



Synthesis of oxy-hydroxyfluorinated anatase nanoparticles grown on carbon nanotubes

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ABSTRACT

The synthesis of composite materials containing carbon nanotubes (CNTs) and inorganic nanocrystals is of interest to combine the specific properties of each components. While literature provides broad studies on the growth of anatase TiO₂ onto CNTs, it has never been reported how the presence of aqueous HF could affect the chemical composition of CNTs. Here, we demonstrated that CNTs are inactive toward fluorination during the solvothermal synthesis of an oxy-hydroxyfluorinated compound featuring the anatase-type structure. We further showed that functionalized CNTs offer nucleation sites that favor nanocrystals growth. As a result, the prepared composite features CNTs that are decorated by anatase nanocrystals. The results also showed that, in this condition, titanium alkoxide readily react with HF via a fluorolysis reaction allowing stabilizing high content of fluorine within the anatase network.

1. Introduction

Sol-gel chemistry relies on the condensation of molecular precursors formed through the reactivity of metal-alkoxide bonds [1]. In 2003, Kemnitz and colleagues were the first to investigate the reactivity of metal-alkoxide bonds toward anhydrous HF proposing to name the following reaction M-OR + HF → M-F + R-OH, fluorolysis by analogy with hydrolysis [2,3].

The reaction system employing titanium alkoxide with aqueous HF treated under solvothermal conditions was initially used to promote the growth of (001)-faceted nanoparticles of anatase TiO₂ [4]. In 2015, using a low temperature, we showed that fluoride and hydroxide were partially substituting oxide inducing a charge-compensating titanium vacancy (□) such as Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} [5]. Subsequently, we investigated its formation mechanism revealing a solid-state transformation of a highly defective anatase phase having a hydroxyfluoride composition which further evolves through oxolation reaction into an oxy-hydroxyfluoride phase [6]. It further shows that titanium alkoxide precursors can react with HF via a fluorolysis process.

The combination of inorganic compounds with electronic conductors such as carbon nanotubes (CNTs) have been widely employed to prepare composite materials with unique properties in numerous

fields such as photocatalysis [7,8] and energy storage [9]. Numerous methods have been used to prepare CNTs-based nanocomposites [10]. Sol-gel process is effective to grow inorganic nanocrystal onto CNTs [8]. The presence of HF, however, might alter the reactivity and crystal growth of the nanoparticles onto the CNTs. In this work, we investigated the feasibility of growing anatase onto CNTs in a fluorinating medium which could open new opportunities in the fields of energy storage and conversion [11,12].

2. Results and discussion

For the synthesis, CNTs and titanium isopropoxide were first mixed together in a solution of isopropanol (see experimental section). Thereafter a solution of aqueous HF diluted in isopropanol was added. The resulting mixed solution was heated treated under solvothermal conditions at 90 °C for 12 h.

2.1. Influence of the nature of CNTs

Two types of CNTs were used for the synthesis of composite materials that are either pure (denoted raw CNTs thereafter) or functionalized (denoted o-CNTs thereafter) CNTs. The later was obtained by

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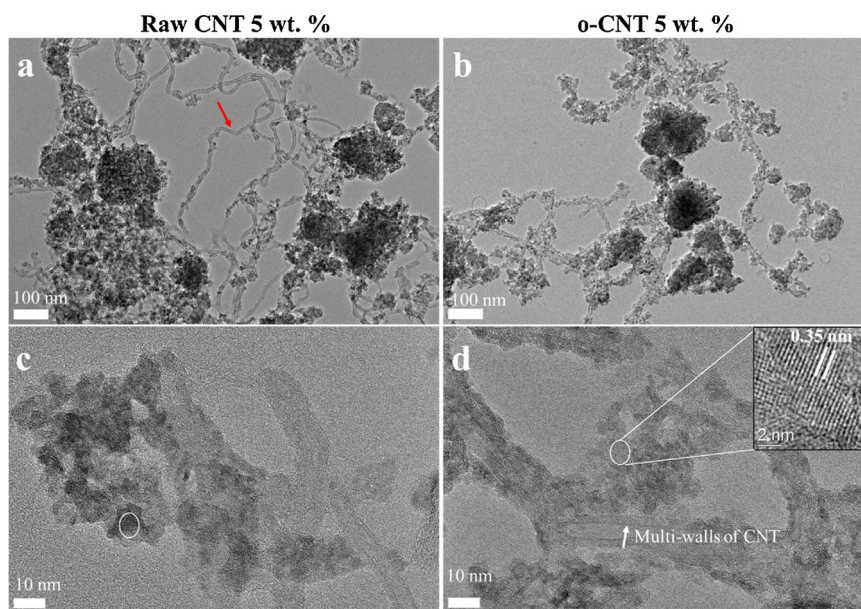


Fig. 1. Representative transmission electron microscopy images of composite materials obtained using raw CNTs (a,c) and o-CNTs (b,d). White circles represent single crystals.

treating raw CNTs with nitric acid to oxidize the surface providing additional active sites and functional groups for favor grafting of the inorganic component. Fig. 1 presents representative TEM images of the composites containing 5 wt.% raw CNTs or o-CNTs. It shows that raw CNTs are not effectively covered by nanoparticles that formed separated aggregates (Fig. 1a). In contrast, surface functionalization allows nanoparticles to grow on the o-CNTs which are almost fully covered (Fig. 1b). High magnification images (Fig. 1c, d) better evidences the effective grafting of nanocrystals on the o-CNTs surfaces. The nanoparticles present lattice fringes of 0.350 nm, characteristic of the spacing of (101) planes in anatase. The particle sizes were ~ 8 nm, consistent with the sample prepared without CNTs. The homogeneity of o-CNTs-based nanocomposites was also confirmed by the recovery of more homogeneous precipitate.

2.2. Influence of the content of o-CNTs

The effect of o-CNTs content on the homogeneity of the composite was studied by using two different content of o-CNTs that are 1 and 10 wt.% (Fig. 2). The decrease of the o-CNTs content to 1 wt.% led to full coverage of o-CNTs by nanoparticles. On the other hand, heavy aggregation of nanoparticles was observed which suggest that 1 wt.% o-CNTs does not provide sufficient sites for anchoring Ti precursor, so that a large excess of precursors condensed away from o-CNTs. Although TEM is only a qualitative technique, we observed that increasing the o-CNTs content to 10 wt.% effectively decreases the level of aggregations. Nevertheless, uncovered o-CNTs were observed

suggesting that the optimized o-CNTs content lies within 5 to 10 wt.%.

2.3. Influence of CNTs on the reactivity of Ti precursor

X-ray diffraction analysis was performed on the composite prepared using different content of o-CNTs (Fig. 3a). All the XRD patterns were indexed with a tetragonal cell (space group 141/amd) characteristic of the anatase type structure. The features of the Bragg peaks in terms of position, intensity remain unchanged whatever the content of o-CNTs, indicating that the presence of o-CNTs did not affect the crystallization of anatase network. The absence of the main (002) line of o-CNTs is due to the weak scattering of carbon.

To further confirm the stabilization of oxy-hydroxyfluorinated anatase, we used the pair distribution function (PDF) [13]. The PDF of the composite containing 10 wt.% of o-CNTs was successfully fitted using the anatase type structural model (Fig. 3b). The refined lattice parameters are $a = 3.782(1)$ Å, $c = 9.477(6)$ Å, which is consistent with previous study [5]. The scattering PDF domain was 5 nm in agreement with TEM observations. Moreover, the refined titanium occupancy was 0.68(3) which is similar to that obtained for the CNTs free compound [14]. The chemical composition assessed by PDF analysis and solid-state ^{19}F NMR, obtained without carbon additives was indeed determined to be $\text{Ti}_{0.69}\text{O}_{0.31}\text{O}_{0.76}\text{F}_{0.48}(\text{OH})_{0.76}$, consistent with the vacancy concentration determined here. This further confirms that the presence of CNTs does not affect the formation of fluorinated anatase but in turns provides a support to grow on it.

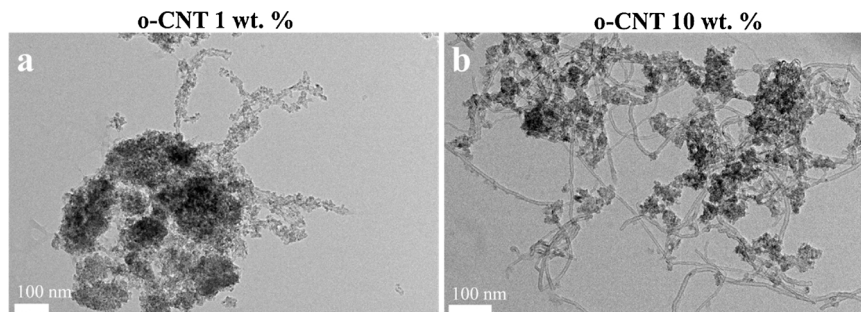


Fig. 2. Representative transmission electron microscopy images of composites prepared using 1 wt.% (a) and 10 wt.% of o-CNTs.

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