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LETTER

# Comment on “Synthesis, characterization and growth mechanism of flower-like vanadium carbide hierarchical nanocrystals”

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This Letter is in response to a recent paper by Ma *et al.* (*CrystEngComm*, 2010, 12, 750–754) which arguably studied vanadium carbide nanostructures whereas all available evidence indicates the study of vanadium oxide. We feel that it is important to communicate to the community several inconsistencies so that the interesting material reported can be seen in the right light, especially with several groups nowadays having reported similar structures from vanadium oxide synthesis.

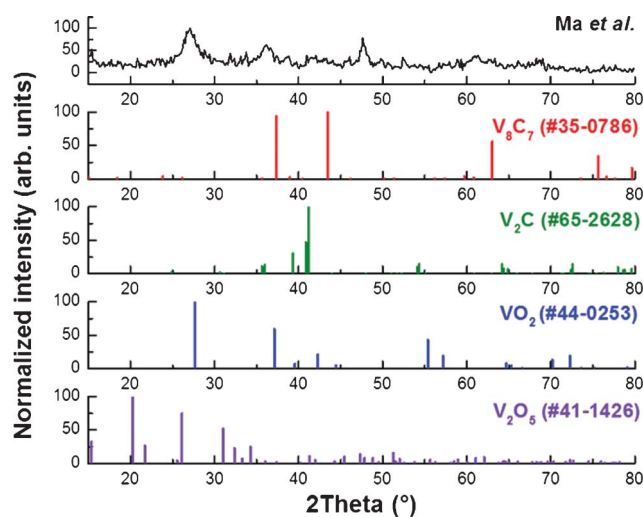
Ma *et al.*<sup>1</sup> reported in 2010 on the synthesis and structural properties of “novel flower-like vanadium carbide ( $V_8C_7$ ) hierarchical nanocrystals” derived from the hydrothermal synthesis of diethanolamine and vanadium oxide ( $V_2O_5$ ). Interested in this chemical system and the related nanostructures, we recently re-investigated their synthesis path and found inconsistencies which we deem important to communicate in this Letter. In their paper, the authors employ a number of structural characterization tools such as X-ray diffraction (XRD), photoelectron spectroscopy (XPS), and energy-dispersive spectroscopy (EDS). Arguably, vanadium carbide ( $V_8C_7$ ) is concluded as the main phase of the nanoflowers.

The authors state that “vanadium carbide has fast oxidation kinetics that leads to the formation of vanadium oxide and oxycarbide surface layers” and quote two references (Ref. 18 and 19). They conclude that the oxygen found in their samples correlates to surface-oxidized  $V_8C_7$  from room-temperature reaction in air. However, Ref. 18 and 19 deal with tribochemistry and while Ref. 18 contains no mentioning of vanadium carbide, Ref. 19 only states that vanadium oxycarbide can be oxidized to vanadium oxide under sliding wear. More appropriate would have been a reference like Santafé and Borgianni<sup>2</sup> or Krut'skii *et al.*<sup>3</sup> All carbides are thermodynamically unstable when exposed to air. Oxide formation for vanadium carbide indeed starts very slowly at room temperature<sup>4</sup> and this process may be more relevant for a nanometer-sized powder; however, even if the nanoflowers were completely composed of vanadium carbide, significant oxidation would be unlikely since the onset

of vanadium carbide oxidation has been reported to be approximately 350 °C in air.<sup>5</sup>

Considering that the nanoflowers were derived from a hydrothermal reaction, it would be surprising to expect pure carbide as the sole reaction product. To confirm this aspect, we carried out thermodynamic calculations with FactSage<sup>TM</sup> and using the amounts of diethanolamine, water, and  $V_2O_5$  specified in the paper, it is clear that at 180 °C only vanadium oxide is the thermodynamically stable solid synthesis product. The calculations also show that solid carbon occurs when lowering the temperature and, as a response of the isochoric system, the vessel pressure.

In the XRD analysis, we first note that the PDF card #19-1394 documented refers to a deleted entry. A better entry for  $V_8C_7$  would be #35-0786. However, the presented XRD pattern is not consistent with vanadium carbide (Fig. 1). The best



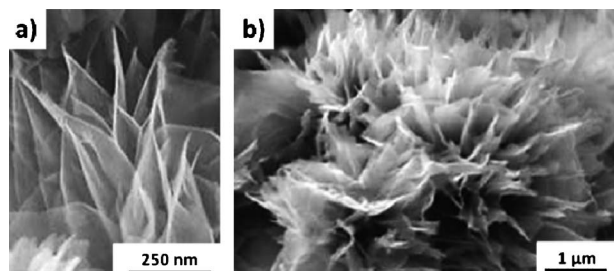
**Fig. 1** Normalized XRD pattern of the allegedly flower-like vanadium carbide (data from Fig. 1 in Ref. 1) compared to diffraction pattern of selected vanadium phases and graphite. The numbers correspond to the PDF card numbers.

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**Fig. 2** (a) Alleged flower-like vanadium carbide<sup>1</sup> compared to (b) vanadium oxide nanoflowers.<sup>8</sup>

agreement can be established with vanadium *oxide* and the best match can be obtained for VO<sub>2</sub> (#44-0253). Minute amounts of vanadium *carbide* cannot be excluded but vanadium oxide is obviously the dominant phase. We note that XRD penetrates the *entire* microparticle and, thus, provides bulk phase information which does not allow differentiating between the core and the shell of the nanoparticles. The only peak without a clear phase assignment is located at 47.7° 2θ. In our own investigation, we did also see this peak (at 48.6° 2θ) and, thus, can exclude that this peak would correlate with an impurity. As the peak does not correspond to any vanadium oxide, vanadium carbide, or carbon phase, the assignment of this peak remains unclear and is subject for further investigation.

The dominance of oxygen is also seen from XPS. The V2p<sub>1/2</sub> and V2p<sub>3/2</sub> peaks are in agreement with vanadium oxide (both, V<sup>4+</sup> → VO<sub>2</sub> and V<sup>5+</sup> → V<sub>2</sub>O<sub>5</sub>)<sup>6,7</sup> and the peak at 516.8 eV is incorrectly assigned to V–C by the authors. The latter would require a peak at ~513 eV which cannot be seen in Fig. 2c in Ref. 1. Yet, with only vanadium oxide being confirmed, the nature of the carbon peak remains unanswered.

From the C1s region we see three distinct peaks; the most intense one indicates a shift towards lower binding energies compared to free carbon (284.5 eV). One possible explanation is sample charging which has shifted the measured energies. If we assume, however, that the system was calibrated correctly, then this indeed would indicate the presence of V–C bonds. With the absence of the corresponding vanadium carbide signal in the V2p region *and* XRD, this may indicate the carbon is loosely intercalated in the layered V<sub>2</sub>O<sub>5</sub> structure or simply it could be environmental contamination that can be resolved by depth

resolved analysis *via* sputtering; it is interesting to note that this material is actively being investigated for its intercalation ability (e.g., Li<sup>+</sup>) in the fields of energy storage.

From the EDS spectrum (inset in Fig. 3c in Ref. 1) one may deduce that the molar concentration of oxygen is actually *higher* than the carbon content; when we now consider the penetration depth of EDS analysis, then it is clear that this (like XRD) is the volume information of an entire nanoflower particle. Considering the predominance of vanadium oxide, a different title would have been more appropriate that does not involve vanadium carbide; in particular, the growth model is inconclusive as it suggests that pure V<sub>8</sub>C<sub>7</sub> would result from the hydrothermal synthesis. This is of particular importance since vanadium oxides nanoparticles with flower-like morphology (Fig. 2) and similar growth mechanism are well documented by now.<sup>8–10</sup>

Yet, the nature of carbon remains an interesting aspect and current vanadium oxide nanoflower literature usually just uses “any” carbon signal to reference the XPS spectrum. Thus, the published paper may give more insights in the nature of carbon from hydrothermal decomposition but seemingly does not report on hierarchical vanadium *carbide* nanoflowers.

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