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Sintering of thin titanium dioxide nanoparticle films via photothermal processing with ultraviolet continuous-wave lasers

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ABSTRACT

Photothermal laser processing of thin films of anatase titania nanoparticles (TiO_2 NPs, diameter: 8–10 nm) with a thickness of about 500 nm is addressed. Laser processing in ambient air is carried out using a microfocused continuous-wave laser setup operating at a wavelength of 355 nm and a $1/e$ laser spot size of 1.6 μm. In conjunction with scanning electron microscopy, this approach provides a highly reproducible and convenient means in order to modify the local film structure and study the dependence of the resulting film morphology on the laser parameters. Generally, sintering of the nanoparticles is observed. At high laser power densities and/or long irradiation times the average particle/grain size increases reaching values of 200 nm and more. This opens up an opportunity to introduce scattering centers and optimize light trapping within the film, e.g., targeting photovoltaic or photocatalytic applications.

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1. Introduction

Semiconductor nanoparticles (NPs) are widely recognized as functional components in applications ranging from thermoelectrics and photovoltaics to display technologies [1,2]. The integration of semiconductor NPs into device structures, though, remains challenging in many respects. In recent years, photothermal laser processing has attracted significant attention as a versatile, fast and scalable technique, which allows one to locally modify thin NP layers and build up functional films with porous and compact morphologies on various substrates including polymers [3–10]. Generally, this approach provides a variety of particularly promising prospects. On one hand, NP films exhibit reduced thermal conductivities and melting temperatures ensuring low processing temperatures [1]. On the other hand, laser processing allows for precise control of heating time and zone [11]. In addition, the optical properties of NPs allow for resonant laser processing [12,13]. Recently, laser processing of thin TiO_2-nanoparticle films has been addressed [3–5]. These studies report optimized parameters for the fabrication of dye-sensitized solar cells with high conversion efficiencies. Processing has been carried out with short-pulse ultraviolet lasers at low fluences and pulse lengths <100 ns in order to largely maintain the inherent porosity of the NP film while interconnecting the individual NPs, thus building up highly conductive, mesoporous electrode structures. In this contribution, we focus on the morphology of laser-processed TiO_2-nanoparticle films exploiting a microfocused continuous-wave (cw) laser setup operating at a wavelength of 355 nm. This approach allows one to systematically study the laser-induced sintering process.

2. Materials and methods

TiO_2 NPs are synthesized via flame spray synthesis from a 0.5 M solution of titanium tetraisopropoxide (for synthesis; Merck) dissolved in isopropanol (p.a.; Merck) following an established method described in detail elsewhere [14]. As determined by X-ray diffraction (PANalytical X-ray Diffractometer X'Pert PRO with Cu K_α radiation), this procedure yields mostly anatase TiO_2 NPs with some traces of rutile nanoparticles. The rutile content is found to be typically less than 10%. The average particle size is 8–10 nm with a geometric standard deviation of about 3 nm. For spin-coating at 3000 rpm, 10 wt% ethanolic dispersions of TiO_2 NPs are prepared using an ultrasonic bath (Ethanol, absolute, VWR). Commercial soda-lime glass plates (Marienfeld) are cut into small pieces of about 10 mm × 10 mm, cleaned two times with piranha solution (3:1 mixture of 96% sulfuric acid, p.a., Fisher Chemical, and 30% hydrogen peroxide, p.a., AppliChem) for 30 min and used as substrates. This procedure yields homogeneous NP films with a thickness of about 500 nm. The samples are mildly heated at 60 °C for 5 min to remove residual ethanol.

Photothermal laser processing is carried out using a microfocused cw-laser setup operating at a wavelength of $\lambda = 355$ nm and

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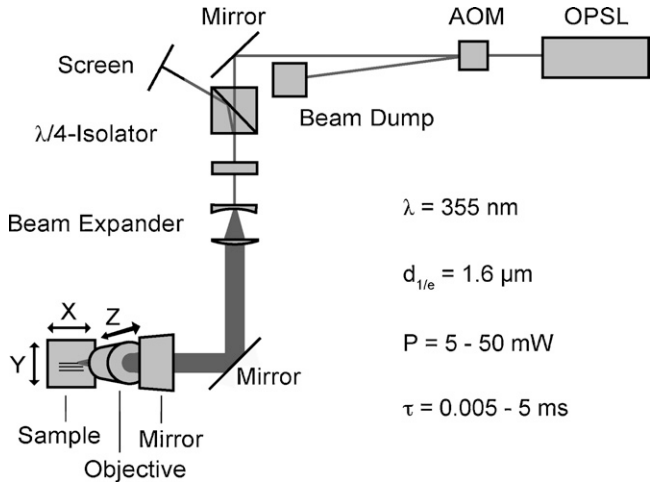

Fig. 1. Schematic drawing of the experimental laser set-up (OPSL: optically pumped semiconductor laser, AOM: acousto-optical modulator).

a $1/e$ laser spot size of $d_{1/e}$ = 1.6 μm. The set-up is displayed in Fig. 1. Briefly, the laser beam of an optically pumped semiconductor laser (OPSL, Coherent, Genesis CX355-250 STM) is focused onto the sample surface using an optical microscope objective (Olympus, Plan 10×) with a numerical aperture of 0.25. The focal laser spot diameter is measured using a knife-edge system (Coherent, Beammaster, BM-3UV). For focusing, the objective is mounted on a stepper motor stage (Micos, PLS-85). For positioning in the focal plane, the sample can be moved within an area of 26 mm × 26 mm using two additional stepper motor stages (Micos, PLS-85). The maximum positioning speed of the motor stages is 15 mm/s. An acousto-optical modulator (AOM, A.A. Opto-Electronic, A.A.MQ110-A3-UV) allows one to adjust the laser power and to switch the laser beam on and off. For laser power measurements a power meter is used (Coherent, FieldMaster GS, FM/GS). Typically, the laser power P is varied between 5 and 50 mW. This yields maximum laser power densities I_0 as calculated via $I_0 = 4P/\pi d_{1/e}^2$ in the range of 0.25–2.5 MW/cm^2.

Generally, processing with the laser setup can be carried out either in pulse-mode operation or in continuous-mode operation. In pulse-mode operation, the sample is moved to predefined positions. Once a given position is reached the AOM is used to generate a single laser pulse at a certain laser power and a selected pulse length in the range of 5 μs–5 ms. Rising and falling times of the AOM are about 0.1 μs. The local irradiation time τ_l in this mode is equal to the laser pulse length τ. In continuous-mode operation, the laser spot is scanned along predefined lines at a given laser power and writing speed. The local laser irradiation time τ_l in this mode is determined by the writing speed v and the $1/e$ laser spot size via $\tau_l = d_{1/e}/v$. This approach is exploited in order to fabricate long line patterns. Such patterns are used to prepare breaking edges and study the morphology across the processed film.

Sample characterization is carried out using scanning electron microscopy (SEM, FEI Company, ESEM Quanta 400), optical microscopy (Olympus), atomic force microscopy (AFM, Veeco, Autoprobe CP) and UV/Vis–spectroscopy (Perkin Elmer, Lambda 950). For SEM measurements samples are covered with a thin gold layer with a nominal thickness of a few nanometers in order to avoid charging effects. Average particle/grain sizes are determined via manual analysis of individual particles/grains in the SEM images.

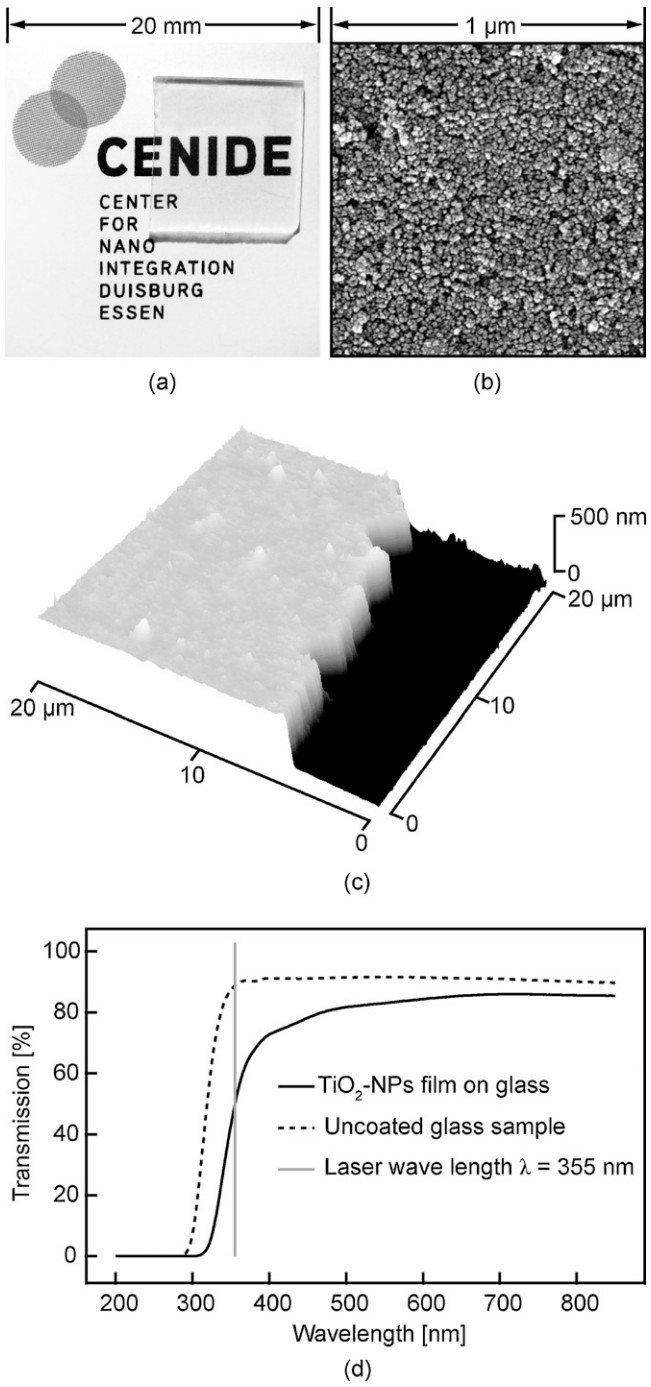

Fig. 2. Characterization of as-deposited TiO_2 NP films on glass: (a) photograph, (b) scanning electron micrograph, (c) AFM data (as-deposited film, top-left and bare substrate surface, bottom right) and (d) UV/Vis spectrum (full line). For comparison, a UV/Vis spectrum of an uncoated sample (dashed line) is added.

3. Results and discussion

For photothermal laser processing, thin TiO_2 NP films on soda-lime glass plates are prepared via spin-coating. A photograph and a scanning electron micrograph of as-deposited TiO_2 NP films with an average particle size of d = 8–10 nm on glass substrates are shown in Fig. 2a and b. For AFM measurements of the film thickness, the as-deposited film is gently removed via scratching along a thin line while the substrate surface is left unaffected. This yields a value of about 500 nm (Fig. 2c). The AFM data also displays the rather smooth and homogeneous film surface.

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