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An expeditious synthesis of early transition metal carbide nanoparticles on graphitic carbons†

Debora Ressnig,ab Simona Moldovan,c Ovidiu Ersen,c Patricia Beaunier,d David Portehault,ab Clément Sanchezab and Sophie Carencoabc

An expeditious synthesis of metal carbide nanoparticles onto various carbon supports is demonstrated. The procedure is versatile and readily yields TiC, VC, Mo2Ca and W2C nanoparticles on different types of carbons. The reaction is initiated at room temperature and proceeds within seconds. This novel synthetic route paves the way for a large variety of metal carbide–carbon nanocomposites that may be implemented in emerging nanotechnology fields.

Metal carbides combine the hardness and resistivity of ceramics with the electronic and optical properties of metals and therefore find widespread application as abrasives, cutting tools and more recently as catalytic materials, e.g. for the hydrogen evolution catalysis.1–4 The stabilization of nanocomposites has boosted research into these fields because higher performances result from the stabilization of nanoscale crystallites on tailored supports, in particular conductive ones.

Composites of metal carbide nanoparticles on a carbon phase are typically synthesized via the carbothermal reduction of a metal salt at temperatures between ~700 °C and 1200 °C in the presence of a carbonizable carbon source: molecular precursors (e.g. glucose), polymers (cellulose (poly) ionic liquids) or gels (urea–glass route).5 In these routes, the formation of the metal carbide and the graphitic support is concerted. As a result, particles are often enclosed in an amorphous or even graphitic carbon shell, and the porosity of the carbon support is not easily controlled. This limits the scope of the composite to applications where accessibility to the metal carbide surface is not required (e.g. mechanical properties).

Thus, softer approaches to produce accessible nanoparticles at low temperature in organic solvents have been developed. They use strong reducing agents (e.g. sodium naphthalenide, potassium graphite, butyl lithium) in order to swiftly produce small amorphous nanoparticles. In most cases, metal nanoparticles are obtained instead of metal carbides,6–9 but in a few studies the latter were produced after a calcination step. Nelson et al. used crown ether to reduce metal halides which afforded amorphous particles that upon annealing at high temperatures (570–1200 °C) crystallized into metal carbides.10,11 A similar reaction between butyl lithium and metal chlorides followed by calcination 600–1000 °C afforded different metal carbides.12 The co-reduction of the metal chloride and a chlorinated carbon source by an alkali metal in autoclaves at elevated temperatures also produced metal carbides.13–15

The synthesis of crystalline metal carbide nanoparticles with a controlled size and accessible surface is still a challenge. Low temperatures are desirable in order to limit particle sintering and growth, but subsequent high calcination temperatures are still required in order to trigger the crystallization of the carbide phase as well as the graphitization of the carbon.

Altogether, an expeditious and straightforward synthetic route that could be applied to different sorts of carbon supports is desirable in order to expand and strengthen the current applications of transition metal carbide nanoparticles.

In this study, we demonstrate a protocol that does not require a separate annealing step and that allows carefully selecting the characteristics of a certain graphitic carbon for specific applications prior to metal carbide formation. In the first step, the carbon surface was charged with electrons by impregnation with a potassium melt, forming potassium graphite of controlled porosity and crystallinity. At room temperature, these were directly reacted with a chosen metal chloride in the absence of a solvent. The reaction was highly exothermic and fast, which allowed immediate functionalization of different carbons with early transition metal carbides, without applying external heat,
long reaction times, or a secondary calcination step. We show here that this route was efficient for producing TiC on different graphitic carbon supports. Furthermore, we demonstrate that the approach can be widened to Mo$_2$C, VC and W$_2$C crystalline nanoparticles.

Titanium carbides deposited on regular graphite (g-C) were produced first. All reactions were carried out using standard Schlenk-line techniques (see the ESI†). In the first step, bronze colored KC$_8$ was prepared using a standard procedure, by melting a stoichiometric ratio of potassium in the presence of graphite ($S_{\text{BET}}$ 9 m$^2$ g$^{-1}$). Liquid TiCl$_4$ was subsequently added drop by drop to the KC$_8$ powder, resulting in a dark solid. Each droplet produced an immediate and strongly exothermic reaction attested by the glowing of the solid and the warming of the reaction vessel. As a side effect a fraction of the titanium chloride evaporated. Therefore an excess amount of TiCl$_4$ was added until no reaction was observed anymore on the dark solid. Excess TiCl$_4$ was subsequently removed under vacuum to prevent the formation of metal oxides during the work-up. The overall reaction can be described as:

$$32\text{C}_{\text{graph}} + 4\text{K} \rightarrow 4\text{KC}_8$$

$$\text{TiCl}_4(\text{l}) + 4\text{KC}_8 \rightarrow \text{TiC(s)} + 4\text{KCl} + 31\text{C}_{\text{graph}}$$

KCl was confirmed as a side-product using powder X-ray diffraction (PXRD) of the raw product (data are not shown). It was almost entirely removed by washing the solid with EtOH and de-ionized water (see Fig. S10, ESI†). In Fig. 1, the pair of bottom patterns is those of the solid after washing (in purple) and of fresh graphitic carbon (in black). As expected, the intense reflections from graphitic (42.6°, 44.6°, 54.7°, 77.6°, 83.7° and 87.0°) were preserved, indicating that the graphitic stacking survived the reaction. New reflections – pointed out by dotted lines – resulting from the reaction of TiCl$_4$ with potassium graphite. They are consistent with the TiC structure (PDF card [00-001-1222]). Applying the Scherrer equation to the (111) reflection (at ca. 36°) suggests a crystallite size of 14 nm for the TiC nanoparticles. Given the high intensity of graphite reflections – that would overlap with rutile TiO$_2$ reflections – the formation of TiO$_2$ impurity cannot be fully excluded at this stage.

The transmission electron microscopy (TEM) images of the TiC/g-C composite show that the graphite platelets are covered with nanoparticles (Fig. 2a and Fig. S1, S2, ESI†). Lattice fringes of 1.5 Å and 2.5 Å can be assigned to the distances $d_{220}$ and $d_{111}$ of TiC [00-001-1222], respectively (Fig. 1 and Fig. S2, ESI†). The corresponding energy-dispersive X-ray spectroscopy (EDX) confirms the presence of Ti in the nanoparticles (Fig. S2, ESI†). It also indicates that a small amount of oxygen is present after the work-up.

The bottom inset of Fig. 2a shows that the nanoparticles have an average diameter of 6.1 ± 1.2 nm. This is smaller than the size of the crystalline domains evaluated from the Scherrer equation, suggesting that larger TiC particles were not properly observed in TEM images. Larger nanoparticles may preferentially populate thicker graphitic domains, which TEM cannot image. Repeated TEM observations showed that some graphitic platelets are richly and others are barely populated with TiC particles. The inhomogeneity results from adding TiCl$_4$ as micro-droplets to the solid powder.

Moreover, Fig. 2a suggests that the TiC nanoparticles are preferentially sitting on the edges and topographic steps of the
graphite layer. Imaging using scanning TEM (STEM) with high- 
angle annular dark field (HAADF) detection provides Z-contrast 
imaging (Fig. 2b).\textsuperscript{17} White dots represent regions with high-Z  
(here, titanium). The accumulation of TiC particles on the edge 
of the graphite platelets is evident in this mode. Moreover,  
larger particles, suspected from XRD, are better observed in  
STEM-HAADF, though they represent a minority.  

The TiC particles nucleate preferably at the edge defects  
of graphite. A similar preference for nucleation at graphite  
edges was previously seen in the reduction of metal salts with  
KC\textsubscript{8} in solution.\textsuperscript{18}  

To demonstrate the generality of the synthetic approach,  
we extended the method to other carbons with different  
morphologies and crystallinities. These are: commercially  
available acetylene black (ac-C, ~50% graphitic, \( S_{\text{BET}} \) 63 m\(^2\) g\(^{-1}\))  
among other carbons with nanosized graphitic domains  
(ng-C, \( S_{\text{BET}} \) 270 m\(^2\) g\(^{-1}\)).\textsuperscript{19}  

Firstly, we observed that the potassium uptake of ac-C and ng-C  
are higher than that of graphite. We evaluated a close-to-maximum-loading by  
adding and intercalating potassium in small fractions until  
metallic potassium would remain unreacted in the vial. The  
determined potassium uptake rounds up to KC\textsubscript{4} for ac-C and  
KC\textsubscript{2} for ng-C. In both cases the initially black carbon powders  
were covered with a red brilliance after potassium insertion.  

Both potassium-loaded carbons were treated with TiCl\textsubscript{4} in the  
same way as described for graphite. The PXRD patterns of  
the products show the formation of TiC as the only crystalline  
Ti-containing product (Fig. 1, middle and top patterns). Traces  
of remaining KCl appear in the diffractograms despite intense  
washing over several days including treatment with ultrasound,  
in particular for the macroporous carbon (ng-C), thus suggesting  
some KCl inclusions in the carbon porosity. PXRD interpretation  
is straightforward thanks to the lower contribution of graphite. In  
both cases, reflections from TiC are detected and the absence  
of any TiO\textsubscript{2} phase is confirmed. This strongly suggested that  
the reaction on g-C, discussed above, did not lead to TiO\textsubscript{2}  
impurities either.  

The Scherrer size of the TiC crystallites is in the same range  
as that for graphite (Table 1). As with g-C, the average size  
estimated from TEM observations is slightly under-evaluated  
due to the difficulty in observing particles in the thicker regions.  

\begin{table}[h]
\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Carbon} & \textbf{TiC size/nm} & \textbf{Raman (I\text{g}/I\text{d})} & \textbf{TiC wt\%\textsubscript{max}}
\textit{calc.}\textsuperscript{a} \\
\hline
\hline
\textit{g-C} & 6.1 ± 1.2 & 14 & 0.37/0.34 & 14 \\
\textit{ac-C} & 3.9 ± 1.1 & 15 & 1.85/1.94 & 25 \\
\textit{ng-C} & 7.2 ± 1.6 & 10 & 1.45/1.36 & 42 \\
\hline
\end{tabular}
\end{center}
\textsuperscript{a} “TiC wt\%\textsubscript{max} calc.” is the maximum loading of TiC on each carbon  
support. It was calculated by assuming that TiCl\textsubscript{4} and the potassium-  
loaded carbon (KC\textsubscript{8} for graphite, KC\textsubscript{4} for acetylene-black, KC\textsubscript{2} for  
macroporous carbon) were introduced in a stoichiometric ratio. For  
example, for the reaction with graphite, one mole of TiC forms along  
with 31 carbon atoms (see eqn (2)), which gives a TiC weight ratio of  
14%. This is the higher TiC loading because the only carbon introduced  
comes from the reducing agent.  

Table 1 Characteristics of TiC/carbon composites

\end{table}

The TiC distribution on ac-C and ng-C divides in richer and less  
populated areas, as shown by STEM in bright field and HAADF  
mode (Fig. S3 and S4, ESI\textsuperscript{†}). Optimizing the procedure in a way  
that allows for spraying smaller droplets would certainly  
Improve the distribution of the particles on the carbon.  

Most importantly, complementary analyses of pristine and  
modified carbons with nitrogen sorption, SEM and PXRD  
analysis, FTIR and Raman spectroscopy corroborate the con- 
servation of the carbon structure, porosity and morphology  
(Fig. S5–S8, ESI\textsuperscript{†}).  

We therefore think that this method can be applied to  
functionaization of a broad variety of sp\textsuperscript{2} carbons. Limitations arise  
when light elements are introduced into the graphitic network  
and disturb the electronic configuration of the graphitic pattern.  
For example, it was not possible to charge graphite’s nitrogen-  
rich analogue g-C\textsubscript{3}N\textsubscript{4} with potassium.  

Next, the expandability of the protocol to other transition  
metals was explored. Acetylene black was selected as a support  
because of its many technological uses and lower crystallinity.  
VCl\textsubscript{4} like titanium chloride is liquid at room temperature and  
therefore the most suitable precursor for further elaborations.  

The reaction of ac-C with VCl\textsubscript{4} was more intense than with TiCl\textsubscript{4}.  
Snapshots of a movie of the reaction are presented in Fig. S11  
(ESI\textsuperscript{†}). PXRD is consistent with the formation of VC \cite{01-089-2719},  
with a maximum crystallite size of 28 nm (Fig. 3, top pattern). As for  
TiC, the smaller nanoparticles of VC are easier observed by TEM on  
ac-C (Fig. 4). Lattice fringes of 2.4 Å match with the \( d_{\text{200}} \) distance of the  
VC structure (Fig. 4b, inset).  

Other transition metal chlorides (e.g. MoCl\textsubscript{3}) are solid at room  
temperature and do not react when mixed with potassium  
graphites. A straightforward approach to initiate the reaction is  
heat the vessel that contains the potassium graphite/metal  
chloride mixture using a heat gun to the boiling point of the  
metal chloride (e.g. 268 °C for MoCl\textsubscript{3}).  

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{PXRD patterns of ac-C/metal carbide composites with vanadium  
(top), molybdenum (middle) and tungsten (bottom). The reference  
patterns are: VC \cite{01-089-2719} (in grey), Mo \cite{00-001-1205} (in black),  
Mo\textsubscript{2}C \cite{04-004-8327} (in grey), W \cite{00-004-0806} (in black), and  
W\textsubscript{5}C \cite{01-089-2371} (in grey). Stars assign reflections of KCl.}
\end{figure}
Fig. 3 (middle and bottom) shows PXRD patterns obtained from the reaction of potassium-loaded ac-C with MoCl₅ or WCl₆ initiated by sublimation. Both reactions yielded the metal rich hexagonal carbides ε-W₂C and Mo₂C. Traces of the pure metals are also detected. Those were reaction byproducts of the strong reduction, because in the absence of potassium-loaded ac-C, simple sublimation and recrystallization of the metal chlorides did not yield the decomposition of the metal chloride precursors. TEM shows the presence of small and crystalline metal carbide nanoparticles on ac-C (Fig. S8 and S9, ESI†).

Note that even if the approach can be widened to several metal chlorides, complementary experiments with specific transition metal chlorides such as FeCl₂ and NiCl₂ yielded the metal and not the metal carbide. Hence, the method has its limitations, presumably related to the respective stability of the carbides versus the corresponding metals.

In summary, we present a versatile, expeditious method to functionalize the surface of different types of graphitic carbons with metal carbide nanoparticles via the formation of potassium graphites. Potassium graphites are reactive precursors that can be easily prepared on the gram scale and safely stored under inert conditions. The functionalization itself is exothermic and very fast (timescale of a few seconds) and no external heating is required. The structure and morphology of the graphitic carbons are retained during functionalization, which increases the control in the composite design. Work is underway to extend this protocol to more sophisticated carbons and to other metal carbide structures, as well as to test the activity of the composite in electrochemical reactions. Besides, upscaling of the reaction to a 10 g scale will require heat management, which could be done by diluting the graphite in inert KCl salts that would be washed with water.

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