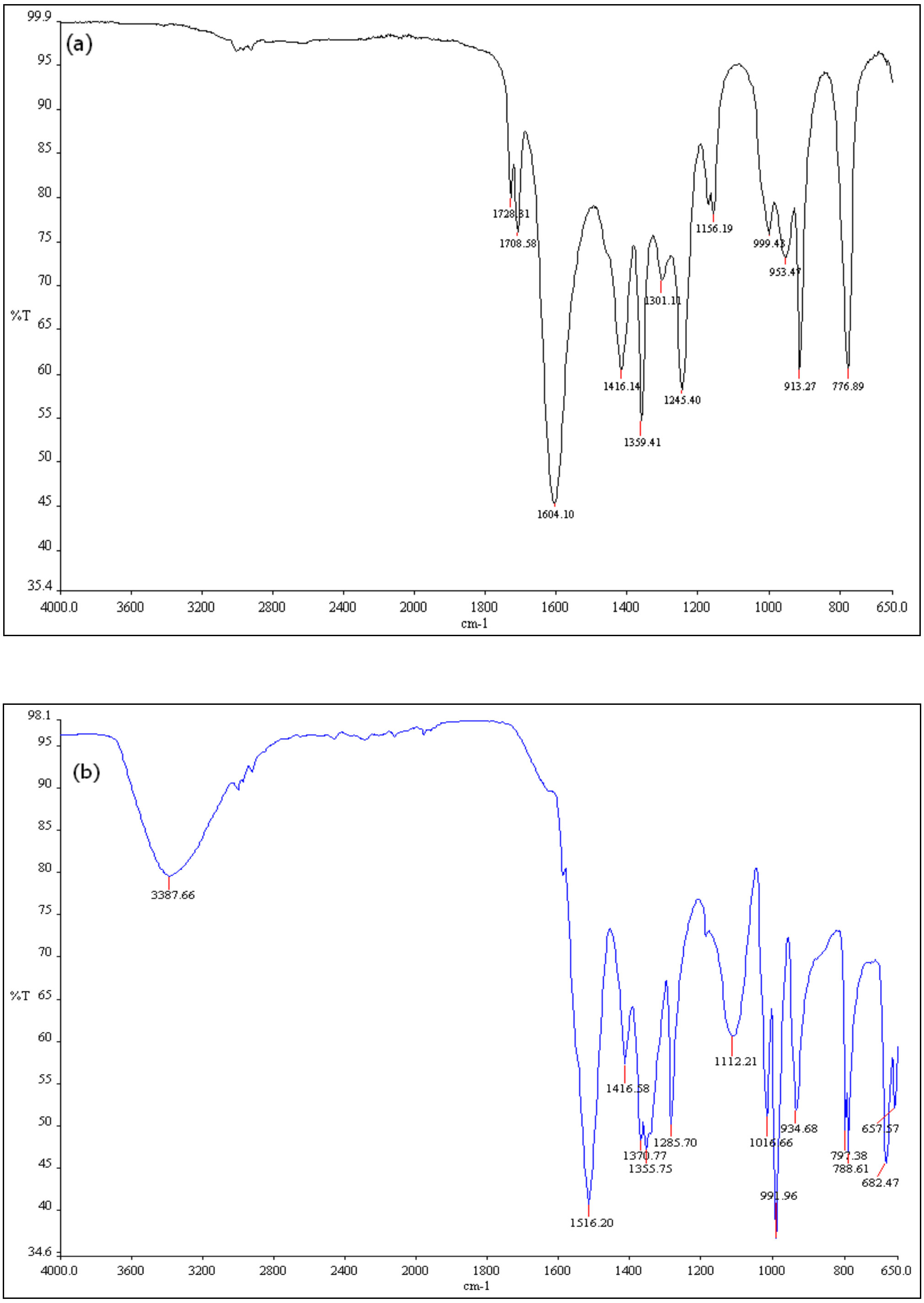


Figure 1. Fourier transform infrared (FTIR) spectra of (a) pure acetylacetone and (b) solution of synthesized bis(acaetylacetonato)oxovanadium(IV).

This is within the usually observed range 950 – 999 cm^{-1} for six coordinate oxovanadium(V) complex. The in-plane vibration of the cyclic fragment is observed at 934 cm^{-1} while the out-of-plane bending vibration is observed as a doublet at 788 and 797 cm^{-1}. In the range 1416 and 1112 – 934 cm^{-1}, the FT-IR spectra exhibit bands corresponding to CH_3 groups [19,22]. The spectra contain strong and sharp band which is assigned as vibration corresponding to the C−C−C angle at 1285 cm^{-1} The FT-IR spectra data table 1, are consistent with the structure of the complex $VO(C_5H_7O_2)_2$ which indicate the ligand is coordinated in the normal manner through O,O-donor sites.

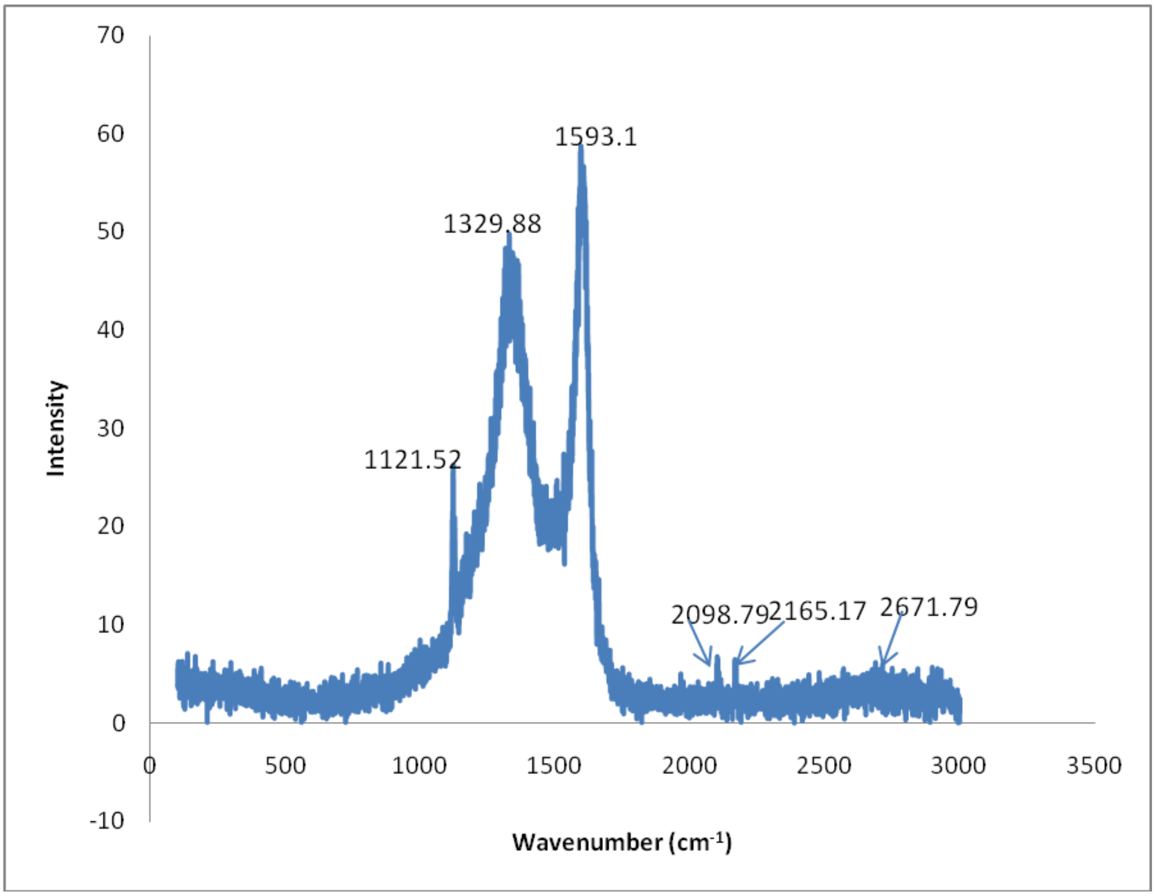


Figure 2. Raman spectra of carbon nanospheres produced from acetylene and bis(acaetylacetonato) oxovanadium(IV) as catalyst precursor.

Raman spectroscopy is a powerful tool for the characterization of carbon nanomaterials, and can reveal several properties of carbon nanomaterials. The Raman spectrum of the prepared carbon nanomaterial is presented in figure 2. The Raman spectra of the sample, figure 2, have several peaks at 1121.06, 1329.88, 1593.1, 2098.79, 2165.17 and 2671.79 cm^{-1}. The two major peaks: the *D* and *G* bands which indicate the presence of crystalline graphitic carbon in the carbon nanomaterial are observed at 1329.88 and 1593.1 cm^{-1} respectively. The *D*-band at 1329.88 cm^{-1}, has been attributed to the presence of amorphous carbon due to surface defects of carbon nanomaterials and graphitic carbon while the *G*-band band at 1593.1 cm^{-1} is that of ordered carbon nanomaterial [4]. The *G*-band at 1593.1

cm^{-1} correspond to an e_{2g} mode of graphite which is related to the vibration of sp^2-bonded carbon atoms and the presence of ordered carbon nanotubes in a sample. The *D*-band at 1329.88 cm^{-1} is associated with vibrations of carbon atoms in disordered graphite. The strength of the band can be identified with wall disorder or the presence of coating on the outside of spheres [23]. A notable observation in this spectrum is the absence of an overtone peak that should have resonated at about 2600 cm^{-1} from the *D* and *G* bands. A small peak is however observed at about 2671.79 cm^{-1} with an intensity of 5.2084. The absence of this peak could be related to the amount of carbon nanotubes produced in the synthesis as well as their purity. The intensity ratio of these two bands ($I_D/I_G = 0.8556$) is considered as a parameter to characterize the quality of carbon nanomaterial in the sample, with a high intensity ratio indicating a high degree of disorder in the carbon nanomaterial. The intensity ratio for the two peaks obtained, 0.8556, indicate the high quality of carbon nanospheres obtained in synthesis. The peaks at 1121.06 cm^{-1} which is a shoulder on the *D*-band should further emphasize the presence of vibrations associated with carbon atoms in disordered graphite.

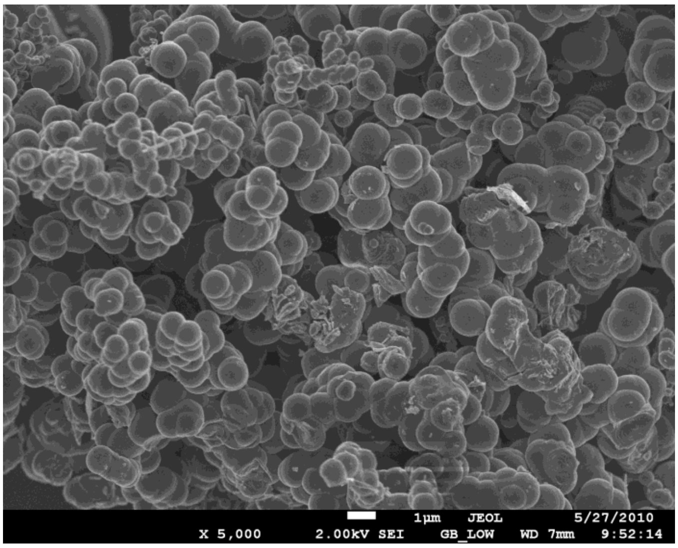


Figure 3. Scanning electron microscope (SEM) spectra of carbon nanospheres produced from acetylene and bis(acaetylacetonato)oxovanadium(IV) as catalyst precursor.

The FE-SEM micrograph of the as-prepared carbon nanomaterial is presented in figure 3. The surface morphology of the carbon deposit obtained is seen to form several spherical carbon nanomaterials which could be called carbon nanospheres. It can be seen that these spheres are relatively uniform in diameter. The spheres are seen to agglomerate by coalescence of the surface forming chains. A few graphitic crystallites are also present, which remnants of neutral graphite matrix. There are a few broken spheres from this morphological presentation which may have been caused by magnetostatic energy of the nanoparticles.

Energy dispersive spectroscopy (EDS) of carbon nanospheres formed from bis(acetylacetonato)oxovanadium(IV) catalyst is presented in figure 4. The spectrum shows the presence of carbon, oxovanadium (V=O), vanadium and sodium. The EDS spectra of the synthesized carbon nanosphere indicate that the carbon nanospheres contain carbon as well as catalyst metals. The carbon is derived from the carbon nanospheres while vanadium oxide and sodium are derived from the catalyst.

Thermogravimetric analysis (TGA) profile of the carbon nanospheres is presented in figure 5. TGA analysis is often employed to examine the thermal stability of the as-prepared carbon nanospheres and the carbon phases present in carbon nanotubes obtained in the synthesis. The interpretation is not often straight forward due to the composition of the nanomaterial and the weight of catalyst change during the reaction.

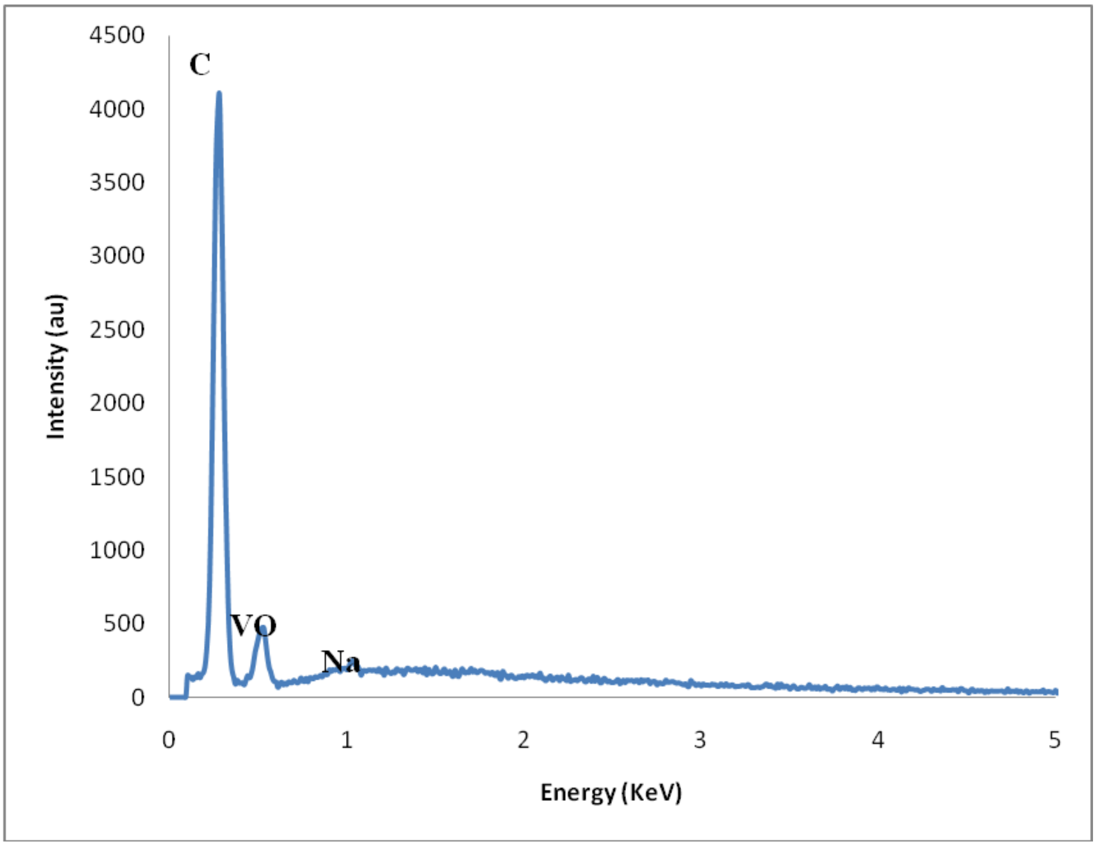


Figure 4. Energy dispersive X-ray spectroscopy (EDS) spectra of carbon nanospheres produced from acetylene and bis(acaetylacetonato)oxovanadium(IV) as catalyst precursor.

In addition, the composition of the catalyst also changes in TGA due to oxidation reaction. The temperature at which the carbon nanospheres are oxidized is an index of its stability. Weight loss started at 496^{o}C to about 830^{o}C for the sample. The TGA profile presents approximately a 96% weight loss which is mainly attributed to a one step exothermic reaction process. The thermal stability observed in this TGA is an indication that the nanomaterials formed in the synthesis are carbon nanospheres.

Powder X-ray diffraction (PXRD) pattern of the as-prepared nanospheres is shown in figure 6.

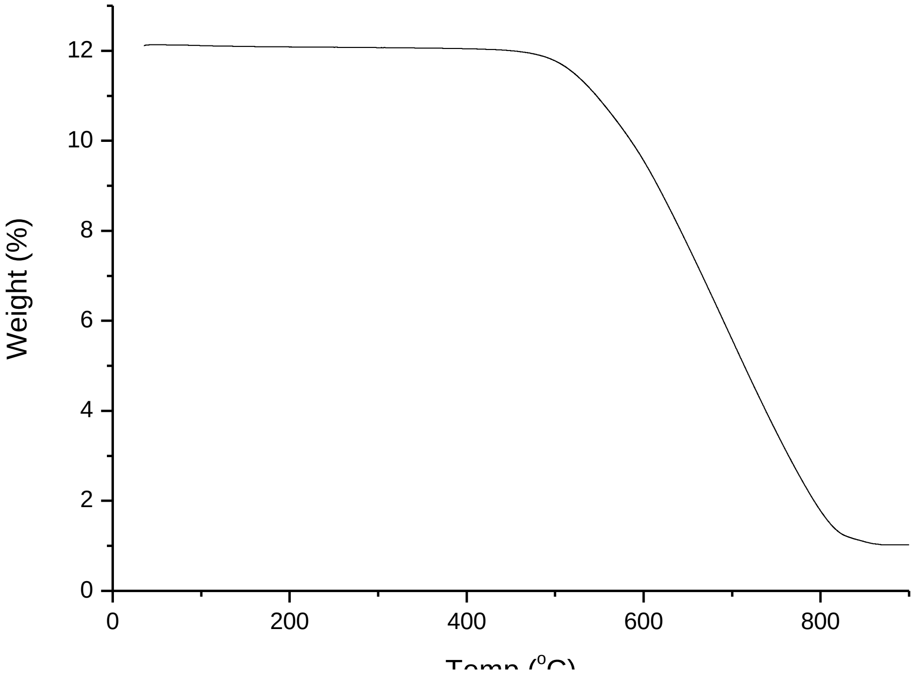


Figure 5. Thermogravimetric analysis of carbon nanospheres produced from acetylene and bis(acaetylacetonato)oxovanadium(IV) as catalyst precursor.

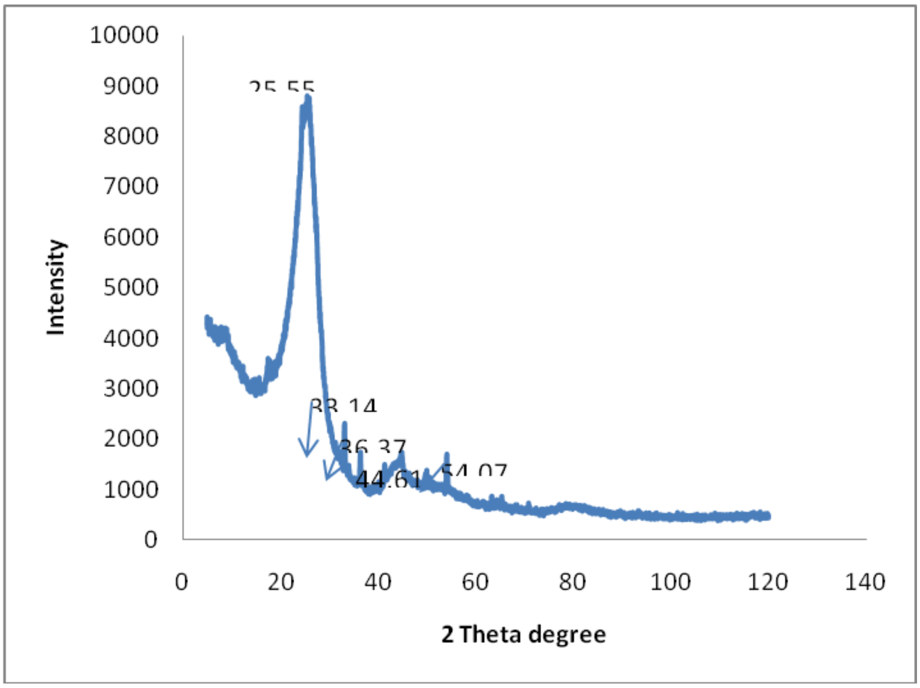


Figure 6. X-ray diffraction analysis of carbon nanospheres produced from acetylene and bis(acaetylacetonato)oxovanadium(IV) as catalyst precursor

Bragg diffraction peaks at 2θ = 25.55°, 33.14°, 36.37°, 44.61° and 54.07° are the main peaks observed in the diffraction analysis. The peaks at 25.55° and 44.61° correspond to hexagonal graphite lattice of the carbon nanospheres. The peak at 2θ = 25.55° with a broad diffraction signal from about 14° to 30° and an intensity of about 8800 (au) units indicates the presence of large amounts of amorphous carbon nanospheres in the as-prepared product. The low intensity of the peak at 2θ = 44.61°, is an indication of the quality of carbon nanospheres present in the as-prepared product. The peaks at 2θ = 33.14°, 36.37° and 54.07° correspond to crystal planes of (111), (200), and (220) of vanadium in the bis(acetylacetonato)oxovanadium(IV) catalyst used in the synthesis [24-26].

High resolution transmission electron microscope (HR-TEM) micrograph of the as-prepared carbon nanospheres obtained from bis(acetylacetonato)oxovanadium(IV) catalyst by decomposition of ethyne (acetylene) is presented in figure 7. Further morphological details of the nanospheres as observed in the SEM micrograph are corroborated in the HR-TEM micrograph. The HR-TEM confirms the nanomaterials obtained in this synthesis as nanospheres. Figure 7(a) is a magnified image of a single nanosphere indicating the nanospheres to be uniform throughout with a diameter of about 300 nm.

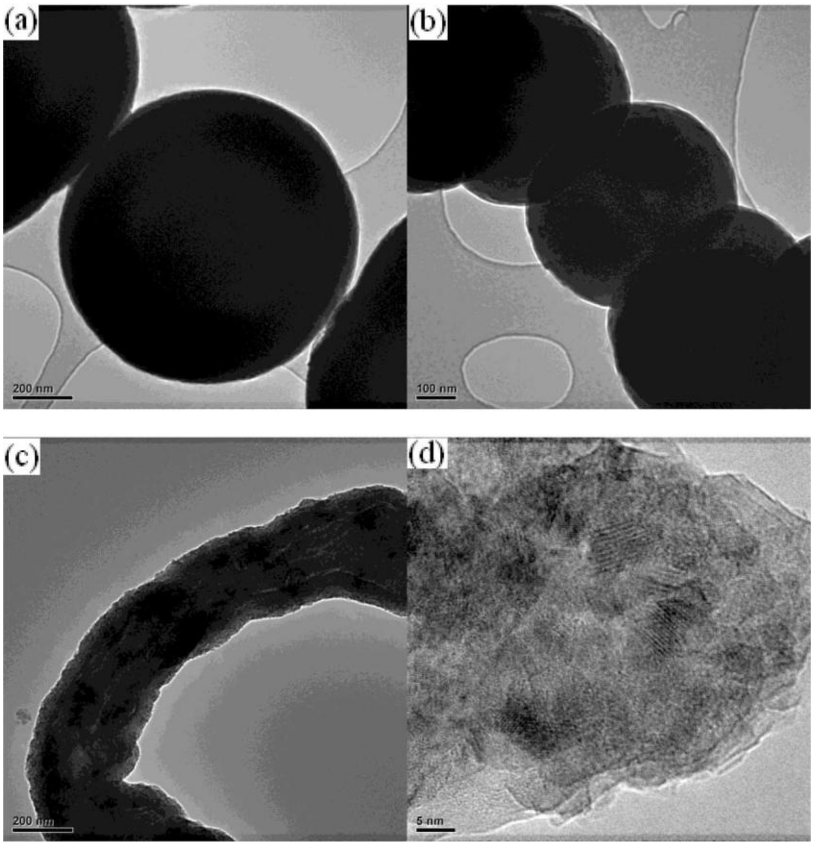


Figure 7. HR-TEM Images of carbon nanospheres produced from acetylene and bis(acetylacetonato)oxovanadium(IV) as catalyst precursor

Several nanospheres have agglomerated together to form a chain with individual nanospheres seen to overlap together in figure 7(b). The HR-TEM micrograph, figure 7(c), show the morphology of a single carbon nanotubes or several nanospheres that have encapsulated together to form a nanotubes [1,28]. The HR-TEM micrograph reveal lattice fringes image of grapheme layers, figure 7(d). The crystalline presentation of the layers is far from ideal as reflected in the graphitization image.

4. CONCLUSION

The catalyst precursor bis(acetylacetonato)oxovanadium(IV) which is an organometallic compound have been used successfully to synthesis carbon nanomaterials in the presence of acetylene gas as carbon precursor. The carbon nanomaterial produced were carbon nanospheres of uniform diameter. Small amounts of amorphous carbon and a strand of carbon nanotube were observed in the HR-TEM and SEM micrographs. This study therefore demonstrates the production of CNS with bis(acetylacetonato)oxovanadium(IV) catalyst. The PXRD pattern identified the presence of amorphous carbon in the synthesis.

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