

Preparation of titanate nanotubes and their surface modification by plasma polymerization

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In the past decade, fabrication of various inorganic nanoparticles has attracted much attention because of their interesting properties and potential applications. The preparation of titanate nanotubes (Ti-NT) was first reported in 1998 [1]. Hollow tubular nanoparticles are prepared by hydrothermal treatment of TiO₂ in strong alkali conditions. The nanoparticles are formed by a rolled sheet of titanate. Their outer diameter is about 8 nm and their length varies from 100 nm to 1 μm. In our previous work we improved a synthesis of Ti-NT to achieve high conversion of TiO₂ and high uniformity of Ti-NT [2]. Furthermore, we developed an isolation method yielding non-destructed and non-merged nanotubes from aqueous solution in gram-scale amounts [3]. Due to their high aspect ratio, Ti-NT have potential use as nanofillers in polymer composites. Our recently prepared polymer composites with titanate nanotubes showed promising increase in elastic moduli. Although the polymer matrix contained both single Ti-NT and their agglomerates, the increase in modulus was significantly higher than in the case of composites with commercial TiO₂ micro- or nanopowders. In order to obtain even finer dispersion of nanoparticles, which should further improve mechanical properties, we investigated the possibility of Ti-NT surface modification by plasma polymerization of n-hexane.

Ti-NT nanotubes were synthesized by hydrothermal treatment and isolated from aqueous solution as described in our previous study [3]. In the next step, the hydrocarbon plasma polymer was deposited on the surface of dried Ti-NT nanopowder. The deposition was performed in a tubular type reactor with capacitively coupled external ring electrodes. R.f. power (13.56 MHz) was delivered to plasma from a generator (Dressler Cesar 133) through a matching unit. Prior to deposition, a sample of nanotubes was evenly distributed along the inner wall of the reactor. The reactor was pumped to the ultimate pressure of 10⁻³ Pa and then the working gas of hexane was adjusted to flow at 14 Pa pressure. Plasma polymerization was performed at 5 W (sample denoted as Ti-NT/plasma#1) and 30 W (sample denoted as Ti-NT/plasma#2) power of discharge. The presence of the polymer layer was investigated by TEM and IR spectroscopy. The structure of plasma polymers will be also examined by solid-state nuclear magnetic resonance spectroscopy (NMR).

IR spectroscopy demonstrated the presence of hydrocarbon polymer in all Ti-NT samples. TEM showed approximately 10nm thick layer on the surface of individual Ti-NT particles. Therefore, two independent methods confirmed that plasma polymer layer was successfully deposited on the surface of Ti-NT. Surface-modified Ti-NT will be used as a nanofiller in non-polar polymers.

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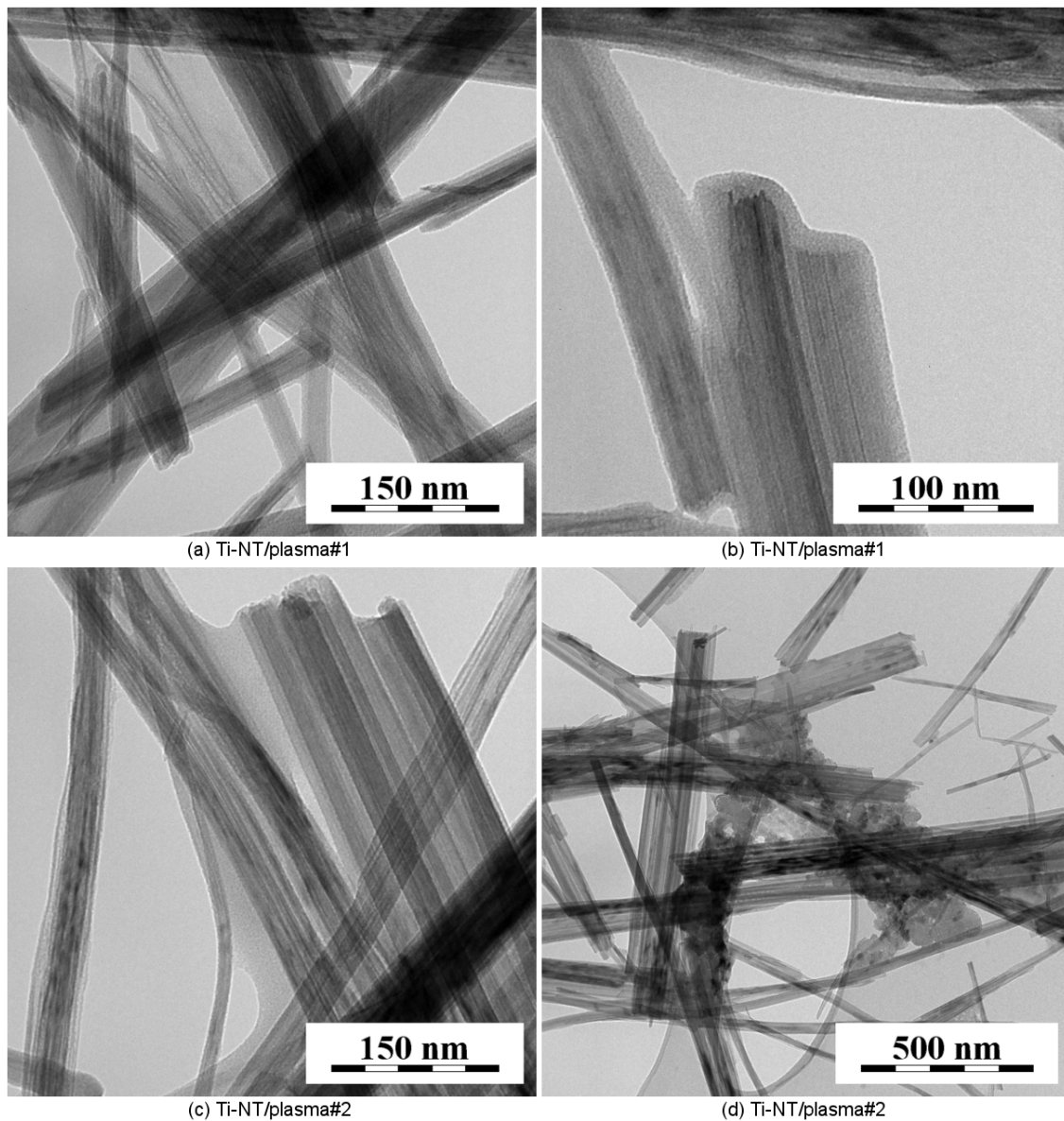


Figure 1. TEM micrographs of plasma treated Ti-NT: (a,b) sample #1; (c,d) sample #2.