Applied Surface Science 336 (2015) 48–52

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Resonant photothermal laser processing of hybrid gold/titania nanoparticle films

Lina Schade[a,b], Steffen Franzka[a,b], Kevin Dzialkowski[a,b], Sebastian Hardt[b,c], Hartmut Wiggers[b,c], Sven Reichenberger[a,b,d], Philipp Wagener[a,b], Nils Hartmann[a,b,*]

[a] Fakultät für Chemie, Universität Duisburg-Essen, 45117 Essen, Germany
[b] Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Carl-Benz-Straße 199, 47057 Duisburg, Germany
[c] Institut für Verbrennung und Gasdynamik, Universität Duisburg-Essen, 47048 Duisburg, Germany
[d] Institut für Lacke und Oberflächenchemie, Hochschule Niederrhein, 47798 Krefeld, Germany

ARTICLE INFO

Article history:
Received 15 June 2014
Received in revised form
19 September 2014
Accepted 20 September 2014
Available online 11 October 2014

Keywords:
Titanium dioxide
Gold nanoparticle
Plasmon resonance
Resonant photothermal processing
Laser sintering
Mesoporous electrodes

ABSTRACT

Photothermal processing of thin anatase TiO_2 and hybrid Au/anatase TiO_2 nanoparticle films on glass supports is investigated using continuous-wave microfocused lasers at $\lambda = 355$ nm and $\lambda = 532$ nm. UV/Vis spectroscopy, Raman spectroscopy, optical microscopy, atomic force microscopy and scanning electron microscopy are used for characterization. Processing of TiO_2 nanoparticle films is feasible at $\lambda = 355$ nm only. In contrast, the addition of Au nanoparticles enhances the overall absorbance of the material in the visible range and enables processing at both wavelengths, i.e. at $\lambda = 355$ nm and $\lambda = 532$ nm. Generally, laser heating induces a transition from anatase to rutile. The modification degree increases with increasing laser power and laser irradiation time. Resonant laser processing of hybrid Au/TiO_2-mesoporous films provide promising perspectives in various applications, e.g. in photovoltaics, where embedded nanoparticulate Au could be exploited to enhance light trapping.

1. Introduction

Semiconductor nanoparticles (NPs) have evolved as versatile building blocks for the fabrication of mesoporous materials in different fields of energy science including photovoltaics, thermoelectrics, batterie technology, fuel cells and catalysis [1–3]. In common fabrication schemes the native nanoparticulate material is annealed and sintered in conventional heating devices, e.g. in order to improve the electrical conductivity and the mechanical stability while maintaining a high specific surface area. More recently, laser sintering techniques have been employed for the fabrication of mesoporous films [4–10]. This approach combines some favorable features. On one hand, NP films exhibit reduced thermal conductivities and melting temperatures ensuring low processing temperatures [2]. On the other hand, laser processing allows for precise control of heating time and zone [11]. In a previous contribution, we addressed laser sintering of TiO_2 NP films using an ultraviolet continuous-wave (CW) laser [12]. Here we report on laser sintering of hybrid Au/TiO_2 NP films using ultraviolet- and visible-light CW lasers. Au NPs are well known for their particular optical properties showing a plasmon resonance in the visible wavelength range. For this reason, hybrid Au/TiO_2-mesoporous films provide promising perspectives in various applications, e.g. in photovoltaics, where embedded nanoparticulate Au could be exploited as scattering centers and nanosized antennas. Using plasmonic NPs as an additive also offers favorable features in laser processing of these hybrid materials. In particular, resonant laser processing of TiO_2-nanoparticulate materials is feasible using visible lasers. In a related previous contribution Crespo-Monteiro et al., for example, reported on laser processing of Ag/TiO_2-coatings at wavelength in the ultraviolet and in the visible range [13]. Also, in a parallel work by Lau et al. processing of Au/ZnO NP films with an infrared laser has been addressed [14].

2. Material 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

* Corresponding author at: Fakultät für Chemie, Center for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, Germany.
Tel.: +49 203 379 8033.
E-mail address: nils.hartmann@uni-due.de (N. Hartmann).

http://dx.doi.org/10.1016/j.apsusc.2014.09.118
0169-4332/

described in detail elsewhere [15,16]. As determined by Raman spectroscopy (cf. below), this procedure yields mostly anatase TiO_2 NPs with some traces of rutile NPs. The average particle size typically is in the range of 8–10 nm. For further processing, TiO_2 NPs are dispersed in water via sonication.

Au NPs are produced by pulsed laser ablation in liquid with a Nd:YAG laser (Rofin-Sinar, RS-Marker 100D) operating at a wavelength of 1064 nm. The beam is focused on a Au target, which is placed in a flow chamber with a volume flow rate of 45 mL/min. The pulse energy was 8 mJ with a repetition rate of 5000 Hz and a pulse duration of 40 ns. Analysis via UV/Vis spectroscopy (Thermo Fisher Scientific, Evolution 201) and analytical disc centrifugation (CPS, DC24000) of the synthesized NPs yielded a mass-weighted average particle size of 6–12 nm.

The pH-value of the Au NP suspension is adjusted to 7 and centrifuged for 18 h at 5000 rpm. Decoration of the TiO_2 NPs with 1 wt% Au NPs is achieved by mixing appropriate amounts of TiO_2 and Au NP suspensions. For complete deposition of Au NPs on the TiO_2 NPs the pH is lowered to a value of 3. This results in a positive charge of the TiO_2 NPs. Au NPs are negatively charged. Hence Au NPs are attracted by TiO_2 NPs. The hybrid nanoparticulate material is removed by filtration, washed with water and dried.

For spin coating at 3000 rpm, 10 wt% dispersions in *tert*-butanol of TiO_2 NPs and hybrid TiO_2/Au NPs are prepared. Commercial soda–lime glass plates (Marienfeld) are cut into small pieces of about 1 cm × 1 cm in size, cleaned two times with piranha solution (3:1 mixture of 96% sulfuric acid and 30% hydrogen peroxide) for 30 min and used as substrates. Finally, coated samples are mildly heated at 60 °C for 5 min to remove residual *tert*-butanol. This procedure yields homogeneous NP films with a thickness of about 500 nm. For determination of film thicknesses AFM is used (cf. below). At first, the as-deposited film is gently removed via scratching along a thin line while the substrate surface is left unaffected. Then the height profile across this line is recorded.

Photothermal laser processing is carried out using a setup consisting of two CW lasers (cf. Fig. 1). One laser is operated at a wavelength of 355 nm yielding a $1/e$ laser spot size of $d_{1/e} = 0.6$ μm (OPSL, Coherent, Genesis CX355-250 STM). The other laser is operated at a wavelength of 532 nm yielding a $1/e$ laser spot size of $d_{1/e} = 0.7$ μm (DPSSL, Laser Quantum, Ventus HP). During material processing the chosen laser beam is directed and focused onto the sample surface using a switchable mirror and an optical microscope objective (Olympus, LUC Plan FLN 40x) with a numerical aperture of 0.6.

The focal laser spot diameters are measured using a CCD camera (Spiricon, Laserbeam diagnostics SP6204). Note, the detector

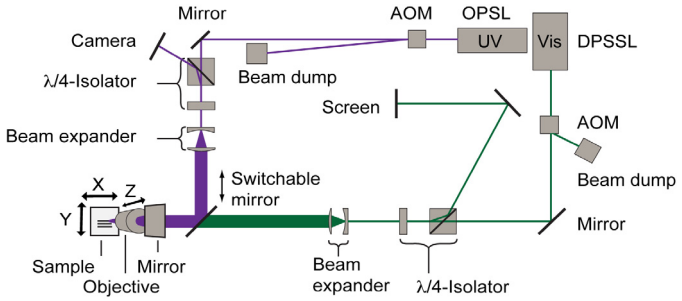

Fig. 1. Schematic drawing of the experimental laser set-up (OPSL: optically pumped semiconductor laser, DPSSL: diode pumped solid state laser, AOM: acousto-optical modulator).

array of the CCD camera has a pixel size of 4 μm × 4 μm. A microscope objective (Leitz PL 160×/0.95 ∞/0) has been used to image the focused beam onto the camera detector array. This expands the measurement range of the camera to include smaller beams, which could not be ordinarily measured due to the pixel size of the detector array. For calibration a stage micrometer (LOMO) has been employed. The resolution in this configuration is 0.05 μm/pixel.

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. Acousto-optical modulators (AOM, A.A. Opto-Electronic, A.A.MQ110-A3-UV and A.A.MTS.110/AS.VIS) allow one to adjust the laser power P and to switch the laser beams on and off. For laser power measurements a power meter (Coherent, FieldMaster GS, FM/GS) in combination with pyroelectric sensors (Coherent, PM3Q and LM-2) is used.

Generally, patterning can be carried out either in pulse-mode operation or in continuous-mode operation. In pulse-mode operation the laser is switched on at fixed positions for predefined irradiation times τ in order to create dot patterns. In continuous-mode operation the laser beam is turned on all time while the motor stage is moving at constant writing speed v in order to fabricate line patterns.

Sample characterization is carried out using scanning electron microscopy (SEM, FEI Company, ESEM Quanta 400), optical microscopy (Olympus), atomic force microscopy (AFM, Bruker, Dimension FastScan), UV/Vis spectroscopy (Perkin Elmer, Lambda 950) and Raman spectroscopy (Renishaw, InVia Raman Spectrometer). For UV/Vis spectrometer the spectral resolution is set to 1 nm. Raman spectroscopy is carried out in backscattering geometry at a

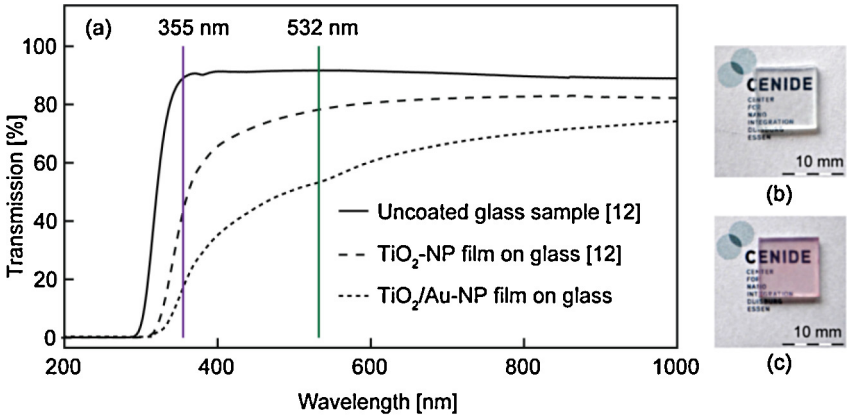

Fig. 2. (a) UV/Vis spectrum of as-deposited TiO_2 and Au/TiO_2 NP films on glass (dashed lines). For comparison, a UV/Vis spectrum of an uncoated sample (full line) is added. The positions of the laser wavelengths are indicated by vertical lines. Photographs of as-deposited TiO_2 NP films and Au/TiO_2 NP films on glass supports are shown in (b) and (c), respectively.