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ABSTRACT

Laser ablation of a bulk ZnTe target in de-ionized water or ethanol for nanoparticle synthesis was performed using a femtosecond laser beam (190 fs) with UV wavelength (343 nm). ZnTe nanoparticles with the cubic crystal structure are obtained. The largest percentage of the nanoparticles has sizes from ~4 to ~30 nm. Their size distribution histogram follows a lognormal function with a median diameter of ~10 nm. The nanoparticles have a bandgap energy of ~2.5 eV and larger up to ~3 eV for a decrease of the laser ablating pulse energy from 50 to $10 \,\mu$ J. Resonant Raman spectra of the nanoparticles are characterized by the fundamental longitudinal-optical and multiphonon peaks of ZnTe that exhibit a broadening and shift to lower frequencies compared to the bulk material attributed to phonon confinement and surface optical phonons. The ratio of the second to the fundamental longitudinal-optical phonon coupling. Time-resolved optical emission spectra of the laser-induced plasma plume are characterized by neutral Zn and Te lines as well as singly ionized Te lines observed at the early times of plume expansion. ZnI emission in de-ionized water decays faster than that in the air due to plume compression by the liquid and its effective cooling. At longer time delays, molecular emission from ZnO in the liquids is observed.

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I. INTRODUCTION

ZnTe with a bandgap of 2.26 eV (at 300 K), low electron affinity (3.53 eV), and highly negative conduction band edge [-1.7 V vs normal hydrogen electrode (NHE)], easiness to be doped p-type, superior non-linear optical properties, and a cubic (zincblende) or hexagonal (wurtzite) crystal structure is an important II–VI semiconductor mainly for optoelectronic applications.¹

In general, nanoparticles (NPs) of a semiconducting material are interesting for applications mainly because when their radius (*R*) is smaller than the exciton Bohr radius (α_X), they behave as quantum dots (QDs) and exhibit properties which are size-dependent.² ZnTe has the largest α_X (~5.3 nm) (Sec. S1 in the

supplementary material) among Zn-based II–VI materials; but, although smaller than that of the corresponding Cd-based ones, its NPs may be more preferable for use in applications since Zn is a human- and environmentally safe element contrary to the highly toxic Cd. The more negative conduction band edge is also advantageous for the application of NPs as photocatalysts.

NPs or, generally, nanomaterials (NMs) of ZnTe have been produced by a variety of methods including the most common hydrothermal synthesis from the chemical reaction between a source of Zn and Te precursors such as, for instance, zinc chloride $(ZnCl_2)$ with sodium hydrogen tellurium (NaHTe) resulting in NPs with an average diameter of 3.2^3 or ~10 nm,⁴ zinc acetate $[Zn(OCOCH_3)_2]$ with sodium telluride (Na₂Te) resulting in 2.6 nm

average diameter NPs,⁵ or using only a Zn/Te molecular precursor such as phenyltellurolate zinc complex [Zn(TePh)₂][TMEDA] resulting in spherical NPs with 4.2 or 5.4 nm average size,⁶ also together with various ligands such as N-acetyl-L-cysteine (NAC), hexadecylamine (HDA), ethylenediamine [C2H4(NH2)2] thioglycolic acid (TGA), or 1-thiolglycerol (TG);⁷ mechanochemical synthesis by the mechanical alloying of a stoichiometric mixture of elemental Zn and Te powders at 300 K under Ar atmosphere using a ball mill resulting in the formation of spherical NPs with ~5 nm size;⁸ ultrasonic (sonochemical) synthesis by the treatment of ZnTe powder in ethanol/water mixture (~40 nm average size NMs); microwave plasma heating of a mixture of Zn and Te powders in a closed ampoule under Ar atmosphere (~73 nm size faceted NPs);¹⁰ heating in an autoclave a sodium hydroxide (NaOH) aqueous solution of Zn and Te powders resulting in smaller (67 nm) spherical and larger (112 nm) polyhedral shape particles;¹¹ chemical reaction of zinc acetate with pollytellurides as the tellurium precursor resulting in the synthesis of ZnTe nanorods (NRDs) with a wurtzite crystal structure (dimensions from 21.5 to 140.1 by 3.5-7.0 nm);¹² or vapor deposition growth of ZnTe flakes from ZnTe or together with Te powders at 1010 or 950 °C in Ar/H₂ gas.^{13,14} In these methods, the NP size and shape was controlled by the reaction/ treatment temperature and time duration, as well as the ligands used.

Laser ablation of a bulk target material in liquid provides an alternative method for the synthesis of NPs and colloidal solutions with the main advantage compared to the traditional methods of synthesis that, at least, in the case of ablation in water, the NPs are synthesized with bare, ligand-free surfaces while the produced colloidal solution contains no reaction by-products since no chemical precursors or ligands are used for NP synthesis.¹⁵ Also, chemical reactions that may occur between the ablated species and the liquid molecules can lead to the formation of new materials in the synthesized NPs by the combination of chemical elements from the target material and the liquid.¹⁶

Throughout the years, laser ablation in liquids of a number of II–VI based bulk semiconductors has been performed for NP/ NM synthesis including CdS (1064 nm/7 ns/100–500 mJ/15 min/ methanol¹⁷ or 800 nm/100 fs/1 kHz/11.5–16.0 mW cm⁻²/5 min/ de-ionized (DI) water);¹⁸ ZnS:Cu (800 nm/100 fs/1 kHz/2.0–2.9 J cm⁻²/60 min/DI water);¹⁹ ZnS (355 nm/Nd:YAG/10 Hz/ 100 mJ/60 min/SDS or CTAB);²⁰ ZnS (355 nm/10 ns/10 Hz/ 3 J cm⁻²/DI water);²¹ CdSe (1064 nm/7 ns/10 Hz/1.32–2.92 J cm⁻²/ 20 min/methanol);²² and ZnSe (1064 nm/240 ns/2 kHz/91 J cm⁻²/ 10 min/ethanol or acetone).²³

Laser ablation of ZnTe for NP synthesis has only been performed so far in Ar gas atmosphere (532 nm/7 ns/20 Hz/20 mJ) using targets composed of compression compacted Zn and Te micro-powders;²⁴ no Zn-related peaks (additionally to ZnTe) were found in the x-ray diffraction (XRD) patterns from the differential mobility analyzer (DMA) classified NPs that were produced from a Zn-rich ZnTe target (Zn:Te = 6:4) and, subsequently, annealed in Ar gas atmosphere at T = 300–600 °C, whereas based on electron probe microanalysis (EPMA) results, the Te-rich content was found to be conserved in NPs produced from a Te-rich ZnTe target (Zn:Te = 4:6) that were subsequently annealed even at 800 °C.²⁴ Laser ablation in N₂ (or H₂) gas atmosphere (192 nm/ArF laser/ 40 mJ) of a ZnTe stoichiometric hot-pressed target produced ZnTe@ZnO core-shell crystalline-amorphous NPs, whose size was found to be smaller at larger distances from the target and, at higher gas pressures, at a certain distance from the target.^{25,26}

Optical spectroscopy of photon emission from the electronically excited plasma plume species (atoms, ions, or molecules) during expansion of the plume, which is traditionally termed as laser-induced breakdown spectroscopy (LIBS), and, particularly, time-resolved dynamics aid in providing information about the formation of plasma plume species and the chemistry of the plume, and allow for the determination of the characteristic parameters of the plasma, such as temperature and electron density, that critically determine the mechanisms of the synthesis of NPs or NMs and other species by laser ablation of a bulk target material.²⁷

From optical emission spectroscopy of the laser ablation (355 nm/10 Hz/10 mJ) plasma plume of a bulk sintered ZnO target in oxygen gas atmosphere, the increase of gas pressure was found to lead, after a certain distance from the target, in an increase and a decrease of the population of the excited neutral (ZnI) and singly ionized (ZnII) Zn atoms, respectively, that would had, as a result, an improvement of the stoichiometry of ZnO films grown on a substrate contrary to the ablation in high vacuum that would invariably had led to the growth on non-stoichiometric films.²⁸ Under laser ablation $(248 \text{ nm}/20 \text{ ns}/10 \text{ Hz}/\sim 8 \text{ J cm}^{-2})$ of a bulk ZnO target in oxygen gas atmosphere, emission lines from ZnI, ZnII, and OI were detected in the optical emission spectra of the plasma plume, whereas in vacuum, a photoluminescence (PL) emission band in the green from ZnO was recorded, which was attributed to the ZnO clusters ejected from the target surface. The ZnI species had a lower kinetic energy than the ZnII species.²⁹ The laser-induced plasma parameters were determined from the LIBS spectra in ambient air of the ZnSe compacted target from powders.³⁰ LIBS in liquids of different materials $\frac{3}{33}$ has been explored so far mainly for chemometrics, i.e., determination of the elemental stoichiometry of the target material.³¹ The use of $\frac{4}{7}$ LIBS of fs pulses compared with ns or ps pulses avoids a secondary interaction of the ablating laser pulse with the plasma plume from the material (plasma heating effects).

This paper involves laser ablation of a bulk ZnTe target for the first time in liquids (DI water or ethanol) for NP synthesis. The synthesized NPs were characterized by UV–vis absorption spectrophotometry, XRD, Transmission Electron Microscopy (TEM)/High Resolution TEM (HRTEM), and Raman spectroscopy, whereas the laser-induced plasma by time-resolved optical emission spectroscopy was compared with that formed upon ablation of the target in ambient air. The morphology, energy bandgap, crystal structure, and electron–phonon coupling (EPC) properties of the synthesized NPs as well as the optical emission spectral parameters of the laserinduced plasma were determined, the physical phenomena that were responsible for attributing those properties to the synthesized NPs were analyzed and explained, and the NP properties and characteristics were compared with those of the other ZnTe-based NMs in the literature.

II. EXPERIMENTAL DETAILS

The bulk target material was a piece of ZnTe single crystal with dimensions of $10 \times 10 \times 3 \text{ mm}^3$ that had been grown from the

melt using the vertical Bridgman growth method.³² It was ablated while lying stationary at the bottom of a container filled with either DI water (Sigma-Aldrich 38796-1L) or absolute ethanol (Honeywell 603-002-00-5). The UV wavelength of 343 nm of a fs laser beam with a pulse width of 190 fs and a pulse repetition rate of 1-6 kHz was chosen for ablation. The UV wavelength was obtained by converting the fundamental IR laser beam wavelength (1030 nm) using a standard optical setup consisting of β -barium borate (BBO) crystals, half- and quarter-waveplates, and mirrors. The beam was vertically impinging onto the horizontally lying target at the bottom of the container and the target surface was scanned under the stationary beam in a meandering fashion (5 mm length, 0.01 mm pitch, and 1 mm/s scanning speed) using a computer-controlled translational stage. Ablation was performed for a time duration of 7.30 min to produce NP colloidal solutions for characterization. Pulse energies in the range of $10-50\,\mu$ J were used corresponding to the calculated fluences of 26-130 J/cm² considering the optical setup parameters (focused beam diameter $\sim 7 \,\mu$ m). Under the present conditions of ablation, no bubbles were visually observed to be formed in the liquid or on the target surface. At the beginning of ablation, the optical emission spectrum of the laser-induced plasma plume was measured by collecting the plume emission light using an achromatic lens positioned at a 45° angle relative to the normal and by focusing it at the entrance of an optical fiber that was coupled to an echelle spectrometer (Andor Mechelle 5000) equipped with a gateable, intensified chargecoupled device (ICCD) camera (iStar 334 T). The ICCD camera detector was synchronized with the trigger of the laser pulse using a digital delay generator (AtomTrace, AC-DDG-4). The time delay of the ICCD (t_d) was chosen to be between 2 and 50 ns, the gate window (tw) between 100 and 200 ns, the number of pulses for each shot between 1000 and 6000 (corresponding to the laser pulse repetition rate), the number of accumulations for each shot between 1 and 50, and the spectral resolution to be 0.1 nm to maximize the signal-to-noise ratio (SNR) in the measured spectra. All spectral measurements were completed soon after starting the ablation (typically within the first minute or earlier). For comparison purposes, experiments were also performed on the target in ambient air using the same ablation and detection parameters. Following ablation of the target in liquid, the produced solutions were characterized using UV-vis absorption spectroscopy (UVProbe Shimadzu spetrophotometer). The ablation products from solution droplets which were dried out on carbon-coated grids were characterized using TEM/HRTEM (Tecnai G2 F20 X-TWIN, FEI) whereas those deposited as a thin film by dropcasting the solutions on clean glass substrates (circular disks with a diameter of 6 mm), while keeping them on a hot plate at $T \sim 40$ °C, were characterized first using XRD, a diffractometer with a Cu K_{α} source ($\lambda = 1.54183$ Å) [SmartLab (Rigaku)], and then, Resonant Raman Scattering (RRS) using an inVia Raman microscope (Renishaw) equipped with a thermoelectrically cooled -70 °C CCD camera and microscope. Raman spectra were excited with the 532 nm radiation from a diode pumped solid state (DPSS) laser (Renishaw). These spectra were collected and averaged from different locations on the sample surface. To avoid any damage of the sample by the excitation beam, the laser power on the sample was restricted to 0.03 or 0.06 mW. The Raman wavenumber axis

was calibrated using the Si standard peak at 520.7 cm^{-1} . The emission lines in the optical emission spectra of the plasma were identified using the NIST database³³ and Plasus SpecLine software Version 2.1.

III. RESULTS AND DISCUSSION

The irradiating fs laser pulse travels through the liquid layer that is transparent to its wavelength and lies above the surface of the target material. The beam with a photon energy (3.61 eV corresponding to the 343 nm wavelength) larger than the material's bandgap (2.26 eV) is absorbed by the material via linear absorption. Electrons are excited to the conduction band leaving behind holes in the valence band. The electrons collide with the lattice and transfer their energy to it via electron-phonon coupling in a picosecond time scale (after the end of the pulse) and ablation of the material occurs creating a plasma plume consisting of material species.³ The plume expands within the liquid and is cooled adiabatically while a cavitation bubble is also formed from the vaporized liquid at the plume-liquid interface surrounding the plasma plume. The NPs are created by nucleation in the plasma plume from the material under the conditions of supersaturation followed by their growth and coalescence in the plume and cavitation bubble but also depending on the pulse energy NPs that may also be directly ejected from the material in the form of liquid droplets. When the plume quenches, NP ripening occurs in the bubble and liquid³⁵ and, finally, when the bubble collapses, the NPs are released into the liquid.

A. TEM/EDX

TEM images of the synthesized NPs in each liquid are shown fin Figs. 1(a), 1(c), and S3 in the supplementary material. It is observed that the NPs have an almost spherical shape. Size distribution histograms of the NPs by counting more than 600 NPs on images taken on different areas on each grid are shown in Figs. 1(b) and 1(d). The largest percentage of NPs has sizes from \sim 4 to \sim 30 nm and only a few have sizes larger than that. Their distribution is characterized by a lognormal function with a median diameter of \sim 10 nm. The small difference that may exist in the median diameter of the NPs between the two liquids lies within the measurement error of the diameters on the images and cannot be distinguished in the histograms. A few, very large NPs (a percentage of \sim 1%) with diameters as large as 200 nm are also present in the ensemble and these correspond to the ejected melted droplets^{35,36} [the complete histograms and the corresponding images are shown in Figs. S1(a), S1(b), S2(a), and S2(b) in the supplementary material].

B. XRD

The XRD patterns measured from the NPs are shown in Fig. 2. On the same graph, the reference patterns for the several materials which are identified in the NPs using the software of the diffractometer for pattern analysis are also plotted for comparison. The patterns are predominantly characterized by ZnTe in the cubic crystal system.³⁷ From the relative intensities of the peaks in the patterns for several reflections, it is confirmed that the samples do not exhibit any prevailing crystallographic orientation.

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FIG. 1. TEM images [(a) and (c)] and size distribution histograms [(b) and (d)] of NPs.

Although the strongest (111) reflections of the lattice of NPs for both liquids appear exactly at the same angle with that corresponding to the lattice of the bulk material (25.26°), the other reflections appear at higher angles. This may be due to a lattice contraction in the NPs along the corresponding crystallographic direction³⁸ determined between 0.091% and 0.179%, which makes the lattice not

perfectly cubic. In the pattern from the NPs in DI water [Fig. 2(a)], there is also another weak peak at 27.59° that corresponds to Te.³⁷

In ethanol [Fig. 2(b)], additional to the peaks from Te, the peaks at 27.15° and 23.85° are also distinguished in the pattern that correspond to orthorhombic β -TeO₂.^{37,39,40} This polymorph of TeO₂ is mainly found in naturally formed minerals, but thin films of β -TeO₂ have recently been synthesized on substrates by using pulsed laser deposition (PLD) (248 nm/KrF excimer laser/2 Hz/ 0.8 J cm⁻²) of a TeO₂ target in oxygen.⁴⁰ Notably, HRTEM imaging of the NPs in DI water shows also the presence of β -TeO₂ (Fig. S4 in the supplementary material) but peaks from this material are not distinguished in the XRD pattern [Fig. 2(a)]. TeO₂ appears in the NPs as a result of Te oxidation from the oxygen species that are produced due to liquid decomposition because of the extreme conditions during the ablation process. Te and TeO₂ in the NPs are, most probably, in the form of precipitates or nanoclusters.

C. UV-vis spectrophotometry

UV-vis absorption spectra from the NP colloidal solutions produced using different pulse energies are shown in Figs. 3(a) and 3(b). The spectra are characterized by an absorption that starts at high wavelengths, increases slowly toward lower wavelengths, and exhibits a "kink" at a wavelength of \sim 300 nm below which it increases sharply. There is not any well defined peak appearing in the spectra because of the wide NP size distribution. This absorption appears as a broad background absorption becomes higher when a higher pulse energy is used for ablation due to the increase in the ablation rate of the target material that results in an increase of the NP concentration in the solution. The absorption spectra resemble those measured for a few chemically prepared ZnTe NP solutions.³

Based on the quantum confinement model for QDs (Sec. S2 in the supplementary material), NPs with a diameter of ~ 10 nm (as determined from the TEM images) are expected to have a bandgap energy of ~ 2.5 eV. Thus, the synthesized NPs exhibit a moderate quantum confinement. The onset of absorption in the spectra [Fig. 3(a)] that starts at lower wavelengths (starting from the high wavelength side) when using a lower pulse energy indicates a decrease in NP size with the decrease in pulse energy and, thus, a





and ethanol (b) $(30 \,\mu J/6 \, kHz)$.

corresponding increase in the bandgap. It is estimated that the bandgap takes values from ~2.5 to ~3 eV for a change of pulse energy from 50 to $10 \,\mu$ J for the NPs synthesized in DI water. In this analysis, we consider the contribution to the measured absorption spectra of the NPs of other materials, Te and TeO₂, that were identified in the ensemble with the XRD measurements (Fig. 2) as negligible due to the relatively small percentage quantities of these materials in each ensemble compared to those of ZnTe.

An increase in the NP size with fluence was observed previously in the case of fs laser (800 nm/100 fs/1 kHz) ablation of Cu-doped ZnS in DI water where NPs were formed with a small mean size that increased from 2.1 to 4 nm with the increase in fluence from 2.0 to 2.9 J/cm² and narrow size distributions that resulted in the appearance in the UV-vis absorption spectra of a distinguishable peak corresponding to their bandgap.¹⁹ In the case of laser (532 nm/Nd:YAG laser/30-90 mJ/10 Hz) ablation of Ag in an aqueous solution of a surfactant [sodium dodecyl sulfate (SDS)],⁴¹ the increase in the NP size with pulse energy for constant surfactant concentration was attributed to the increase in the size of the embryonic particles for nucleation and NP formation in the plasma plume with the density of Ag atoms in the plume due to the increase in the ablation rate with fluence. An increase in the size of Pd NPs from ~3.5 to ~4.5 nm was measured for an increase in fluence from ~9 to $\sim 20 \text{ J/cm}^2$ under a 355 nm laser wavelength ablation (3–6 ns/





ablation of an Al₂O₃ doped ZnO target in MilliQ water⁴³ using a stationary beam, the increase in the size of the formed NPs with laser energy was assumed to be due to the larger target volume ablated that results in a higher gaseous density of the plasma plume, thus increasing the probability of the growth of larger NPs.

D. Raman spectroscopy

Raman spectra from the bulk material and NPs excited by the 532 nm Raman laser beam are shown in Fig. 4 after subtracting the broad fluorescence background. The spectra were measured using powers (power densities) of $0.06 (3 \times 10^3)$ and 0.03 mW $(1.5 \times 10^3 \text{ W/cm}^2)$ for the bulk material and NPs, respectively, which were lower than the reported thresholds to induce structural changes of the material with the formation of Te precipitates $[4.4 \times 10^5 \text{ W/cm}^2 \text{ for ZnTe epilayers } (\sim 120 \text{ nm thickness}) \text{ grown}$ on GaAs(001) substrates by closed space sublimation⁴⁻ ⁴ and $\sim 13.56 \times 10^4$ (554 μ W) and $\sim 0.5 \times 10^4$ (20 μ W) W/cm² for 800 and 73 ± 9 nm diameter NWs, respectively⁴⁵]. The spectra are characterized by the Γ -point longitudinal-optical phonon fundamental (1LO) and multiphonon (2LO, 3LO, and 4LO) vibrational mode peaks of ZnTe, which appear at 207.6, 413, 618.3, and 823.6 cm⁻¹ for the bulk material; 207.4, 411.8, 616.1, and 818.7 cm⁻¹ for the



FIG. 4. Raman spectra of the NPs and the bulk material. The spectra have been shifted vertically for clarity.

NPs in DI water; and 207.4, 411.1, 616.1, and 815.1 cm⁻¹ for the NPs in ethanol, respectively.46-48 The multi-phonon overtones appear at energies that are multiples of the fundamental LO phonon energy ($E_{LO} = 0.025 \text{ eV}$). The LO multi-phonon peaks are observed in the spectra because their scattering cross section is significantly enhanced compared to the TO phonons due to the strong incoming resonance since the excitation photon energy $(E_{ex} = 2.33 \text{ eV})$ is close to the bandgap of the bulk material $(E_g = 2.254 \text{ eV})$ and NPs or equal to the sum of the bulk bandgap energy and up to three times LO phonon energy in ZnTe $(\hbar\omega_{LO} = 0.026 \text{ eV})$;⁴⁹ the coupling of excitons to LO phonons via the Fröhlich interaction is resonantly enhanced.⁵⁰ Due to the relatively wide NP size distribution (Fig. 1) and, thus, energy bandgaps, this also means that NPs smaller than a certain size will make a negligible contribution to the spectra since their bandgaps will be away from the resonant condition.

The peaks that appear in the spectra of the NPs in the region of 90-180 cm⁻¹ are known to be the first order Raman modes of trigonal Te (A₁ at 128 cm^{-1} and E¹ and E² optical phonon modes at 103 and 145 cm⁻¹, respectively)⁵¹ and originate from polycrystaline Te clusters or precipitates in the form of nanocrystalline grains or layers of pure Te that are on the surface of the NPs or inside their volume.⁵¹⁻⁵³ The origin of the weak peak at 709 cm⁻¹ is still unknown but it may be related to β -TeO₂.^{54,55} The other reported Te bands at 267, 396, and 644 cm⁻¹,^{44,52} the β -TeO₂ B_{1g} and B_{2g} bands at 189 and 225 cm⁻¹, respectively,⁵⁴ as well as the other reported β -TeO₂ bands⁵⁵ could not be identified in the spectra. In addition to the shift of the LO peaks for the NPs to lower frequencies, they also exhibit a slight asymmetry and broadening toward lower frequencies, which become more pronounced for the 2LO peak compared to the 1LO peak, which are typical characteristics of the LO peaks of semiconductor nanocrystals.⁵⁰ In addition to the optical phonon confinement effect, the peaks attributed to surface optical phonons appear as shoulders at the low frequency side of the main LO peaks (SO and 2SO at \sim 200 and \sim 400 cm⁻¹ for the 1LO and 2LO peaks, respectively).5

From the Raman spectra, the ratio of the integrated intensity of the 2LO to the 1LO peak (R_{21}), which is a measure of the strength of the EPC in the materials, is determined to be ≈ 4.75 for the bulk material and ≈ 0.84 and 0.90 for the NPs in DI water and ethanol, respectively. The relatively high value of R_{21} for the bulk material indicates that the crystal contains a negligible concentration of impurities such as O or, far most, a third element.⁴⁵ The lower value of R_{21} in the NPs compared to that in the bulk material has been explained previously^{56,58–60} by the enhancement of the electron–hole overlap in the NM compared to that in the bulk that had, as a result, the decrease of the ability of the electric field associated with lattice vibrations to polarize the exciton (the exciton– phonon Fröhlich interaction becomes weaker) and, thus, a reduction in electron–vibration coupling.

E. Optical spectroscopy of the laser-induced plasma in liquids and air

The optical emission spectra of the laser-induced plasma were measured upon target ablation in the liquids and ambient air using the same ablation and detection parameters for comparison to identify the species that are produced from material ablation and contribute to NP synthesis. In general, the spectra in liquids are weaker in intensity compared to those in air mainly due to the scattering and/or absorption of the plasma emitted radiation by the liquid and there is also the absence of plasma heating effect by the laser pulse due to the use of a fs laser pulse for ablation.

The peaks corresponding to the characteristic triplet structure of ZnI appear at 468.01, 472.21, and 481.05 nm corresponding to the transitions $3d^{10}4s5s$ ${}^{3}S_{1} \rightarrow 3d^{10}4s4p$ ${}^{3}P_{Ji}^{\circ}$ with $J_{i} = 0$, 1, and 2, respectively (Fig. 5). 33 In addition, in air as well as ethanol, the ZnI line at 636.23 nm (4s4d ${}^{1}D_{2} \rightarrow 4s4p$ ${}^{1}P_{1}^{\circ}$) also appears.

From the NIST database, the strongest TeI lines are expected below 350 nm and above 900 nm that fall outside of the spectral region where the current spectrometer system can provide meaningful data. However, in the measured spectral region from ~350 to ~900 nm, the next most intense TeI line in the database appears weak at 875.82 nm (6p ${}^{3}P_{2} \rightarrow 6s$ ${}^{5}S_{2}^{\circ}$) in the spectra in air [Fig. 6(a)]. At early time delays (~50 ns) when the density of ions is high, the TeII line appears at 468.69 nm (6d ${}^{4}D_{7/2} \rightarrow 6p$ ${}^{4}P_{5/2}^{\circ}$) as a weak shoulder in the high wavelength side of the 468.01 ZnI line in air [Fig. 6(b)] but is extinguished after ~80 ns. Also, at a time delay of ~120 ns, the 483.13 nm (6d ${}^{4}P_{5/2} \rightarrow 6p$ ${}^{4}D_{3/2}^{\circ}$) TeII line is barely distinguished in the high wavelength side of the 481.05 nm ZnI line but disappears after ~130 ns [Fig. 6(c)].

For longer time delays, a line at 546.16 nm is distinguished in the spectra in DI water and ethanol (Fig. 7), which is attributed to the molecular emission from ZnO (Plasus).^{29,61} Formation of ZnO (more likely amorphous) can be considered as an indication of the consumption of ablated target Zn species for the formation of products other than ZnTe. Upon ablation in ethanol, the C_2 Swan band at 516.47 nm also appears (Sec. S6 in the supplementary material).

The integrated intensity (normalized to one) of the ZnI 481.05 nm line determined from the spectra in DI water and air is shown in Fig. 8 to investigate the emission dynamics of ZnI atoms. The intensities increase with the delay time and attain a maximum



FIG. 5. Laser-induced plasma spectra around the region where the Znl triplet structure appears measured for different time delays in air ($50 \mu J/6 \text{ kHz}$) (a), DI water ($50 \mu J/6 \text{ kHz}$) (b), and ethanol ($30 \mu J/6 \text{ kHz}$) (c). The spectra in (b) and (c) have been shifted vertically for clarity.

and then decay. By fitting an exponential function to the line decay portion of the data, the decay time constants which denote the characteristic lifetime of emission are determined to be equal to 37.84 ± 1.79 and 23.77 ± 6.17 for air and DI water, respectively. The smaller time constant in DI water compared to that in air is because of the shortening of the plume expansion lifetime in liquid due to the compression that the plume experiences from the liquid as well as its effective cooling by water. The decay time constant of a laser-induced plasma emission line is not only related to the transition probability associated with the line but also to the corresponding upper level population density, and, thus, because of the constant production of excited atoms due to the continuous laser radiation, ⁶² the determined constants are higher than the natural time constant of 8 ns of the 481.05 nm line transition.

From the ZnI lines in air, the electron density of the plasma was calculated (Sec. S3 in the supplementary material) and it changes from $\sim 1.1 \times 10^{16}$ to $\sim 0.1 \times 10^{16}$ cm⁻³ from 190 to 300 ns (Fig. S7 in the supplementary material).

The H_{α} line at 656.28 nm appears strong in the spectra in DI water [Fig. S8(a) in the supplementary material] but is absent in the spectra in air or ethanol most probably due to lack of enough humidity in the laboratory atmosphere or ethanol dissociation in



FIG. 6. Laser-induced plasma spectra measured for different time delays in air (50 μ J/6 kHz) where Tel (a) and Tell (b) and (c) lines are distinguished. The spectra have been shifted vertically for clarity.

species other than atomic hydrogen, respectively. This (as well as the OI line) appears in the spectra in DI water only for pulse energies of 50 and $40\,\mu$ J but are absent for $30\,\mu$ J and below. The H_{α} line is extinguished at ~60 ns before the appearance of any material lines which appear after that time delay [Figs. 8 and S8(a) and S8(b) in the supplementary material]. From the H_{α} line in DI water, the electron density was determined (Sec. S4 in the supplementary material) and it changes from ~ 2.5×10^{16} to ~0 cm⁻³ from 10 to 60 ns [Fig. S8(c) in the supplementary material].

In the spectra in air, only the OI line at 777.19 nm $(3p {}^{5}P_{J\kappa} \rightarrow 3s {}^{5}S_{2}^{o})$ appears weak [Fig. S9(a) in the supplementary material] whereas in DI water, both this (triplet at 777.19, 777.42, and 777.54 nm for $J_{\kappa} = 3$, 2, and 1, respectively) and the other OI



FIG. 7. Laser-induced plasma spectra measured for different time delays in DI water ($50 \mu J/6 \text{ kHz}$) (a) and ethanol ($30 \mu J/6 \text{ kHz}$) (b) showing the ZnO molecular emission line. The spectra have been shifted vertically for clarity.

line at 844.64 nm (3p ${}^{3}P_{2} \rightarrow 3s {}^{3}S_{1}^{\circ}$) appear strong [Figs. S9(b) and S10(a) in the supplementary material]. Although the strong OI lines in DI water are extinguished at ~70 ns before the appearance of the ZnI lines, in air the weak OI line is present in the spectra up to ~130 ns and together with the appearance of ZnI lines (Fig. 8). From the 777.19 and 844.64 nm OI lines, the plasma temperature was calculated (Sec. S5 in the supplementary material) and it decreases from ~5000 to ~1500 K from 10 to 50 ns [Fig. S10(b) in the supplementary material].



FIG. 8. Integrated intensities of the 481.05 nm Znl line from the laser-induced plasma spectra measured in air and DI water vs time delay.

The local thermodynamic equilibrium (LTE) of the plasma is ensured because the electron density of the plume is higher than the critical density determined from McWhirter's criterion, the plasma relaxation time (τ_{rel}) is smaller than the plasma decay time constant of the electron density, and the diffusion length of atoms/ ions (λ_{diff}) during the plasma relaxation time is much shorter than the typical plume dimensions (Sec. S7 in the supplementary material).

IV. CONCLUSIONS

In this work, NPs in the solution were synthesized by laser ablation of a bulk ZnTe target in DI water or ethanol motivated by the importance of the material for applications in relation to the unique advantage of the method in providing NPs with ligand-free surfaces. A fs laser beam with UV wavelength was used mainly to avoid secondary heating of the laser-induced plasma by the ablating laser beam and also to achieve linear absorption of the beam by the target material. The NPs are almost spherical and their largest percentage has sizes from ~4 to ~30 nm. Their size distribution follows a lognormal function with a median diameter of ~ 10 nm. The NPs retain the cubic crystal structure of the bulk target material. Their bandgap energy is ~2.5 eV and exhibits an increase to \sim 3 eV with the decrease of the ablating pulse energy from 50 to $10\,\mu$ J. The strength of the EPC is lower in the NPs compared to the bulk material as a result of their reduced dimensionality. Zn and Te neutral atoms were identified in the laser-induced plasma plume upon ablation in air as well as Te ions in the early stages of plume expansion. At the later stages of plume expansion in DI water or ethanol, emission from the ZnO formed molecules in the plume was observed that may have consumed the Zn ablated species in 8 the plume. Due to their synthesis in the form of a colloidal solution, almost spherical shape, bare ligand-free surfaces that allow $\frac{1}{20}$ charge transfer across interfaces, moderate quantum confinement, ⁴ and easiness of tunability of their bandgap by the laser ablation pulse energy, these NPs may have many important applications.

SUPPLEMENTARY MATERIAL

See the supplementary material for large area TEM images of the NPs; complete size distribution histograms; additional TEM image of the NPs synthesized in DI water; HRTEM image; calculation of the exciton Bohr radius; calculation of the energy bandgap based on the quantum confinement model; integrated intensity of the ZnI 468.01 nm line in air vs time delay; determination of N_e in air vs time delay from the ZnI 481.05 and 468.01 nm lines; integrated intensity of the H_{α} line in DI water vs time delay; determination of N_e vs time delay from the H_{α} line in DI water; determination of plasma temperature vs time delay from the OI lines in DI water; determination of plasma temperature vs time delay from the Swan band in ethanol; and calculation of McWhirter's criterion, relaxation time, and diffusion length.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Nikolaos G. Semaltianos: Conceptualization (lead); Formal analysis (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Visualization (equal); Writing - original draft (lead); Writing review & editing (equal). Ona Balachninaite: Data curation (equal); Formal analysis (equal); Funding acquisition (lead); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Writing - review & editing (equal). Raimondas Giraitis: Data curation (equal); Formal analysis (equal); Methodology (equal); Validation (equal); Writing - review & editing (equal). Audrius Drabavičius: Data curation (equal); Formal analysis (equal); Methodology (equal); Validation (equal); Writing - review & editing (equal). Gediminas Niaura: Data curation (equal); Formal analysis (equal); Methodology (equal); Validation (equal); Writing review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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