Laser-Assisted Synthesis of Ultra-Small Anatase TiO_2 Nanoparticles

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Abstract

Titanium dioxide is one of the most important materials today in terms of green technology. In this work, we synthesis ultra-small titanium dioxide nanoparticles (NPs) via a two step process involving infrared laser ablation of a bulk titanium target in DDI water and subsequent irradiation of the colloidal solution with visible light. The as-prepared NPs contain defect states related to oxygen vacancies which lead to visible light sensitization as observed by photodegradation of methylene blue. Irradiation of the colloidal TiO_2 solution, with a 532 nm picosecond laser, lead to fragmentation and ultimate formation of ultra-small ($< 3\text{ nm}$) anatase particles. Shadowgraph was utilized to capture shockwave and cavitation bubble propagation during both the ablation and fragmentation processes. High-frequency ripples within the primary shockwave are identified as coming from laser induced stress-wave reflections within the metal target. A blueshift of the bandgap, for the ultra-small NPs, is explained by quantum confinement effects and rationalized using the Brus model.

1 Introduction

Titanium dioxide has long been known as a promising material for applications such as a photocatalyst in decomposition of pollutants, as a photo-voltaic for green energy solar technology, and as a bactericidal agent, especially due to its biocompatibility. One challenge in utilizing TiO_2 in these applications is that it has a wide bandgap and thus requires UV-light to initiate direct photo-excitation.

In nanoparticle form, one of TiO_2 's most important characteristics is that it can generate reactive oxygen species (ROS). The applicability of TiO_2 would be greatly enhanced if its photo-activity

Fig. 1: Schematic of the imaging apparatus. The setup contained a 25 ps Nd:YAG (1064 nm) laser for ablation of the titanium plate submerged in an optical cell. The ablation process was back illuminated using a fluorescent dye contained in a cuvette and excited by a Nd:YVO₄ (532 nm) laser. A digital delay generator controlled timing between the Nd:YAG laser, the Nd:YVO₄ laser, and the CCD camera's shutter. Note. The optical cell was omitted in the illustration for clarity.

was extended into the visible region of the spectrum. Various materials can be used as sensitizers (e.g. Ag NPs, graphene), however, the strength of the photo-catalytic response of the TiO_2 quickly destroys the sensitizers. Therefore such measures are invariably stop-gap and temporary. Alternatively, intermediate gap states can be introduced via defects, such as oxygen vacancies [1]. Titanium dioxide is also polymorphic and can be synthesized in the rutile, brookite, or anatase crystalline phases, allowing for the creation of a wide number of phases and nanostructures.

Laser ablation in liquids (LAL) [2, 3] is a promising technique for the creation of suspensions of nanoparticles and nanocomposites. It is a reliable method to produce precursor-free colloidal solutions. While it is most typically used for metals and semiconductors [4, 5], it can also be used for organic materials as well [6].

It is well known that anatase TiO_2 displays a higher photocatalytic efficiency than the rutile phase [7, 8]. There is also strong evidence that surface hydroxylation and oxygen vacancies act as charge carrier trapping sites, thus reducing recombination and enhancing the photo-activity of the NPs [9, 10]. Additionally, the smaller the particle size the less distance photogenerated charge carriers have to travel to reach surface reaction sites [11]. Therefore, we have focused on the production of suspensions of anatase nanoparticles of very small size (< 3 nm) in this work and we have explored their effectiveness in the photocatalytic degradation of the dye, methylene blue.

2 Results

2.1 Experimental Conditions

The initial colloidal suspensions were produced using a picosecond Nd:YAG laser (Ekspla PL2241, 25 ps) operating at its fundamental wavelength (1064 nm) and a repetition rate of 250 Hz. A Ti plate was placed in a 50 mL beaker on top of a short stainless steel platform, which allowed for a magnetic stirrer to be placed underneath the target; the liquid height above the target was 15 mm. Fluence at the target surface was $490 \frac{mJ}{cm^2}$. The approximately square plate, with an area of ~ 4.0

Fig. 2: (a) UV-Vis spectrum of as-synthesized TiO_x nanoparticles and (b) HR-TEM of the resulting particles with histogram in the inset.

cm^2 , was moved by a motorized XY translation stage in order to uniformly ablate the sample. Ablation took place for 8 minutes and a turbid solution with a blue hue developed.

For shadowgraph imaging of the shockwave/cavitation bubble, the titanium target was placed into a rectangular (type 96) spectrophotometer cell with polished front and back surfaces. Images were taken using a Sentech STC-TB202USH-ASH CCD camera equipped with a macro lens. A 532 nm Nd:YVO₄ laser (Ekspla NL-201, 10 ns) incident upon a cuvette of Rhodamine dye served as the camera's flash. The timing between laser pulses was controlled by a four-channel digital delay generator (Berkeley Nucleonics Corporation 575), and the total optical jitter was determined to be ~ 20 ns. Note that the camera's shutter is opened before the ablation pulse arrives. A schematic of the process, along with the imaging apparatus is shown in figure 1.

2.2 Particle Synthesis, post-Irradiation, and Characterization

The absorbance spectrum shows a broad peak that extends well into the near-IR as shown in figure 2. Dynamic light scattering (DLS) measurements show a wide distribution of particle sizes with a mean hydrodynamic diameter of 132 ± 55 nm. HR-TEM images agree well with the DLS measurements and reveal the NPs to be polymorphic, predominantly consisting of rutile and amorphous phases with a small admixture of anatase. In the size histogram, two distinct peaks are present at 100 ± 40 nm and 225 ± 25 nm. Additionally, some hollow nanospheres are present [12]. The large absorption tail that persists into the near-IR is indicative of mid-gap defect states [10], so the as-synthesized NPs are best described by the chemical formula TiO_x where x is between 1 and 2.

Further examination of the HR-TEM images reveals that the smaller particles are crystalline and anatase. The particle in the left frame of figure 3 clearly shows spacing associated with the $\{005\}$ plane family. Indexing of the particle in the right frame reveals a lattice spacing of about 2.3 Å, which is consistent with the $\{020\}$ rutile family of planes.

2.2.1 Post-Irradiation

Pulsed laser irradiation of colloidal NP solutions has been shown to induce size reduction and homogenization, shape evolution, structural transformations, and compositional changes of the

Fig. 3: HR-TEM images of TiO_2 nanoparticles (left) zoom of anatase particle showing 1.93 Å lattice spacing between (005) planes (center) post-irradiated TiO_2 particles and zoom of particle from figure 2, showing {020} plane family spacing.

NPs [13–17]. The incident radiation absorbed by the NPs may come about through either excitation of interband transitions or excitement of SPR modes within the metal NPs. In the case of ultrashort laser pulses, multi-photon absorption can also occur. The current belief is that the NPs may experience either melting, thermal evaporation [18, 19], or Coulomb explosion where strong repulsive forces between similarly charged regions within a particle cause it to fragment [17, 20]. The fragmentation mechanism experienced by the NPs during irradiation depends on several factors, some intrinsic to the particle (e.g. melting point, and absorption coefficient) while others are related to the laser source (e.g. pulse duration, and wavelength). In the case of short (< 30 ps) lasers pulses and high intensities it is possible to have direct photoionization of the particles that leads to Coulomb explosion.

The Uv-Vis spectrum displayed in figure 2 is indicative of particles with a high defect density, most likely oxygen vacancies. The initial bandgap extracted from a Tauc plot is of the order of 0.7 eV. The spectra was fitted to a Tauc plot [21] for indirect transitions with $(h\nu\alpha)^{\frac{1}{2}} = A(h\nu - E_g)$ where $h\nu$ is the photon energy, α is the extinction coefficient as determined from the Beer-Lambert law, A is a proportionality constant, and E_g is the band gap.

After synthesis, the particles were irradiated with a 25 ps 532 nm laser, resulting in a significant size reduction along with changes to the UV-Vis spectrum. A 17.5 mm focal length plano convex lens was used to bring the 0.66 mJ laser pulses to a beam waist of about 3 μ m. HR-TEM gives an average hydrodynamic diameter of 2.17 ± 0.59 nm after 20 minutes of irradiation in agreement with DLS measurements (< 5 nm). Only anatase particles are found after 20 minutes of irradiation. These particles are highly stable and have a zeta potential of approximately -60 mV.

As shown in figure 4, the UV-Vis spectrum shows that the absorbance edge becomes sharper as defects are removed and the anatase phase dominates. After 20 min of irradiation, we find a bandgap of approximately 3.4 eV. At first glance, this might appear to compare poorly with the bulk anatase phase ($E_g^{bulk} = 3.2$ eV), but TiO_2 NPs are known to display quantum size effects on the order several tenths of an eV [22]. In our case, we can apply the Brus model to find a reasonable estimate for the magnitude of the blueshift in the bandgap expected due to quantum confinement.

The expected shift is given as a function of the particle radius, R , as:

Fig. 4: (a) Uv-Vis spectra of post-irradiated TiO_2 colloids with (inset) band-gap fitted from Tauc plots and (b) HR-TEM showing small Anatase particles

$$\Delta E = \frac{\hbar^2 \pi^2}{2\mu R^2} - 1.8 \frac{e^2}{\epsilon R}, \quad (1)$$

while the reduced mass of the exciton is given by:

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}. \quad (2)$$

Here, the bulk dielectric constant, ϵ is given as 86, e is the electronic charge, and the effective masses of electrons and holes is taken to be $1.2 - 9 m_e$ and $2 m_e$, respectively [22–24].

The Brus model is applicable when the exciton radius is greater than or equal to the particle radius ($r_e \geq R$). In terms of the Bohr radius, r_e is given as:

$$r_e = \frac{\epsilon}{m_e^*/m_e} a_0. \quad (3)$$

Given these parameters, r_e is expected to range from $0.5 - 3.8 \text{ nm}$. Using several representative values for the reduced excitonic mass, the expected bandgap shift is calculated as a function of particle radius and the results are displayed in figure 5. Therefore, we regard our shift of 0.2 eV to be well explained by the Brus model.

2.3 Plume Images and Shadowography

2.3.1 Imaging of Shock Wave

Plume shadowgraphs were captured for the ablation of the Ti plate while it was immersed in water. The shock front is strongly ellipsoidal at first, but becomes nearly hemispherical at later times ($> 1000 \text{ ns}$). The anisotropy likely arises from the heating of water in the immediate vicinity of the target, thus allowing the shockwave to initially propagate more rapidly in the horizontal rather than vertical direction. Anisotropy in laser generated shock waves is commonly observed in a variety of contexts, but we don't believe it to be germane to the production of nanoparticles [25, and references therein].

Fig. 5: Bandgap shift for several values of reduced exciton mass. The red data point shows the position of our post-irradiated nanoparticles.

The position of the leading edge of the shock wave is linear in time over the range 100–1000 ns , and travels at a velocity of $1513 \frac{m}{s}$ which is very close to the accepted value for the speed of sound in water at standard conditions ($1494 \frac{m}{s}$). This is somewhat less than observed for ablation of an Ag plate immersed in water by a ns laser ($\sim 1600 \frac{m}{s}$) [26]. Given that we see a similar velocity for Au targets and that it does not depend on laser fluence, we think it unlikely to be material-specific, but rather, it might point to differences between ns and ps ablation mechanisms. Our experiments were done at an intensity of $20 \frac{GW}{cm^2}$, while those of Tsuji *et al.* were done at $10 \frac{GW}{cm^2}$.

One interesting feature that becomes readily apparent 100 ns after the laser pulse arrives is horizontal bands that are evenly spaced at about 50 ns apart. They are occurring far too frequently to be described as mechanical oscillations of the Ti plate, as we can show by calculating the natural frequency of the plate. The rigid body modes for a plate with Poisson's ratio of approximately $\nu = 0.3$ ($Ti \approx 0.32$) are given by the i, j pairs (1, 1), (1, 2), and (2, 1) in the formula:

$$f_{ij} = \frac{\lambda_{ij}^2}{2\pi a^2} \left[\frac{Eh^3}{12\gamma(1-\nu^2)} \right]^{1/2}, \quad (4)$$

where λ_{ij} is a geometric factor, a is the length of the plate, E is the elastic modulus (110 GPa), h is the thickness of the plate, γ is the mass per unit area in the plate, and ν is Poisson's ratio. For a square plate with four free sides, the lowest mode is given by (2, 2) and $\lambda_{22} = 13.49$ [27]. This yields a fundamental frequency of approximately 76 kHz for the plate. However, this frequency is changed in water due to the added mass to the plate, which is given as $A'_p = \alpha \frac{\pi}{4} \rho a^2 b$, where α is given for a square plate ($a = b$) as 0.5790, and ρ is the mass density ($4430 \frac{kg}{m^3}$). Given that both sides of the plate are oscillation, we have $A_p = 2A'_p$, in the formula:

$$\frac{f_{H_2O}}{f_{air}} = \frac{1}{(1 + \frac{A_p}{M_p})^{1/2}}, \quad (5)$$

Fig. 6: (left) images of shock waves for *ps* laser ablation of *Ti* plate (right) anisotropic nature of shockwave expansion (*inset*) schematic of stress wave reflected off of bottom of target resulting in an additional shock wave .

where f_{H_2O} and f_{air} are the frequencies in water and air respectively, and M_p is the mass of the plate. This analysis yields $f_{H_2O} = 20.7 \text{ kHz}$. This frequency is far too low to result in the horizontal lines observed in the lower left of figure 6. These images bear more than a passing resemblance to those observed in Ref.[28]. In the present case, the thin nature of the plate and the large differences between the acoustic impedance of the *Ti* plate and water lead to a large number of reflections within the plate, thus resulting in a large number of secondary shock waves present in water. The reflection coefficient for the stress wave at the boundary is given as:

$$R = \left[\frac{1 - \Gamma}{1 + \Gamma} \right]^2, \quad (6)$$

where $\Gamma = \frac{Z_{Ti}}{Z_{H_2O}}$ is the ratios of the acoustic impedance of *Ti* to H_2O . The acoustic impedance is given as $Z = \rho c_s$ where c_s is the longitudinal speed of sound within the material. For *Ti*, this is commonly accepted at $6100 \frac{m}{s}$. This results in a reflection coefficient of 0.8 for the stress wave within the *Ti* plate.

If we compute the round trip time for the stress wave in the plate as $\Delta t = \frac{2h}{c_s} = \frac{3 \times 10^{-4} m}{6100 \frac{m}{s}} \approx 50 ns$, we see that the appearance of the horizontal bands in figure 6 are well accounted for.

2.3.2 Cavitation Bubble

During the laser ablation process, a cavitation bubble appears directly over the irradiated spot. Several microseconds after the laser pulse arrives, the cavitation bubble grows rapidly as shown in figure 7. After $80 \mu s$, the bubble collapses and rebounds twice. This is similar behavior to that observed by several authors [26, 29–31], with the exception that our first collapse occurs at approximately 1/2 the time of the other authors. This is likely due to the differences between *ns* and *ps* ablation dynamics.

We observe many of the same features that others, such as the spherical shock wave that occurs after the central bubble collapses [26]. In addition, our results bear a strong similarity to the “conventional” solution to the Rayleigh-Plesset Equation in Fig 1 of Ref. [29], in that the rebound

Fig. 7: Development of the central cavitation bubble at specified times after the laser pulse arrived. It takes $40 \mu s$ for the bubble to achieve maximum radius. A “pancake” mode collapse is occurring at $80 \mu s$ after the laser pulse arrived. A second collapse occurs $150 \mu s$ after the laser pulse arrives.

bubble is much smaller than the original. The bubble radius as a function of time is shown in figure 8

A full solution to the Rayleigh-Plesset equation is beyond the scope of this study. However, much can be learned by considering the initial phase of growth of the bubble along with the collapse. First, the critical time for thermally controlled growth can be calculated as:

$$t_c = \frac{p_v - p_\infty^*}{\rho_L} \frac{1}{\Sigma^2}, \quad (7)$$

where p_v is the vapor pressure within the bubble, p_∞^* is the pressure far from the bubble, ρ_L is the density within the liquid, and Σ is the thermophysical parameter [32]. Using values consistent with the spinodal temperature for water, we calculate that $t_c \approx 1.5 \text{ ns}$. Therefore, all bubble growth is consistent with the thermally controlled regime. This is not surprising given the high temperatures that are reached at the surface of the target.

The bubble radius can be written as a function of time as,

$$R = \frac{1}{2C(\frac{1}{2})} \frac{\rho_L c_{pL} \Delta T}{\rho_v L} (\alpha_L t)^{\frac{1}{2}}, \quad (8)$$

where c_{pL} is the heat capacity of the liquid, ΔT is the temperature change induced by the laser, ρ_v is the density of the vapor, L is the latent heat of vaporization, α_L is the thermal diffusivity, and $C(\frac{1}{2}) = \frac{1}{2} \left(\frac{3}{\pi}\right)^{\frac{1}{2}} \int_0^1 \frac{z^{1/2}}{(1-z^3)^{1/2}} dz = \frac{1}{2} \left(\frac{\pi}{3}\right)^{\frac{1}{2}}$.

2.3.3 Post-Irradiation Images

Shadowgraphy images were captured for laser irradiation of neat DDI water and solutions that contained TiO_x nanoparticles. The irradiation conditions are described in section 2.2.1. As previously described, this causes the nanoparticle size distribution to change from a roughly bimodal distribution with two wide peaks centered at 100 nm and 225 nm , to a monomodal distribution with an

Fig. 8: Central cavitation bubble radius as a function of time after the laser pulse arrives. The inset shows the shockwave that follows the first collapse. A blue dashed line indicates the position of the shock front created by the collapsing bubble.

Fig. 9: Initial expansion period of cavitation bubble and fit to equation (8). Using parameters consistent with the spinodal temperature of water would predict a prefactor of $3.0 \times 10^{-4} \frac{m}{s^{1/2}}$.

Fig. 10: Irradiation of (top) DDI water and (bottom) colloidal solution of TiO_x nanoparticles with 532 nm and 0.66 mJ laser pulses that are 25 ps in duration. The images are captured $20\text{ }\mu\text{s}$ after the green laser pulse is incident from the left.

average diameter of $2.2 \pm 0.6\text{ nm}$ as determined by high resolution TEM. While the initial nanoparticle suspension produced by laser ablation might vary somewhat in terms of the width and position of the peaks, the final colloidal solution is highly reproducible.

The cavitation bubble and shockwave images for DDI water show much in common with earlier studies [33, 34], and they will not be extensively discussed here. In figure 10, we show the difference between the images for DDI water and colloidal TiO_2 at a time delay of $20\text{ }\mu\text{s}$ after the laser pulse arrives. It is clear that the cavitation bubble is much more axial in the case where nanoparticles are present in solution and this is characteristic of light scattering by larger particles on the order of tens of μm or greater [35]. Since the largest particles present in the solution are less than $1\text{ }\mu\text{m}$, it seems likely that this scattering pattern is created by small cavitation bubbles created by rapid heating in the vicinity of nanoparticles within the solution. These bubbles could, in turn, strongly scatter laser light, thus resulting in the observed pattern.

The post-irradiation of the nanoparticle solutions produces a variety of observed phenomena such as laser-induced shock, cavitation-bubbles, and shock waves generated by collapsing bubbles. Bubble collapse is a very violent event resulting in high temperatures and pressures. In fact, the lower left panel in figure 11 clearly shows plasma emission from the vicinity of a collapsed bubble. This points to a very violent process in which the pressure reaches GPa at the liquid boundary near the collapse [33] and between $10 - 100\text{ GPa}$ at the center of the collapse [29]. Likewise, the temperature is expected to reach the order of 10^4 K for a short time during the collapse as well [29]. These temperatures and pressures are clearly enough to induced fragmentation of nanoparticles.

Fig. 11: Shadowgraphy images for 532 nm irradiation of colloidal TiO_x solutions. The delay relative to the incident laser pulse is indicated in the upper right of each frame in microseconds. In the upper left, we see a cylindrical shockwave expanding outward and superimposed on a spherical shock from a collapsed bubble. In the upper left and lower right, spherical shock waves from collapsed bubbles travel outward. Finally, in the lower left, the presence of plasma emission is observed immediately after collapse.

Sample	details	Eq. time (min)	% change @ 210 min
a	Irr. TiO_2 - visible	85	3.4
b	Non-Irr. TiO_x - dark	175	5
c	Irr. TiO_2 - dark	180	5
d	Non-Irr. TiO_x - visible	—	13
e	No NPs - UV	—	18
f	Non-Irr. TiO_x - UV	270	39
g	Irr. TiO_2 - UV	360	66

Tab. 1: Details of photocatalytic samples

Fig. 12: Photocatalytic response of TiO_2 nanofluids

2.4 Photodegradation of Methylene Blue

To study the photocatalytic effects of our TiO_2 solutions, we monitored the decomposition of methylene blue ($C_{16}H_{18}N_3SCl$) in our nanofluid under UV and visible light exposure. A 4 mL quartz cuvette contained 1.5 mL of 100 μM methylene blue dissolved in DDI water with an additional 1.5 mL of TiO_2 solution. This cuvette was placed on a magnetic stirrer and housed in aluminum casing to enclose the UV-Visible radiation. The light source was a mercury-vapor lamp with an intensity of $5100 \frac{\mu W}{cm^2}$ @ 254 nm incident on the front surface of the cuvette.

UV-Vis absorbance spectra were taken at several exposure time intervals from 0 to 210 minutes and are displayed in figure 12. Here, samples *f*) and *g*) refer to particles before and after 532 nm irradiation as described in section 2.2.1.

In table 1, we summarize the details of the photocatalytic response of the samples. As controls, two samples were kept in the dark and monitored for degradation. Two samples were irradiated with broadbanded visible and near-IR light from a *W* lamp. Finally, two samples were irradiated with UV irradiation from a *Hg* lamp. The absorption peak at $\lambda = 664$ nm is measured to monitor the degradation of the dye.

As shown in figure 13, the essential result from this study is that the anatase particles showed the highest photocatalytic activity when irradiated with UV light, as previous studies have shown [7, 8]. The UV-irradiated polymorphic nanoparticles also caused significant photodegradation of the dye as well. Finally, the polymorphic nanoparticles showed a photocatalytic response when irradiated with visible/near-IR irradiation confirming their sensitization to solar light. The activity is

Fig. 13: Degradation of $\lambda = 664 \text{ nm}$ peak with time during irradiation. Letters correspond to sample designations in table 1. Note data was fitted to a first-order exponential model containing a constant offset parameter that accounts for absorbance contributions from the nanoparticles.

comparatively low however their size is quite large hence a majority of the photogenerated charge carriers likely do not have sufficient time to reach surface reaction sites before recombining. None of the “dark” samples showed significant degradation.

3 Conclusions

In conclusion, TiO_2 nanoparticles synthesized by laser ablation in DDI water produced only polymorphic NPs containing defect states. While these as-prepared NPs display poor photocatalytic activity on their own they may be good candidates for forming plasmonic photocatalyst nanostructures which require intermediate bandgap states. Post-irradiation of the polymorphic solution with picosecond pulses induced a transformation into ultra-small and highly crystalline anatase particles with excellent photocatalytic activity under UV light. Shadowgraphy images, in vicinity of the beam waist, during post-irradiation reveals that dielectric mechanical shock from collapse of cavitation bubbles may play in a role along with coulomb explosion in the fragmentation process.

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5 References

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