Exploring a novel approach to fabricate vanadium carbide encapsulated into carbon nanotube (VC@C) with large specific surface area

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Abstract. A novel approach to the fabrication of vanadium carbide encapsulated into carbon nanotube (VC@C) core-shell structured composite by thermal treatment with the precursor $V_3O_7 \cdot H_2O@C$ was developed for the first time. The as-obtained VC@C were characterized by X-ray powder diffraction (XRD), Raman spectrum, energy-dispersive X-ray spectrometer (EDX), elemental analysis (EA), Fourier transform infrared spectroscopy (FT)–(IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET). The results showed that VC@C with core-shell structures could be successfully synthesized at 1000 °C for 2 h. The specific surface area, average pore size and measured pore volume of VC@C were 135·46 m^2/g, 4·443 nm and 0·180 cm^3/g, respectively indicating that the as-obtained VC@C composite could be used as a mesoporous material. Furthermore, thermal behaviour of the as-obtained VC@C composite in air was investigated by thermo-gravimetric/differential thermal analyser (TG/DTA). The experimental result revealed that the carbon coated on the surface of VC has high activity with O_2 in air atmosphere.

Keywords. VC@C; core-shell structure; composite materials; mesoporous material; solid-state reaction.

1. Introduction

The fabrication of new materials with well-defined morphologies based on the construction of some other materials with novel structures has gained considerable attention in the past few years (Zygmunt *et al* 2003; Zhang *et al* 2011a, 2012a, b). For example, novel silica nanotubes with high aspect ratio were synthesized using $V_3O_7 \cdot H_2O$ nanofibres as templates by Zygmunt *et al* (2003) and the silica nanotubes had been found a novel use in coating with catalytically active transition metal compounds (Zygmunt *et al* 2003). Recently, core-shell nanostructures have been paid much attention due to their tunable surface properties, which retain the properties of both cores and shells (Caruso 2001; Sun *et al* 2006; Singh *et al* 2010; Zhang *et al* 2011b, c). Moreover, core-shell structured materials with a carbon shell have stimulated great interest, owing to their chemical inertness, biocompatibility and high thermal conductivity (Sun and Li 2004; Dastidar *et al* 2011; Zhang *et al* 2011b, c, 2012d, e). It has been reported that V_2O_5 can react with active carbon to synthesize low-valence vanadium oxides and vanadium carbide (Gupta and Krishnamurthy 1992 (chapter 4)). The idea that low-valence vanadium oxides@C or VC@C and core-shell structures are

synthesized using high-valence vanadium oxides@C and core-shell structures have not been reported to the best of our knowledge, which is a novel route to fabricate new materials with novel structures and morphologies.

In the past decades, the transition metal carbides have attracted a great interest owing to their outstanding physical and chemical properties, including high melting point, high thermal conductivity, high hardness, high strength even at high temperatures, high chemical resistance, etc which have been extensively applied in metallurgy, cutting tools, electronics, catalysts, high-temperature structural materials, and so on (Oelerich *et al* 2001; Yoon *et al* 2002; Liermann *et al* 2004; Reichl and Hayek 2004; Yazawa *et al* 2004; Nakamura and Yashima 2008; Ye *et al* 2010; Fard and Baharvandi 2011; Pang *et al* 2011). Among them, vanadium carbide (VC) is a very important industrial material because of its excellent high-temperature strength, high chemical and thermal stability even at high temperatures. Therefore, VC can be widely applied to cutting materials, abrasive and anti-wear materials (Calka and Kaczmarek 1992; Ma *et al* 2009; Chen *et al* 2011). Furthermore, vanadium carbides own catalytic behaviours, which are almost comparable to platinum metal due to their similar electronic and magnetic properties (Choi 1999; Frantz *et al* 2002; Rodriguez *et al* 2004; Chen *et al* 2011). Recently, Hu's group reported (Hu *et al* 2011) that the oxygen reduction

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electrocatalysis can be enhanced by nano-sized cubic vanadium carbide. Therefore, developing a novel route to synthesize nanocrystalline VC is greatly meaningful and a crucial challenge for material scientists (Chen *et al* 2011; Hu *et al* 2011).

Up to now, various methods have been reported to prepare vanadium carbide and some approaches have been widely used for its production, such as, high temperature reactions (Gupta and Krishnamurthy 1992), direct element reaction (Schwarzkopf and Kieffer 1953), mechanical alloying (Zhang and Li 2005), gas reduction–carburization (Lee *et al* 1990), temperature-programmed reaction (Kapoor and Oyama 1995), thermal processing of the precursor with additives (Ma *et al* 2009; Zhao *et al* 2009; Ye *et al* 2010), aluminothermic reduction of vanadium oxide (Venugopalan and Sathiyamoorthy 2006), the carburization of vanadium oxide with an organic reagent (Li *et al* 2008), etc. Recently, flower-like vanadium carbide hierarchical nanocrystals were synthesized by the hydrothermal process using a mixture of diethanolamine ($HN(C_2H_4OH)_2$, DEA) and V_2O_5 powder reported by Ma *et al* (2010). However, the synthesis of VC encapsulated into carbon nanotube (VC@C core-shell structured composite) has not been reported to the best of our knowledge.

Herein, we have successfully developed a novel approach to fabricate VC@C core-shell composite by thermal treatment with the precursor $V_3O_7 \cdot H_2O$@C for the first time. The as-obtained VC@C has large specific surface area and lots of pores, indicating that it can be used as a mesoporous material. Furthermore, thermal behaviour of VC@C in air was investigated by TG–DTA test, and it was found that the carbon coated on the surface of VC has high activity with O_2 in an air atmosphere. The above results indicate that VC@C may have high catalytic activity and have potential application in the future.

2. Experimental

2.1 *Materials*

Vanadium pentoxide (V_2O_5), ethanol and D-(+)-glucose ($C_6H_{12}O_6 \cdot H_2O$) with analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without any further purification.

2.2 *Synthesis of $V_3O_7 \cdot H_2O$ nanobelts*

The synthesis of $V_3O_7 \cdot H_2O$ nanobelts was based on our previous report (Zhang *et al* 2010) and slightly modified. In a typical synthesis, 9 g of V_2O_5 powder was dispersed into 30 mL of ethanol and then 370 mL of deionized water was added into the above solution with magnetic stirring. The mixed solution was transferred into a 600 mL stainless steel autoclave after the solution became suspension. An autoclave was sealed and maintained at 180 °C for 48 h and then cooled to room temperature naturally. The products were

filtered off, washed with distilled water and absolute ethanol several times to remove all possible residues and dried in vacuum at 75 °C for the following experiments. XRD pattern of the as-obtained product is shown in supplementary data (figure S1)

2.3 *Synthesis of $V_3O_7 \cdot H_2O$@C core-shell composite*

The synthesis of $V_3O_7 \cdot H_2O$@C core-shell composite was similar with our previous reports (Zhang *et al* 2011c). In a typical procedure, 0·40 g of the as-obtained $V_3O_7 \cdot H_2O$ nanobelts were dispersed into the glucose solution (4 g of glucose and 50 mL of distilled water) in a 100 mL beaker under ultrasonic for 20 min and then the mixture was stirred vigorously for 1 h by magnetic stirrer. After the solution became suspension, they were transferred into a 100 mL teflon-lined stainless steel autoclave, which was sealed and maintained at 180 °C for 4 h. After cooling to room temperature naturally, the products were filtered off, washed with distilled water and absolute ethanol several times and dried in vacuum at 75 °C for further characterization and application. XRD pattern of the as-obtained $V_3O_7 \cdot H_2O$@C is shown in supplementary data (figure S1).

2.4 *Synthesis of VC@C core-shell material*

To obtain VC@C core-shell material, the above core-shell structured composite ($V_3O_7 \cdot H_2O$@C) was heated in a tube furnace with 5 °C/min heating rate under a flow of argon gas at 700–1000 °C for 2 h and cooled to room temperature in an argon flow to prevent oxidation of VC@C composite.

2.5 *Characterization*

X-ray powder diffraction (XRD) was carried out on D8 X-ray diffractometer equipment with CuKα radiation, $\lambda = 1·54060$ Å. The Raman spectrum was taken on a RM-1000 spectrometer (confocal Raman microspectroscopy) with an argon-ion laser at an excitation wavelength of 514·5 nm. The elemental analysis (EA) of the samples was carried out using a Vario EL III equipment (Germany) with a TCD detector to analyse the element of C, H and N. The chemical composition of as-obtained samples was revealed by the energy-dispersive X-ray spectrometer (EDX) attached to a scanning electron microscope (SEM; Quanta 200). Fourier transform infrared spectroscopy (FT–IR) pattern of the solid samples was measured using KBr pellet technique (about 1 wt% of the samples and 99 wt% of KBr were mixed homogeneously and then the mixture was pressed to a pellet) and recorded on a Nicolet 60-SXB spectrometer from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The morphology and dimension of the products were observed by scanning electron microscopy (SEM, Quanta 200) and transmission electron microscopy (TEM, JEM-100CXII). The specific surface area and mesoporous properties of the as-obtained sample were examined by Brunauer–Emmett–Teller (BET) N$_2$-gas
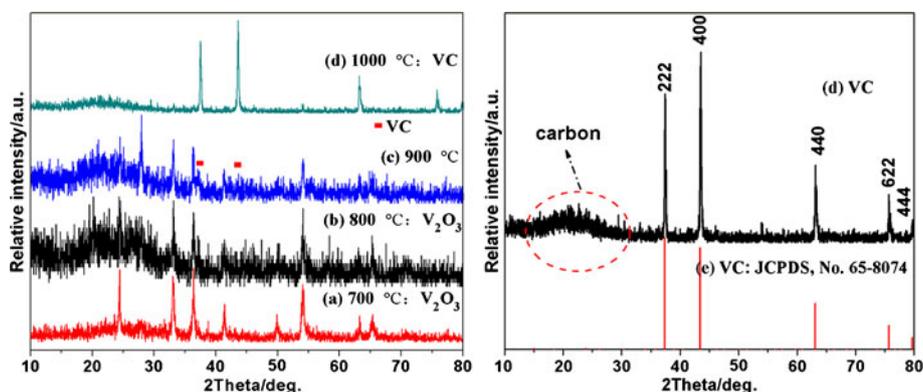
Figure 1. XRD patterns of resulting products obtained with different heating temperatures for 2 h: (**a**) 700 °C; (**b**) 800 °C; (**c**) 900 °C; (**d**) 1000 °C and (**e**) plots of JCPDS No. 65-8074.

adsorption method at 77 K and carried out on a JW–BK equipment. Pore volume and average pore size were calculated by Barrett–Joyner–Halenda (BJH) formula. Thermogravimetric/differential thermal analyser (TG/DTA) was performed on SETSYS-1750 (AETARAM instruments). About 10 mg of the as-obtained samples was heated in an Al_2O_3 crucible in nitrogen atmosphere from ambient temperature to 800 °C at a constant rise of temperature (10 °C/min).

3. Results and discussion

Figure 1 shows typical XRD patterns of the resulting products obtained by different treatment temperatures for 2 h. All the peaks from figure 1(a and b) can be indexed to the rhombohedral crystalline phase (space group: *R*-3*c* 167) of V_2O_3, which corresponds to the literature values (JCPDS No. 34-0187, 1984). The above result indicated that pure V_2O_3 was synthesized when the heating temperatures range was 700–800 °C. However, a new phase is observed from the XRD pattern (figure 1(c)) with the temperature up to 900 °C. Consequently, new phase with high purity is prepared by increasing the thermal temperature to 1000 °C, whose XRD observation is represented in figure 1(d). All the diffraction peaks in figure 1(d) can be assigned to the cubic phase (space group: *Fm*–3*m*, No. 225) of VC with calculated lattice parameters $a = 4·165$ Å, which are in agreement with the literature values (JCPDS No. 65-8074, $a = 4·164$ Å) (Pessall *et al* 1968), whose plots are shown in figure 1(e). No peaks of any other phases are detected from the XRD pattern, indicating the as-prepared VC with high purity. Furthermore, we can also see a broadened peak ranging from 15 to 30°, which is attributed to amorphous carbon (Sun *et al* 2006; Zhang *et al* 2011b). These results reveal that VC@C core-shell composite is successfully fabricated.

According to our previous report, $V_3O_7 \cdot H_2O$ loses water at about 380 °C (Zhang *et al* 2010) and the equation is presented as (1):

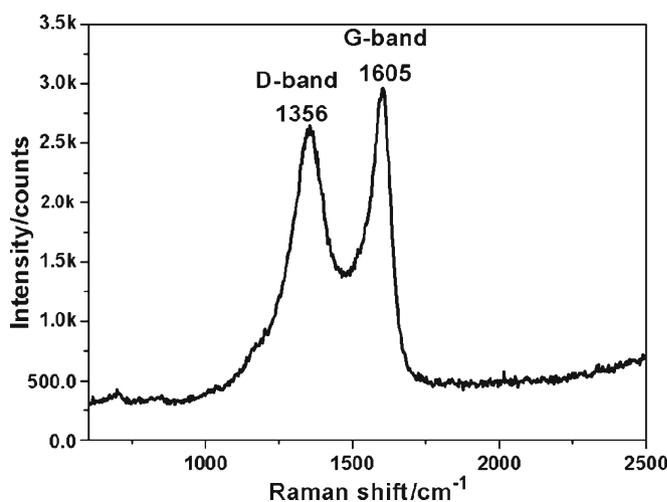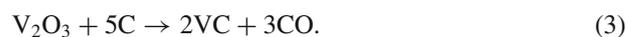$$V_3O_7 \cdot H_2O \rightarrow V_3O_7 + H_2O. \tag{1}$$

Figure 2. Raman spectrum of VC@C.

Based on the XRD analyses, V_2O_3 is an intermediate product for the synthesis of VC. Therefore, the chemical reaction equations of formation of VC can be expressed as shown in (2) and (3):

$$2V_3O_7 + 5C \rightarrow 3V_2O_3 + 5CO, \tag{2}$$

$$V_2O_3 + 5C \rightarrow 2VC + 3CO. \tag{3}$$

Thus, the total reaction equation of $V_3O_7 \cdot H_2O@C$ to prepare VC@C core-shell composite under the thermal treatment condition can be expressed as follows:

$$V_3O_7 \cdot H_2O@C \rightarrow 3VC@C + 7CO + H_2O. \tag{4}$$
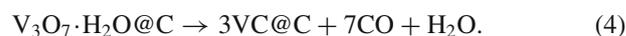
To reveal the structure of carbon coated on the surface of VC, the corresponding Raman spectrum was carried out, as shown in figure 2. Two main peaks can be observed. The peaks located at 1356 and 1605 cm^{-1} are corresponding to the in-plane vibration of disordered amorphous carbon (D-band) and crystalline graphic carbon (G-band), respectively

which are same as those of amorphous carbon (llie *et al* 2002; Odani *et al* 2006; Zhang *et al* 2011c). The intensity ratio of the G- and D-bands was $I_G/I_D = 1.12$ for the as-obtained VC@C compound. The relatively high intensity of the D-peak further proves that the coating on the surface of VC comprises disordered carbon. Therefore, the Raman spectrum further confirms that the carbon coating on the surface of VC is disordered, in agreement with XRD pattern observation.

Further important information about the composition of VC@C composite was collected by EDS, EA and FT–IR. Figure 3 shows typical EDS spectrum of VC@C, which reveals that the surface of the resulting sample consists of only C and V elements, in agreement with XRD pattern observation. The content of carbon is 92·40 at%, while vanadium is 7·60 at%. The atomic ratio of C/V in VC@C (C/V = 12·16) is much higher than that of pure VC (C/V = 1), which indicates that excess carbon resides on the surface of

VC. Further composition about the carbon on the surface of VC was examined by EA, which shows that the VC@C composite contains 31·09 wt% of C (19·05 wt% of C in pure VC) and 1·02 wt% of H and the atomic ratio of C/H is 2·54. These results may imply the existence of residual C–H groups in the as-obtained VC@C composite after thermal treatment, which can be proved by FT–IR spectrum, as depicted in supplementary data (figure S2). The residual C–H groups will facilitate the linkage of catalytic species or polymers to the surface in its potential applications.

Figure 4 shows typical SEM images of the as-obtained VC@C composite. It can be seen from the SEM images that VC@C has belt-like morphology. The length is ranging from 0·3 μm to several micrometers and the width is about 80–180 nm on an average. However, some irregular particles can be observed, which is due to the violent reaction, growth or aggregation by surface and boundary diffusion during the high temperature treatment. In order to get a clear insight into the core-shell structure of the as-synthesized VC@C composite, the corresponding TEM measurement was carried out, as shown in figure 5. The low magnification TEM images (figure 5(a and b)) reveal that the sample consists of a large number of nanotubes, which are carbon nanotubes according to the above analyses and the precursor $V_3O_7 \cdot H_2O@C$. These results prove that a new route to synthesize carbon nanotubes consisting of amorphous carbon may be developed and applied in the future. Furthermore, it can be seen from figure 5(a and b), that many VC particles are encapsulated into the carbon nanotubes. The contrast grade between core (VC) and shell (carbon nanotube) can be clearly observed in figure 5(c). It is to be noted that the morphology of the as-prepared VC@C composite is very much different from the morphology of the precursor $V_3O_7 \cdot H_2O@C$, as reported in literature (Zhang *et al* 2011c,d). We suggest that the structure of $V_3O_7 \cdot H_2O$ is completely destroyed and the vanadium oxide severely reacted with carbon or active organic groups (Zhang *et al* 2011c) to form a new phase VC, accompanying with release of CO. The excess carbon remained to form carbon nanotubes.
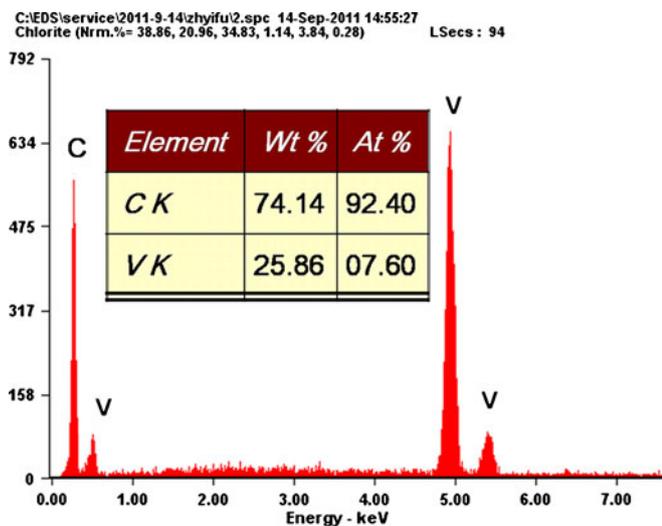

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Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)   LSecs : 94

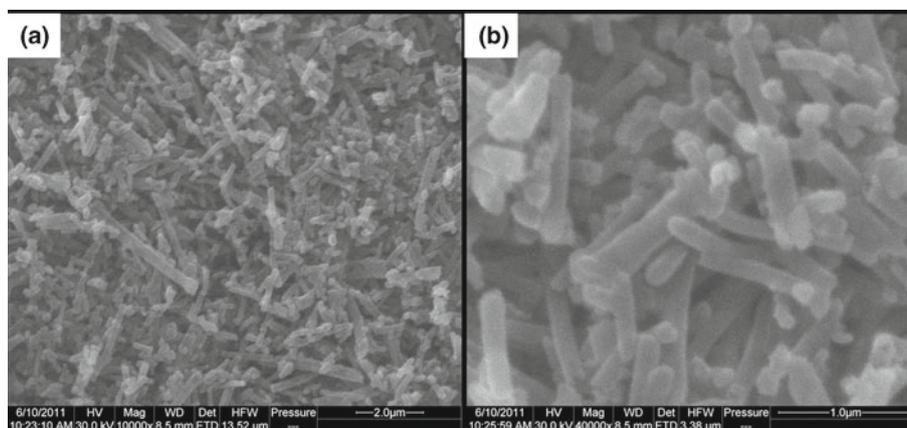| Element	Wt %	At %
C K	74.14	92.40
V K	25.86	07.60

Figure 3. EDS spectrum of VC@C.

Figure 4. Typical SEM images of VC@C.
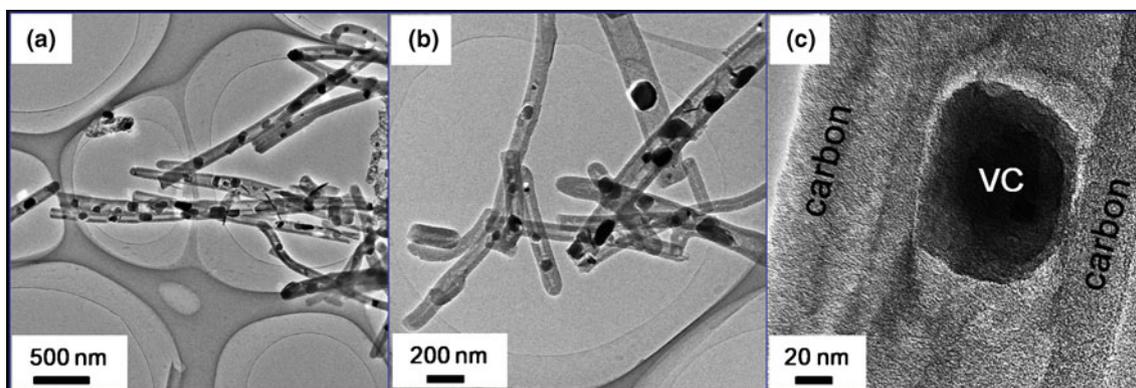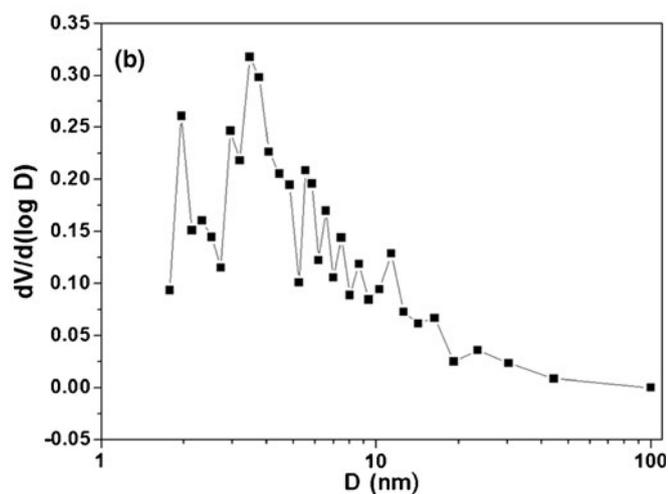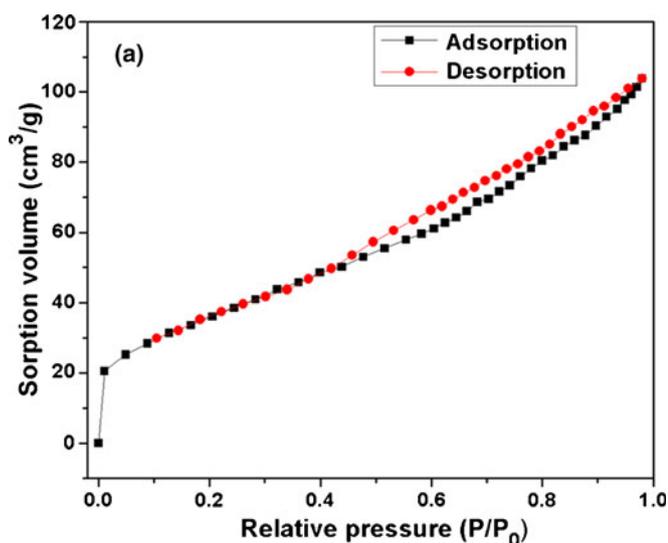
Figure 5. TEM images of VC@C.

Figure 6. (**a**) Sorption isotherm of VC@C and (**b**) pore size distribution data calculated with BJH method from desorption branch of nitrogen sorption measurements at 77 K.

Based on the above analyses and the chemical reaction (4), some gas was released in the process of preparing VC@C, which might cause lots of pores on the surface of
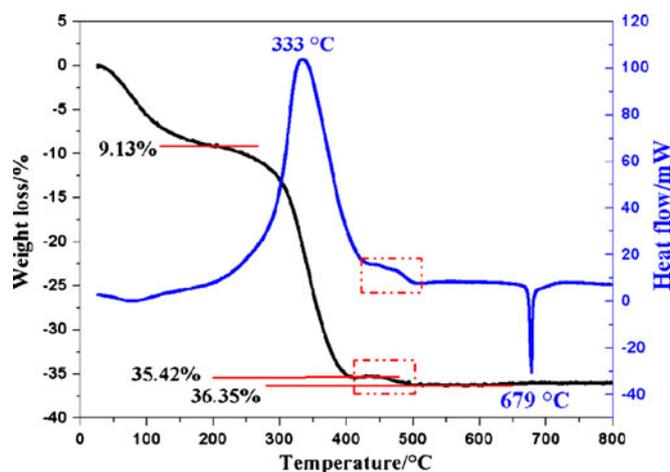

Figure 7. TG and heat flow curves of VC@C in air.

VC@C. These pores can be occasionally observed by TEM images, as shown in figure 5 and clearly seen in supplementary data (figure S3). The above results indicate that the as-synthesized VC@C core-shell structured composite has large specific surface area. Thereafter, the specific surface area and the pore volume of VC@C were measured by BET and BJH methods. BET specific surface area of VC@C is 135.46 m^2/g, which is much bigger than those reported in the literature (Ye *et al* 2010): 63.36, 31.73, 5.3, 0.9 and 0.3 m^2/g. Nitrogen sorption measurement for VC@C is shown in figure 6. Figure 6(a) shows sorption isotherm of VC@C, revealing that the nitrogen sorption isotherms exhibit the shape of type IV curves (Sing 1982), characteristic of the presence of mesoporous material. Furthermore, the pore size distribution data calculated with the BJH method from the desorption branch of the nitrogen sorption measurements at 77 K is shown in figure 6(b). The average pore size of the sample is 4.443 nm, which is in the range of the mesoporous material. The measured pore volume is 0.162 cm^3/g.

The thermal behaviour of VC@C was investigated by TG–DTA test, as shown in figure 7. From TG curve, the weight loss is ∼9.13% below 200 °C. The reason can be

that the water absorbed on the surface of VC@C is releasing or the carbon on the surface can slowly react with O_2 in the flowing air. With the increase in temperature, the carbon violently reacts with O_2 and releases lot of heat. At about 333 °C, the oxidation is extremely accelerated by large heat evolution, as shown in the heat-flow curve in figure 7. Besides, the oxidation of VC may occur at this interval. However, both the TG and heat-flow curves have a small platform at about 420 °C, which is due to the oxidation of VC (Ma *et al* 2009). The weight loss below 420 °C is ~35·42% and below 500 °C is ~36·35%. These results indicate that the oxidation of carbon and VC may be overlapped. In addition, the endothermic peak at 679 °C is assigned to the melting point of V_2O_5, indicating the oxidation product of VC is V_2O_5 in air. Based on above analyses, carbon coated on the surface of VC has high activity with O_2 in air atmosphere, as well as the as-obtained VC@C has large specific surface area confirmed by BET, indicating that the as-prepared VC@C may have high catalytic activity and have potential application in the future.

4. Conclusions

In conclusion, a novel approach was successfully developed to fabricate VC@C core-shell structured composite by thermal treatment with the precursor $V_3O_7 \cdot H_2O$@C at 1000 °C for 2 h for the first time. It was found that V_2O_3 is an intermediate product for the synthesis of VC. The structure of $V_3O_7 \cdot H_2O$ was completely destroyed during the process of formation of VC and excess carbon remained to form carbon nanotube. The specific surface area, average pore size and measured pore volume of VC@C are 135·46 m^2/g, 4·443 nm and 0·180 cm^3/g, respectively indicating that the as-obtained VC@C composite can be used as a mesoporous material. Furthermore, the thermal behaviour of VC@C composite in air was investigated by TG–DTA test, revealing that the carbon coated on the surface of VC has high activity with O_2 in an air atmosphere. The results in this study show that the as-prepared VC@C may have high catalytic activity and have potential applications in the future.

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Electronic supplementary material

Supplementary material pertaining to this article is available on the Bulletin of Materials Science website (www.ias.ac.in/matersci).

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