Supporting Information

Expeditious Synthesis of Early Transition Metal Carbide Nanoparticles on Graphitic Carbons

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Experimental

All manipulations were carried out under Argon, using common glove box (O_2, $H_2O < 0.5$ ppm) and Schlenk line techniques. Graphite was purchased from Alfa AESAR 99 % APS7-11 micron particles, 99.9 % carbon black, acetylene 50 % and the macroporous carbon were prepared at 1200 °C according to ref 1. Liquid metal chlorides were stored in sealed bottles. Solid, ultra-dry metal chlorides were stored in the glove box.

Synthesis

In a typical preparation procedure for potassium graphite (KC_8), graphite (360 mg, 30 mmol) was degassed at 130 °C under vacuum before a stoichiometric amount of potassium was added. The mixture was stirred under static vacuum at 130 °C until a homogenous bronze colored powder was obtained. KC_8 can be stored in the glove box without decomposing over days.

The same procedure was followed to impregnate acetylene black (ac-C, KC_4) and the macroporous carbon (ng-C, KC_2) with potassium. Potassium uptake took at least two hours at 130 °C. The carbons remained black with a reddish shimmer.

Liquid precursors ($TiCl_4$, VCl_4): The potassium-loaded carbons (typically 50 mg but up to 250 mg) were added to a Schlenk tube equipped with a stirring bar and closed with a septum. Then, using a syringe, the liquid metal chloride precursor was added through the septum dropwise, in slight excess, while vigorously stirring to ensure the reactions completion. Excess metal chloride was removed by vacuum. Potential remaining potassium was quenched with EtOH (3 mL). The products were stirred in water for an hour, separated using a Buchner funnel, repeatedly washed with DI water, and dried at 120 °C in air for 1 h. The yield of the reaction was found to be ca 90%, some of the powder being lost in the washing step.

Solid precursors ($MoCl_5$, WCl_6): The potassium-loaded acetylene black was added in stoichiometric amount to a Schlenk tube before 1 mmol metal chloride was added in portions. The tube was closed before the powders were mixed by shaking. [Caution, it might happen that the reaction is initiated by simple shaking]. The Schlenk tubes were removed from the glove box and directly heated with a heat gun to initiate the reaction that lasted only a few seconds. Potential remaining potassium was quenched with EtOH (3 mL). The products were stirred in water for an hour, separated using a Buchner funnel, repeatedly washed with DI water, and dried at 120 °C for 1 h.

Characterization

Powder X-ray reflection measurements (PXRD) were performed with a Bruker D8 X-ray diffractometer operating in reflection mode with Cu K_α radiation (40 kV, 40 mA). The data were collected in the 5-90° range (2θ) with steps of 0.05° and a counting time of 5 s using Si-sample holders. The *Scherrer* equation was applied with a form factor K of 0.94, to a maximum number of reflections for each diffractogram.

Routine transition electron microscopy analyses (TEM) were performed on a TECNAI 120 apparatus working at an acceleration voltage of 120 kV or 100 kV. The powders were dispersed in EtOH and deposited on a carbon-coated copper grid. HRTEM studies were carried out on a JEOL JEM 2011 with a LaB_6 filament, equipped with an EDX system PGT IMIX-PC (at 200 kV) at the *Institut des Matériaux de Paris Centre*, *Sorbonne Universités - UPMC*.

The STEM experiments were carried out on a Cs probe corrected JEOL 2100F TEM microscope equipped with a field emission gun (FEG) and operating at 200kV. Two STEM micrographs were acquired simultaneously by using a bright field (BF) and high angle annular dark field (HAADF) detectors, with a point-to point resolution of 1.1Å. The data were acquired and treated using the Digital Micrograph software.

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[1] D. Ressnig, T. Corbiere, T. Lunkenbein, U. Braun, M. G. Willinger, M. Antonietti, J. Mater. Chem. A, 2014, 2, 18076.

SEM analyses were performed on a HITACHI S– 3400 N microscope using carbon tape to fix the powder and without sputtering.
Fourier transformed infrared spectroscopy was performed in attenuated total reflection mode (ATR-FTIR) with a resolution of 4 cm^{-1} on a Perkin Elmer Spectrum 400 spectrometer, equipped with a diamond crystal.
Raman spectra were collected on a Kaiser RamanRxn device using a 785 nm (1.58 eV) laser operated at 10 mW. The powders were placed on an aluminum plate.
Nitrogen sorption isotherms were recorded at 77 K with a BEL Japan Belsorp max device, after degassing at 150 °C for 12 h.

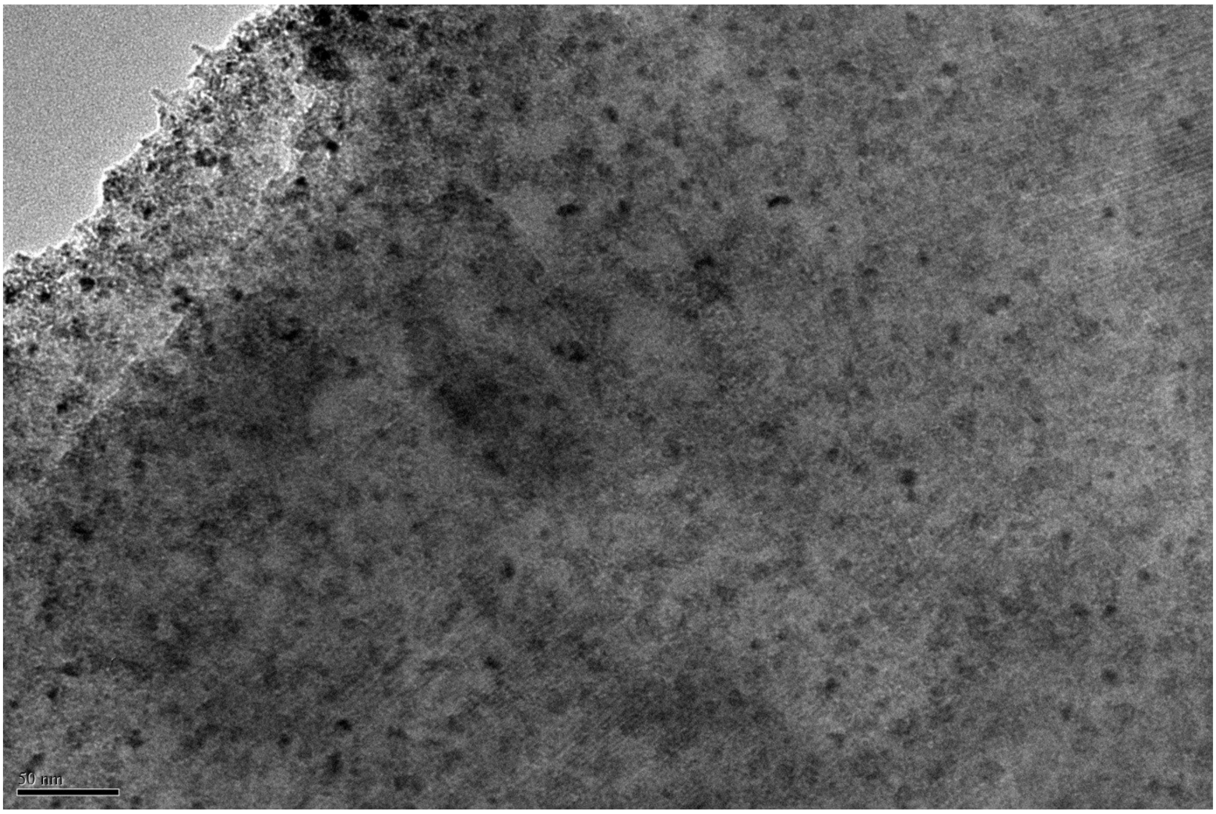

Figure S1. TEM of a TiC/g-C composite. Scale bar is 50 nm.

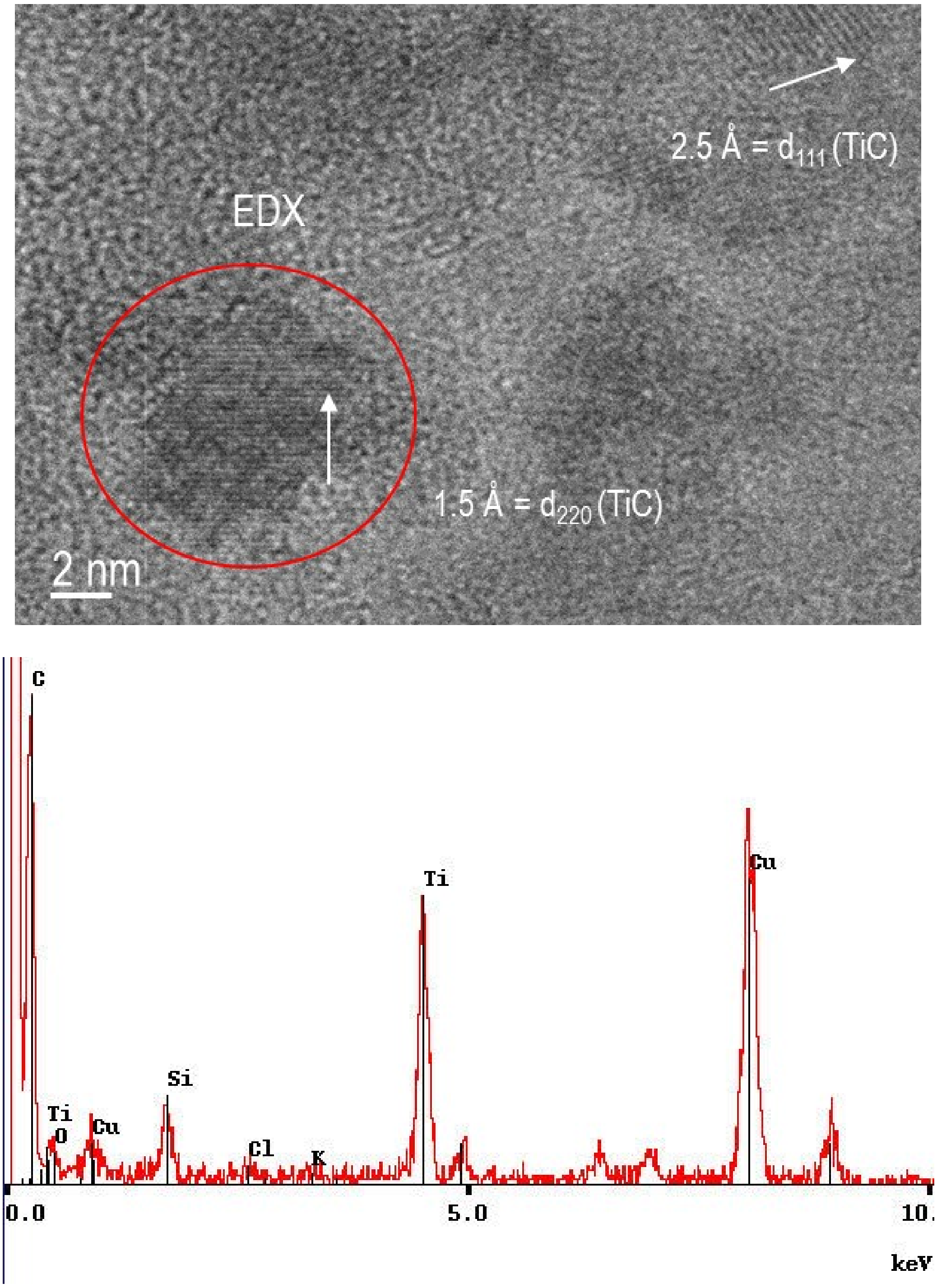

Figure S2. HRTEM analysis of the TiC/g-C composite with corresponding EDX pattern. Lattice fringes can be assigned to the distances d_{220}, and d_{111} of TiC [00- 001-1222].

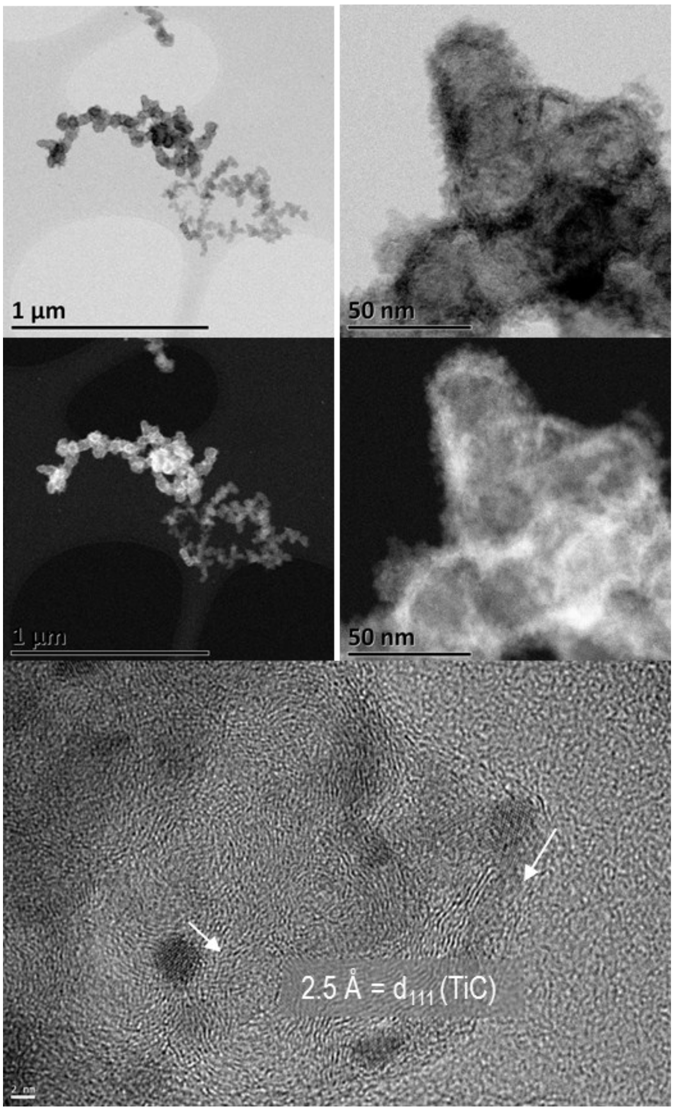

Figure S3. STEM (top left), STEM-HAADF (top-right) and HRTEM (bottom) images of TiC/ac-C.

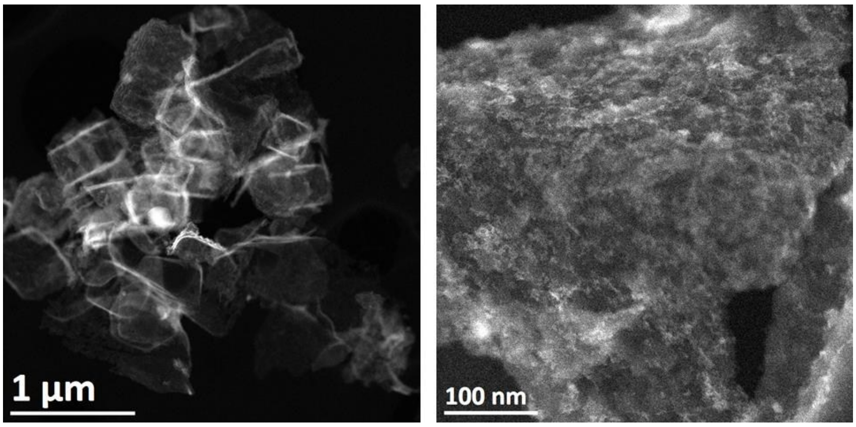

Figure S4. STEM-HAADF of TiC/ng-C.

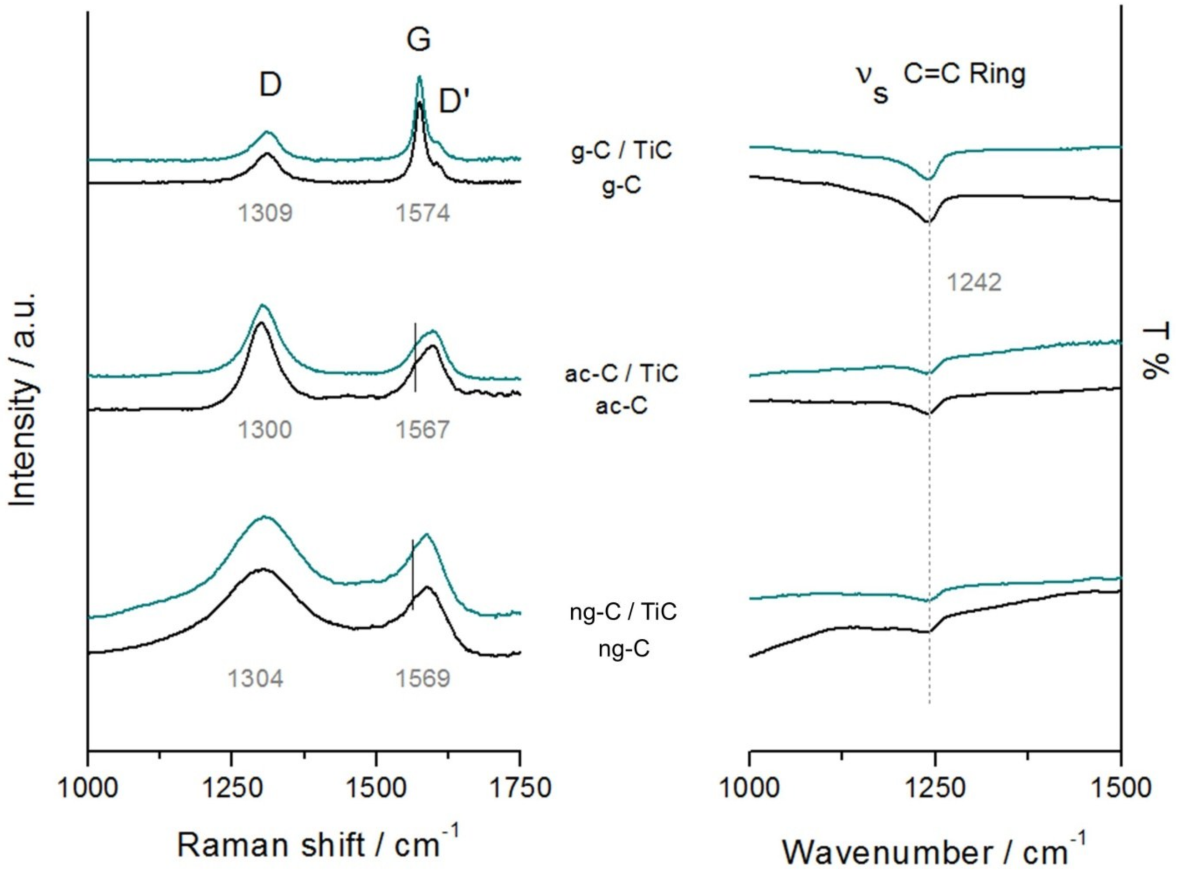

Figure S5. Comparison of FTIR and Raman spectra of pristine graphitic carbons and the corresponding TiC decorated carbons.

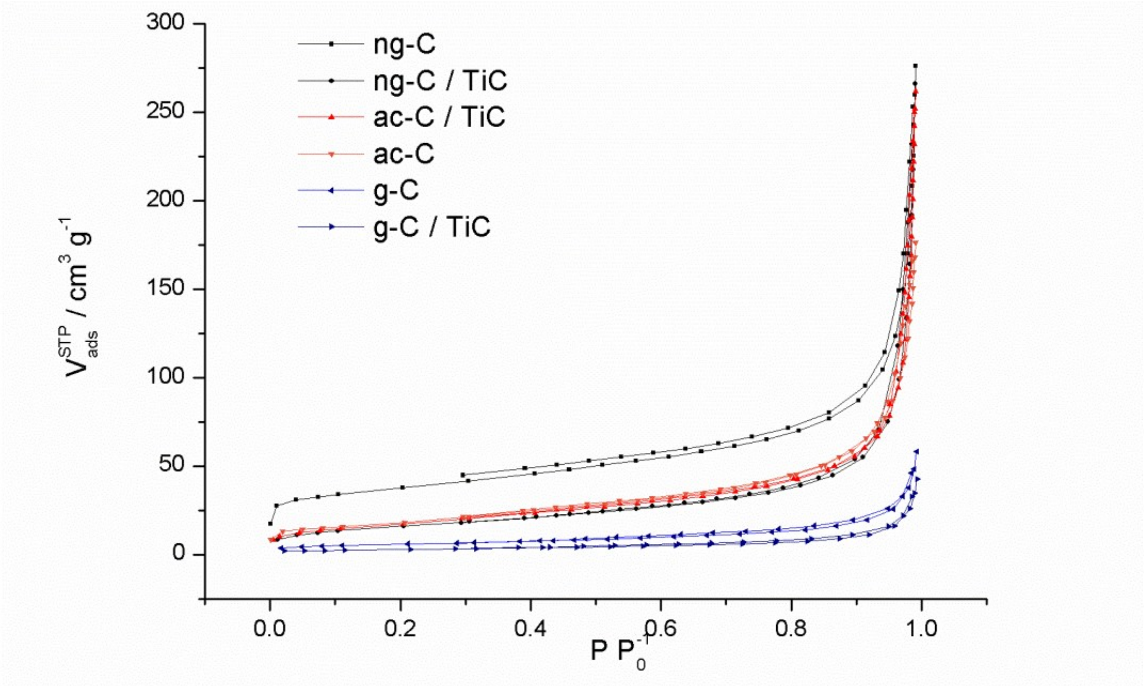

Figure S6. Nitrogen sorption isotherms of pristine and TiC modified carbons. Note that downward shift of modified isotherms is because of the different molecular weights.

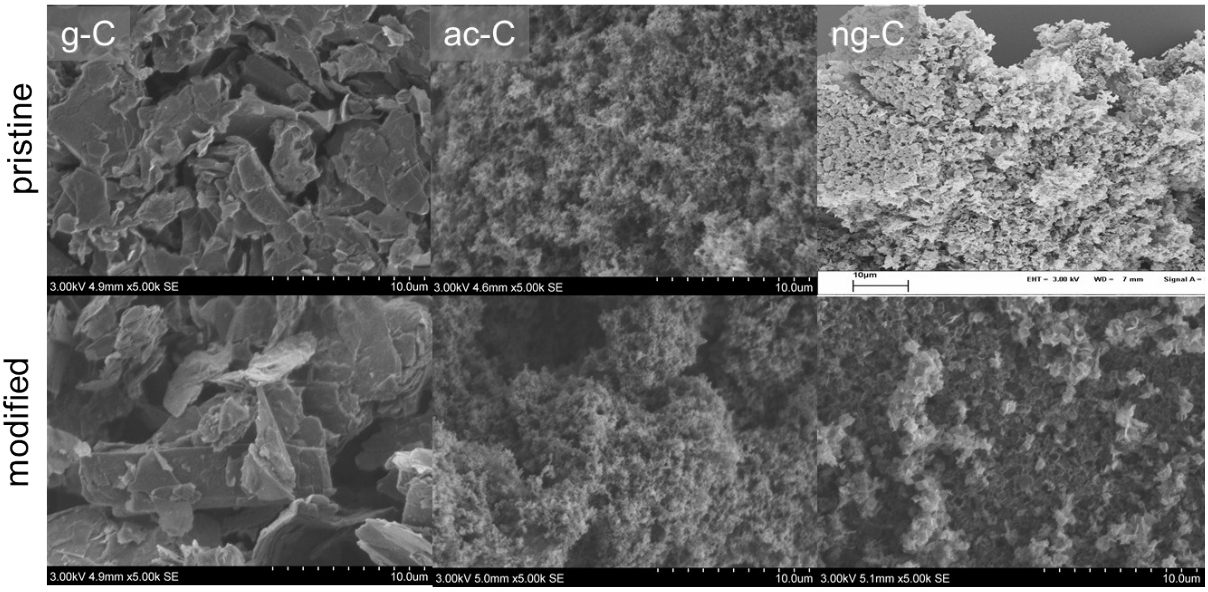

Figure S7. SEM images of pristine and TiC-modified carbons.

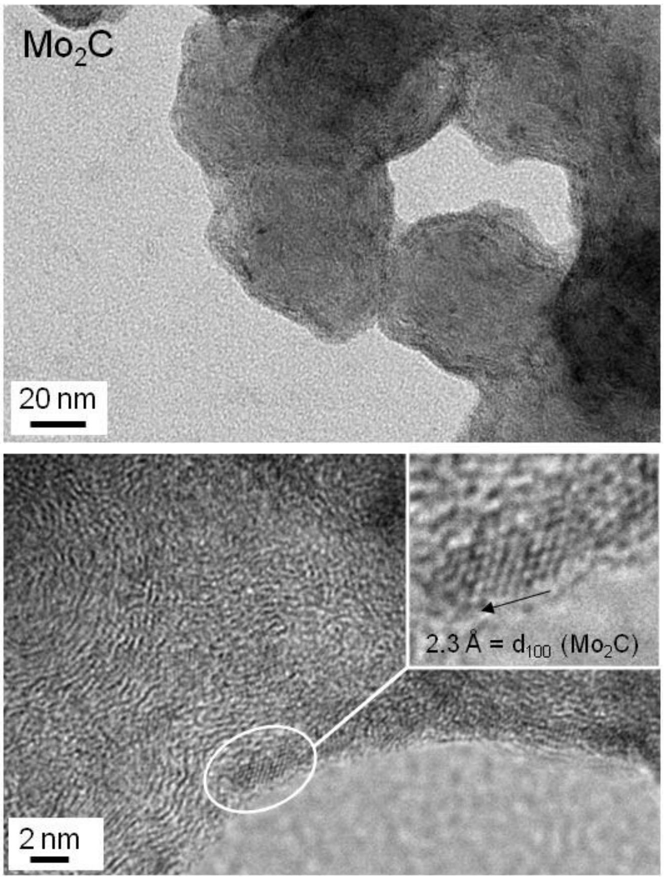

Figure S8. (HR)TEM analyses of molybdenum carbide on ac-C.

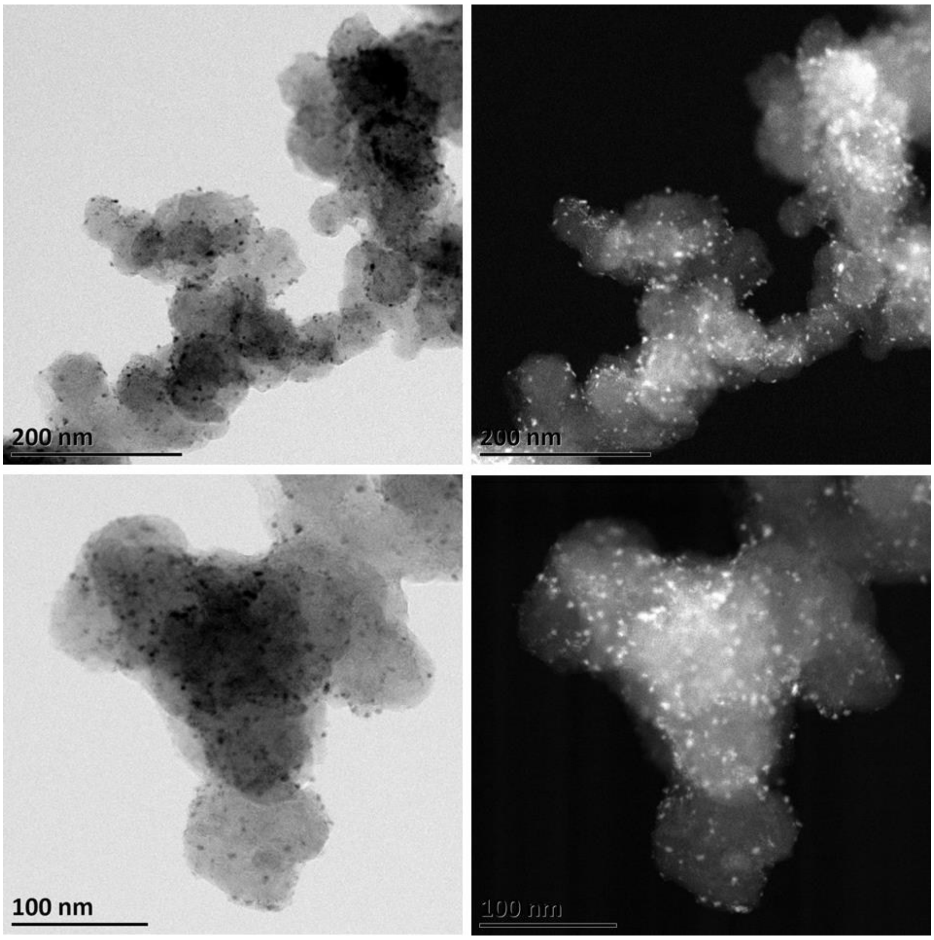

Figure S9. STEM (left) and STEM-HAADF (right) of tungsten carbide on ac-C.

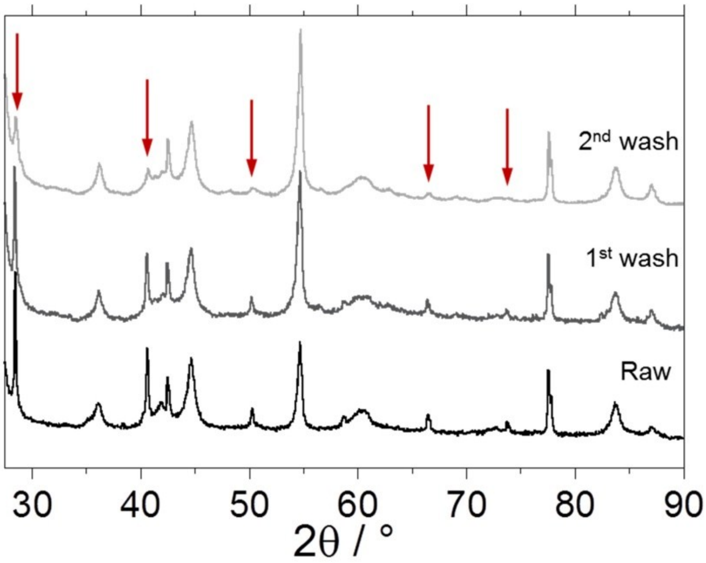

Figure S10. PXRD of TiC/g-C: raw product (bottom), after the first washing step (middle) and after the second one (top). Red arrow points the most intense peaks of KCl.

Figure S11. Four snapshots of the reaction forming VC nanoparticles on ac-C.