Lepidocrocite TiO_2 nanofilaments: Optical properties revealed by ultrafast transient optical absorption

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ABSTRACT

Use of nanomaterials for photocatalysis faces challenges such as complex synthesis, high cost, low scalability, and dependance on UV radiation for initiating the photocatalytic activity. We recently demonstrated scalable, one-pot syntheses of one-dimensional (1D) lepidocrocite-based nanofilaments (NFs), 1DL NFs, that have the potential to overcome some of the challenges. 1DL NFs are exceptionally stable in water, have a large surface to volume ratio, and sub-square-nanometer cross sections. Initial reports show the semiconducting nature of this material, with an indirect band gap energy of 4.0 eV, one of the highest ever reported for a titania material. In this work, we present a study of the electronic and optical properties of these newly discovered 1DL NFs using ultrafast transient optical absorption. We show that despite the large band gap of this material, sub-gap states can be accessed with visible light illumination only, and photoexcited species reveal decay times in the nanosecond scale. Long lived photoexcitations in the visible range, without assistance by UV illumination, pave the way for possible application in photocatalysis.

Keywords: ultrafast transient optical absorption, oxides, defects

INTRODUCTION

1DL NFs are obtained by reacting Ti-containing water-insoluble, earth-abundant compounds, and relatively low-cost starting materials such as TiC, TiB2, TiN, etc., with tetraalkylammonium hydroxide, TMAOH, the resulting 1DL NFs are exceptional stable in water, have a large surface to volume ratio, sub-square-nanometer cross sections, as shown by transmission electron microscopy (TEM), and electron diffraction studies[1]. 1DL NFs self-assemble into a wide variety of structures depending on the washing compound used during the synthesis, it has been shown that they can assemble from 2D flakes to micron-sized fibers bundles[2].

Films of 1DL NFs have demonstrated exceptional performances for lithium-ion battery applications[1] and recent reports have shown NFs have the capability of producing H2 an order of magnitude higher than commercial titanium oxide (P25)[3], which is the standard material used for photocatalysis. The promising performance of 1DL NFs for clean energy applications motivates the need to understand their electronic and optical properties.

In this work we studied 1DL NFs films using TiC as a precursor, AFM revealed the nanofilament morphology of this new nanomaterial. UV-vis spectroscopy and ultrafast optical transient absorption (TA) was used to understand the optical properties of 1DL NFs, revealing that excitation energy in the visible range, 3.1 eV, can generate long-lived photoexcitations despite not filling the band gap of the nanomaterial, suggesting these photoexcitations can contribute to make 1DL NFs a promising photocatalytic material.

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RESULTS AND DISCUSSION

AFM imaging of a 1DL NFs film (Figure 1A) demonstrate the 1D structure of the NFs, in accordance with previous work[1], it also shows NFs present a high length to width aspect ratios, that extends over the AFM scan range, 10µm, and that it can be comparable to carbon nanotubes.

UV-vis spectroscopy of a thicker 1DL NFs film, reveals that the nanomaterial is a semiconductor, with a 4eV indirect band gap, as seen in the Tauc plot shown in Figure 1B. It can be observed that the nanomaterial presents an Urbach tail that covers the visible range. Recent reports suggest that the broad absorption in the visible range is due to the existence of near-valence edge defects[4].

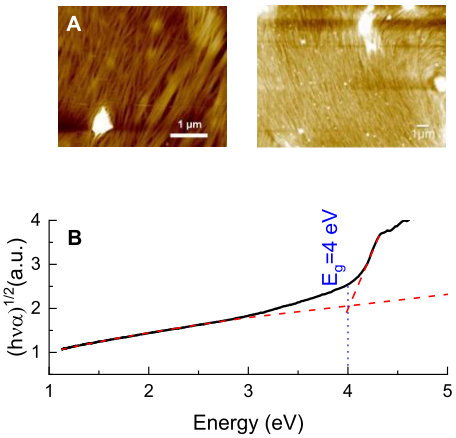

Figure 1. AFM image (A) and Tauc plot (B) of 1DL NFs films using TiC as a precursor.

To study if the 1DL NFs have optical states that can be accessed with visible light, we used TA with 400nm photoexcitation energy, which is an energy that does not fill the band gap of the material. We find that long-lived photoexcitations are generated in the visible range, exhibited by the broad excited state absorption (ESA) in Figure 3.

ESA signal measured at two different probe wavelengths, 550nm and 700nm, shows that they have same behavior, and it is independent of wavelength, suggesting that photoexcitations originate from similar states. The lifetimes of both kinetics exceed the 3ns detection range of the TA setup. We find that the signal decay around 75% after 3ns (setup detection limit). Exponential fitting shows the decay time have a 70 ps and 700 ps components, and a third one that cannot be resolved but appears to be in the microsecond scale. We hypothesize that the pump pulse promotes the carriers to the sub-gap states, and enhanced transient absorption represents transitions from those states to the conduction band.

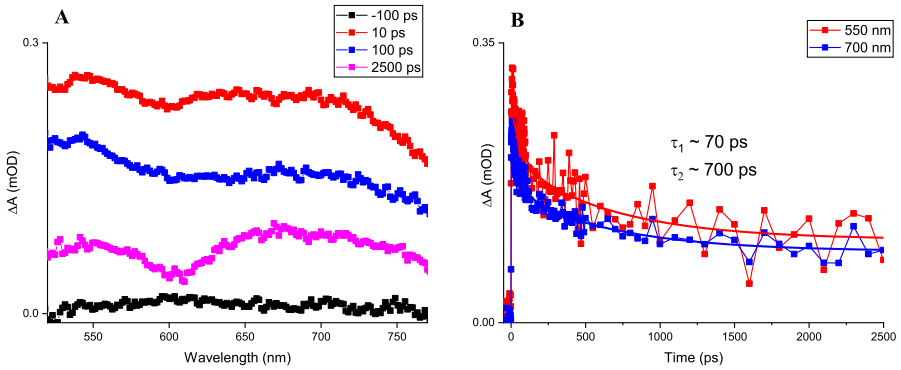

Figure 2. Temporal evolution of ΔA signal of 1DL NFs film (A), decay times of probe wavelengths 550 nm and 700nm (B).

SUMMARY

We report the properties of photoexcitations of 1DL NFs, kinetics that can be accessed using visible light and that are long lived. The mechanism responsible for these kinetics and their dependance on synthesis remains an object of future study. Nevertheless, the easy synthesis and scalability of 1DL NFs combined with their long lived photoexcitations hold promise for photocatalytic applications.

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