Direct Synthesis of Controllable Microstructures of Thermally Stable and Ordered Mesoporous Crystalline Titanium Oxides and Carbide/Carbon Composite

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The mesoporous titanium oxides- and carbide-carbon nanocomposites (Ti-C nanocomposites) were directly synthesized via supramolecular self-assembly with *in-situ* crystallization process. The molecular structure change in graphitization degree of Ti-C composites was examined by X-ray adsorption near-edge structure (XANES) spectra of C and Ti *K*-edge in Ti-C composites, which were measured in total X-ray fluorescence yield mode at room temperature using BL-16A, BL 17A and BL20A.

Figure 1 shows the XRPD patterns of Ti-C nanocomposites calcined at 1000 °C. A new titania phase is observed after calcined at 1000 °C. Five resolved diffraction peaks at 2θ of 36.8, 42.8, 62.4, 74.9 and 78.4 ° are observed in the WAXRD patterns, which can be indexed as the (111), (200), (220), (311), and (222) reflections of the cubic TiC nanocrystals. The formation of TiC is mainly attributed to the occurrence of carbothermal reduction reaction (TiO_2 + 3C → TiC + $2CO_{(g)}$) during the pyrolysis. The crystalline sizes range between 4.6 and 12.1 nm, and decrease upon increasing the carbon content. In addition, several small diffractions, which can be assigned as Ti_4O_7 phase ($4TiO_2$ + C → Ti_4O_7 +$CO_{(g)}$) and unidentified phases (possibly one of Magneli phases), are observed when the carbon content is lower than 35 wt%.

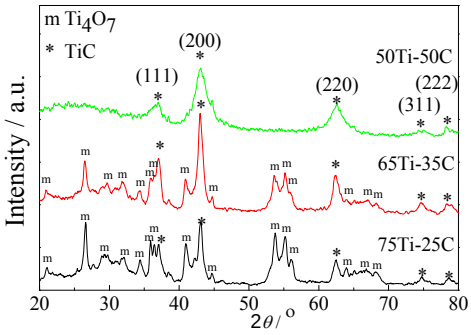

Fig. 1: WAXRD patterns of the mesoporous Ti-C composites at different Ti/C ratios calcined at 1000 °C under N_2 atmosphere

The XAS spectra (Fig. 1a) of the mesoporous Ti-C composite show a sharp 1s→π* peak at 285.1 eV and the 1s→σ* edge at near 292 eV, which correspond to fingerprints of sp^2- and sp^3-bonded carbons in Ti-C composite, respectively.[1] The feature at 288 eV originally assigned to interlayer bands with σ symmetry is contributed from the C–H σ* band and related to the presence of hydrogen after incomplete pyrolysis of the hydrocarbon precursors.[1] The sharp band at 288 eV associated with C-H σ* bonds diminishes apparently after calcination at 450°C, which is contributed from the decomposition of the triblock copolymer.

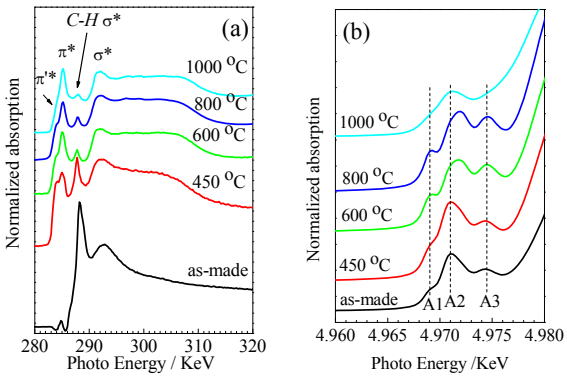

Fig. 2: Normalized (a) C *K*-edge and (b) Ti *K*-edge absorption spectra of the as-made and calcined mesoporous Ti-C composites.

The intensity ratio of the 1*s*→π* to C–H σ* bands for the mesoporous Ti-C composites increases upon increasing calcination temperature, indicating that the increase in sp^2 bonds is mainly due to the clean surface and the possible break of surface molecular bonds. Te 1*s*→π*/1*s*→σ* ratios at various temperature from 450 to 1000°C increased from 0.07 to 1.05, clearly demonstrates the increase in graphitization. After calcination at 450-800 °C, the shoulder at 284.1 eV for the sp^2 matrix can be observed. In addition, the distorted sp^2 bonds diminish at high temperature, depicting the high rigidity of ordered mesostructures after calcination.

The Ti *K*-edge XANES spectra (Fig. 2b) show three resolved pre-edge peaks (labeled A1, A2, and A3) follow by features on the higher energy part of the rising edges. The A1 peak is due to a quadrapolar 1s → 3d(t_{2g}) transition, the A2 is dipolar in nature but also includes a little quadrapolar component (1s→ 3d(e_g)), while the A3 peak is a pure dipolar component.[2] In addition, the occurrence and shape of A3 peak provides a sensitive probe for the degree of distortion.[2] The Ti K-edge spectra show that the A3 peak for mesoporous Ti-C composites increases upon the increasing calcination temperatures from 450 to 800°C. In addition, the A2 peak shifts to higher energy region, clearly showing the distortion around the TiO_6 octahedral sites, presumably due to the phase transformation from anatase to rutile.

References

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[2] D. M. Pickup, E. A. Abou Neel, R. M. Moss, K. M. Wetherall, P. Gerry, M. E. Smith, J. C. Knowles, and R. J. Newport, J. Mater. Sci.: Mater. Med. **19**, 1681 (2008).