Core—Double-Shell Fe$_2$O$_3$@SiO$_2$@Jarosite Hybrid Nanoparticles Synthesized by Laser Ablation of Turquoise in Ethanol

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**ABSTRACT:** This work highlights a facile green route for the one-step synthesis of iron oxide core—double-shell nanoparticles (NPs) and aluminum phosphide (AlP) nanosheets by pulsed laser ablation of the mineral turquoise target from Nishapur in the presence of an ethanol solvent. High-resolution transmission electron microscopy, selected-area electron diffraction pattern, and field emission scanning electron microscopy (FESEM) in combination with energy-dispersive X-ray mapping revealed the formation of NPs with a typical core@double-shell structure in which crystalline $\alpha$-Fe$_2$O$_3$ (iron oxide) formed the core, while SiO$_2$ (quartz) and (K, H$_3$O)Fe$_3$(SO$_4$)$_2$(OH$_6$) (jarosite) participated as the inner and outer shell, respectively. However, the application of laser ablation on the turquoise phase of the target led to the formation of NPs with a typical core@double-shell structure in which crystalline $\alpha$-Fe$_2$O$_3$ and jarosite phases, while the absorption band at 250–300 nm for the turquoise-ablated species was related to the presence of Cu compound species and also the $\alpha$-Fe$_2$O$_3$ phase in the sample. Photoluminescence emission spectra for the vein-ablated species depicted a peak centered at 370 nm, while a peak located at 364 nm was ascribed to the turquoise-ablated species. In particular, these hybrid NPs with high purity and stability may offer new opportunities for bio-applications such as anticancer agents and water/wastewater applications.

**INTRODUCTION**

Recently, multifunctional materials due to their wide range of applications have attracted considerable attention. In hybrid nanostructures, different physical and chemical properties of multiple components were integrated, which shows higher device performance regarding their characteristic single components. Different hybrid materials were synthesized with versatile structures and various components such as core—shell and double-shell structures (Fe$_2$O$_3$@SiO$_2$, Cu$_{3+}$@Au,$^1$ Fe$_{3+}$Fe$_{3+}$@Si—C—O,$^2$) doped metal oxides,$^3$ noble metal-supported oxides,$^4$ hierarchical oxide heterostructures (TiO$_2$/Fe$_2$O$_3$, ZnO/Fe$_2$O$_3$,$^5$ and so forth. Among the hybrid materials, iron oxide core—shell or double-shell nanostructures motivated fundamental research because of their potential applications in different areas including heavy metal removal by adsorption or reduction,$^6$ NC drug or biomolecules transport,$^7$ pigment synthesis,$^8$ hyperthermia,$^9$ catalysis,$^{10}$ as bio- and chemosensors,$^{11}$ fine ceramics,$^{12}$ and magnetic resonance imaging.$^{13}$ There have been various synthetic strategies to fabricate iron oxide core—shell or double-shell nanostructures such as the selective etching strategy,$^{14}$ microemulsion,$^{15}$ Stober methods,$^{16}$ and the ship-in-bottle approach.$^{17}$ However, the methods listed above suffer from the purity of the surface of nanostructures. While this impurity somewhat blocks the benefit of bioconjugations of their surface. These approaches usually are time-consuming and require multiple high-temperature experimental steps. Additionally, most of the procedures are not green processes because of the use of toxic preservatives or chemical precursors; therefore, a well-established, direct, and environmentally friendly process for the synthesis of iron oxide hybrid nanoparticles (NPs) is still absent.

Liquid phase-pulsed laser ablation (LP-PLA) is a unique and efficient technique for the synthesis of complex nanostructures in a clean manner.$^{18}$ The LP-PLA method has received considerable attention in recent years as a simple and easily operable synthesis technique for preparing the various nanomaterials free of contaminants.$^{19}$ Ultrapure elements,$^{20}$ oxide and non-oxide synthetic compositions,$^{21a,22}$ and polymers and alloys$^{23}$ are usually used as the targets for the synthesis of different nanostructures through the LP-PLA method. Minerals are not commonly used as targets in the LP-PLA approach because of the presence of multiphase structures in the mineral samples. Turquoise is a precious mineral which belongs to a group of inorganic materials with at least six recognized members.$^{24}$ The general formula of the turquoise...
group was written as $AB_n(PO_4)_m(PO_3)(OH)_{n-1}(OH)_8\cdot 4H_2O$, wherein the A position was filled with Cu$^{2+}$ or Fe$^{2+}$ as the most common constituent, while Fe$^{3+}$ and Al$^{3+}$ are situated at the B position.\(^{25}\) Turquoise might also have veins running through it. The wide veins on the surface of turquoise are undesired for high-quality designing of jewelry pieces. The vein of Persian turquoise as our mineral target encompasses three main phases of pyrite, quartz, and jarosite.\(^{26}\) Inspired by this, with the hypothesis of copossessing of iron oxide and silica, synthesis of crystalline core−double-shell NPs through one-step LP-PLA approach, low-cost Persian turquoise with wide veins, inappropriate for jewelry applications, is proposed as a candidate for the ablation target without any manipulation.

In this work, to the best of our knowledge, for the first time, as-prepared nanostructures from the laser ablation of Nishapur turquoise in ethanol medium performed using Ce:Nd:YAG laser in the fundamental wavelength (1064 nm) were studied. The hematite@quartz@jarosite core−double-shell NPs, also produced for the first time through the laser ablation of the vein phase of turquoise, consist of crystalline iron oxide ($\alpha$-Fe$_2$O$_3$) core, silicon oxide (SiO$_2$) inner shell, and jarosite ($\left(K,H_3O\right)Fe_3\left(SO_4\right)\left(OH\right)_6$) outer shell. Laser ablation of the turquoise phase of the target also led to the synthesis of AlP nanosheets.

X-ray diffraction (XRD) pattern analysis, field emission scanning electron microscopy (FESEM) in combination with energy-dispersive X-ray (EDX) elemental mapping, high-resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction pattern (SAED) were utilized for phase and morphological studies, while UV−vis−NIR and photoluminescence (PL) spectroscopy used for characterization of the optical properties of the synthesized nanostructures from laser ablation of Nishapur turquoise in ethanol.

**RESULTS AND DISCUSSION**

A schematic of the setup applied for the laser ablation experiments is shown in Figure 1a. The laser beam was irradiated on the surface of the target going through the 0.01 m
The SiO$_2$ phase were seen in the XRD pattern of the dried well as two weak peaks corresponding to (101) and (110) of studied by FESEM, as depicted in Figure 2. The ethanol medium could be compared considering Figure 3. FESEM images of (a) iron-containing particles (bright particles) prepared from laser ablation of the vein phase of the target; (b) and (c) AlP nanosheets besides Cu compound-ablated species produced from laser ablation of the turquoise phase of the target in low and high magnifications; (e) FESEM of a bright particle along with a line scan of Si and Fe depicted on, (d, f) EDX mapping images for iron oxide-silicon oxide LP-PLA generated core—double-shell particles produced in ethanol, showing the oxidized iron core and also silicon oxide shell.

height of the ethanol solvent. The composition of the vein and turquoise phase of the target before and after the laser ablation were characterized by XRD and is shown in Figure 1b. The vein of the target before laser ablation was mostly composed of jarosite (JCPDS file no. 00-036-0427), hematite (JCPDS file no. 00-033-0664), and SiO$_2$ (JCPDS file no. 00-046-1045), which were consistent with the previously reported results of studies on Iranian turquoise. After laser ablation of the vein, the identified phase was jarosite; however, the most four main peaks ascribed to (101), (012), (021), and (113) planes showed lower intensity relative to the intact vein target. This decreased intensity of the jarosite phase after laser ablation of the vein was due to the lower crystallinity of the as-synthesized product relative to the vein target produced during the ablation process. The full width at half maximum (fwhm) of peaks related to the (012) and (113) planes for the vein before and after laser ablation was not meaningfully changed. A weak peak related to the main peak ((104) planes) of the Fe$_2$O$_3$ phase, as well as two weak peaks corresponding to (101) and (110) of the SiO$_2$ phase were seen in the XRD pattern of the dried solution produced after laser ablation. The presence of iron in EDX analysis (Figure S1) and iron-containing NPs in FESEM images (Figure 2h) confirmed the presence of the iron-containing phase in the vein-ablated species. In the XRD of the turquoise phase of the sample before laser ablation, the turquoise crystalline phase (JCPDS file no. 96-500-0102) besides Fe$_2$O$_3$ (JCPDS file no. 00-033-0664) and AlP (00-012-0470) phases were characterized. After laser ablation of the turquoise phase, the most intense peaks of the turquoise phase, that is, the ones related to (111), (111), and (123) planes completely disappeared, while the three most intensive peaks of the AlP phase, that is, the ones related to (111), (220), and (311) planes were observed. In addition, the two most intensive peaks of the Fe$_2$O$_3$ phase, that is, the ones corresponding to (104) and (110) were identified.

The morphology of the surface of the target before and after 150 min laser ablation (15 runs of 10 min laser irradiation) was studied by FESEM, as depicted in Figure 2. The effect of the laser pulses irradiated on the surface of the turquoise target in the ethanol medium could be compared considering Figure 2a,c for the untreated and irradiated targets, respectively. These overall views of the surface of the target could demonstrate the formation of holes with different depths on the surface of the target (Figure 2c); the deep hole is related to the intense ablation for 150 min ($9 \times 10^4$ shots) in the vein phase versus the shallow cavity which indicated mild ablation on the surface of the turquoise phase. The higher resolution FESEM images of the vein and turquoise phases of the target before laser ablation are shown in Figure 2b,c, respectively. The morphology of fragmented particles of SiO$_2$, Fe$_2$O$_3$, and jarosite constituted in the vein phase is shown in Figure 2b, while an integrated surface structure of the turquoise phase is observed in Figure 2c. The surface structures of the veins and turquoise phases after laser ablation are also depicted in Figure 2f,g, respectively. Considering the FESEM images of the surface of the target after laser ablation (Figure 2f,g), the ablation dynamics of these two phases (vein and turquoise phases) during the laser ablation were different. Regarding the ablation of the vein phase by laser, through the formation of new phases, microreliefs were formed on the surface of the vein phase. The microreliefs were therefore modified by repeating the ablation procedure, and the craters were observed in the formed septums and valleys of the vein phase of the target. These reformed irregular microreliefs on the vein phase of the stone, after 150 min of noncontinuous irradiation, formed irregular microchannels and are shown in Figure 2f. It could be understood from the FESEM image of the vein of the target after laser ablation that the deformation of the surface and the formation of the pore-like structure and incomplete pores were arising from laser-induced heating of the ablation target, subsequent melting, and resolidification of the surface (Figure S2a,b). Resolidified materials were seen over the surface of the vein phase in these images. EDX analysis of different regions from the vein phase (Figure S1a–c) clearly revealed the presence of Fe and Si in the vein phase. On the other hand, the FESEM image from the turquoise phase after 150 min of noncontinuous irradiation showed an irregular geometrical structure, without any effect of melting and resolidification (Figure 2g). For a more detailed study, EDX analysis and mapping were performed on the turquoise phase of the target.
The laser ablation product study was conducted by selective laser irradiation on the surface of the target. After 10 min of irradiation on the vein phase, the liquid environment (ethanol) was smooth. As a result, the energy per pulse sensed by the surface depended on the changing pulsed laser modality. During the ablation, the temperature distribution produced on the surface returned depended on the temperature distribution produced on the target. Subsequent pulses have produced different fluences on the surface; in fact, the energy per pulse sensed by the surface depended on the changing pulsed laser modifications of the solid surface as the ablation continues. When the target was irradiated initially on the nonprocessed surface, the temperature distribution on the surface of the target was different from the same distribution produced upon the laser pulses on the processed target. For the initially stable pulses, the temperature profile was smooth. As a result, the energy density (the laser fluence) on the surface of the target was stable, which led to the narrow size distribution of NPs. During 10 min laser irradiation, the solid surface of the target absorbed lower absorption in the turquoise phase led to lower ablation efficiency of the turquoise phase in the NIR region (1064 nm − ∼1075 nm) resulting from the Fe(II) band, 24 the reflectance of the turquoise phase in the NIR region (1064 nm laser wavelength) is higher than that of the vein phase. This lower absorption in the turquoise phase led to lower ablation efficiency of the turquoise phase (shown in Figure 2e) and led to the change of ablation dynamics in this phase during laser ablation. The surfaces of the turquoise phase before and after laser ablation (150 min noncontinuously irradiation) are illustrated in the back-scattered electron mode FESEM images (Figure 2d,h). After laser ablation of the target, ablated products in the form of nano- and microparticles transferred into the ethanol environment, while some of the as-prepared particles already remained on the surface of the stone target (Figure 2h).

The laser ablation product study was conducted by selective laser irradiation on the surface of the target. After 10 min of irradiation on the vein phase, the liquid environment (ethanol) changed from colorless to dark brown liquid. The color changes were attributed to the formation of nanostructures containing iron oxide species. The turquoise phase of the target was also exposed for 10 min to the laser pulses. FESEM micrographs of the iron-containing NPs, prepared from the laser ablation of the vein, as well as AlP nanosheets produced from the laser ablation of the turquoise phase of the target are depicted in Figure 3a,b,c, respectively. The presence of Cu compound-ablated species in the suspension produced from laser ablation of the turquoise phase is seen in Figures 3c and S5a. Regarding the size distribution of AlP nanosheets, in the applied laser fluence of 178.3 J/cm², broad-peak Gaussian extrapolation was adjusted (inset in Figure S4b). The mean lateral size of AlP nanosheets is measured as 30 nm, while the lateral size of these nanosheets present in the solution was in the range of 30–210 nm. Iron-containing NPs were the bright spheres observed in Figure 3a. For the iron-containing NPs (inset in Figure S4a), the same trend was also seen. Most of the iron-containing NPs were synthesized in relatively small size with the mean size around 20–30 nm; however, substantial 20–550 nm size particles still existed in the suspension. These broad-peak Gaussian distributions were also reported in other laser-synthesized nanostructures. 28 The size of NPs depended on the gained fluency of the surface, which in return depended on the temperature distribution produced on the target. Subsequent pulses have produced different fluences on the surface; in fact, the energy per pulse sensed by the surface depended on the changing pulsed laser modifications of the solid surface as the ablation continues. When the target was irradiated initially on the nonprocessed surface, the temperature distribution on the surface of the target was different from the same distribution produced upon the laser pulses on the processed target. For the initially stable pulses, the temperature profile was smooth. As a result, the energy density (the laser fluence) on the surface of the target was stable, which led to the narrow size distribution of NPs. During 10 min laser irradiation, the solid surface of the target absorbed...
the short laser pulses and melted. Because of the heat transfer from this molten layer of the target to the surrounding liquid layer, this liquid layer heated up. As a result of the high pressure of the adjacent layer that contacted the surface of the target, the microchannels were formed. After the formation of these channels during 150 min of noncontinuous irradiation on the surface (Figure 2f), numerous hot spots located at the channels altered the temperature profile and changed the fluence distribution, thus finally leading to the synthesis of NPs with more broad size distribution. Furthermore, in nanosecond laser ablation, multiple size distribution occurred because of the radiation-related target heating effect. In the nanosecond laser ablation, because of the electron–phonon relaxation process,\textsuperscript{30} the lattice temperature started to increase. When the absorbed energy on the target was sufficiently high, the nanoclusters and atoms were formed. These ablated nanoclusters and atoms tended to agglomerate during or after the laser pulse irradiation. In nanosecond laser ablation, the target itself was heated by the laser-produced plasma and also by the radiation as a direct consequence of the heat diffusion time being much shorter than the laser pulse. This later condition resulted in slow cooling of particles and thus led to the agglomeration of these particles.\textsuperscript{31} The radiation-related target heating effect was strong in the nanosecond and microsecond radiations, wherein the ablated crater was surrounded by the heat-affected zone, leading to the release of large droplets of the materials.\textsuperscript{32}

The FESEM image in combination with the EDX line scan on a single particle is shown in Figure 3d–f. EDX mappings of the same particle regarding the presence of O and Fe–Si were also shown in Figure 3d,f, respectively. The FeO\textsubscript{2}@SiO\textsubscript{2} core–shell structure is clearly distinguishable by the defined phase boundary formed with a decrease of silicon with a simultaneous increase of iron in the center. This trend of iron and silicon variations corresponded with the presence of oxygen, depicted in FESEM and EDX (line and mapping) results, confirms the iron oxide enrichment in the core and silicon oxide in the shell. The diameter of the core and the thickness of the shell for some core–shell structure of these particles have been shown in Figure S2c,d. Considering the FESEM images, the core size of these particles changed from 60 to 410 nm and the shell size (inner and outer shell together) changed from 20 to 150 nm.

For a more detailed analysis of the particle, HRTEM analysis was done on the prepared particles. While FESEM images could not recognize more than two layers (recognition of first and second shell aside), HRTEM images disclosed the presence of two shells and a core. In fact, the outer shell was composed of two different compositions revealed by electron diffraction of the particles, showing the formation of core–double-shell particles. Figure 4a showed a bright-field HRTEM image, confirming the formation of multiple size distributions of particles with a core–double-shell structure by 1064 nm laser ablation in ethanol. The measurement on TEM images indicated that the typical core and shell (inner and outer together) sizes were in the range of 5–205 and 2–145 nm, respectively. The multiple size distributions of particles illustrated using FESEM images were discussed (Figure S4a) in the previous section. A particle with a core-double-shell structure is shown in Figure 4b, in which the outer shell was formed within an identical thickness, although the inner shell was not formed with equal thickness. The dark core was FeO\textsubscript{2} with about 202 nm diameter and the mean thickness of the inner shell of SiO\textsubscript{2} was 82 nm; however, the thinner bright outer shell showed a thickness of 3 nm. To identify the specific compositions of the as-synthesized core–double-shell particles, also evaluation of the crystallinity, inverse fast Fourier transform (FFT) was redrawn (Figure 4c) and also SAED characterization from different areas of the sample was drawn (Figures 4d and S6a,b). The radial profile (circular integration of intensity in reciprocal space) of the diffraction patterns is shown in Figures 4e and S6c,d. For the core, a lattice fringe of 0.27 nm corresponding to the (104) planes of α-Fe\textsubscript{2}O\textsubscript{3} (bottom left inset in Figure 4c) was characterized, while for the inner shell, the measured lattice fringe was 0.25 nm (was marked at the upright of the inset in Figure 4c) which is related to (110) planes of SiO\textsubscript{2}. The lattice fringe of 0.57 nm on the top-left inset in Figure 4c illustrated a characteristic interlayer spacing of 0.57 nm for the jarosite phase (JCPDS file no. 00-036-0427) corresponding to (003) planes. The SAED patterns (Figures 4d and S6a,b) showed the crystalline planes of the α-Fe\textsubscript{2}O\textsubscript{3} core ((202), (223), (424), (501), (515)), and SiO\textsubscript{2} inner shell ((101), (202), (211), (002), (400), (311) planes), and jarosite outer shell related to (511), (431), (217), (330), (438), (405), (146), and (407) planes), which were in good agreement with HRTEM inverse FFT images.

**Optical Properties of Laser-Synthesized Particles and Nanosheets.** The optical absorption properties of laser-synthesized particles and turquoise phase-ablated species at room temperature were studied by UV–vis–NIR spectroscopy (Figure 5a). As shown in Figure 5a, the spectrum of the suspension containing AIP nanosheets and Cu compounds showed broad absorption in the range of 250–300 nm with the maximum peak at 270 nm. Because of the presence of Cu-ablated species in the turquoise phase of the target after the laser ablation of the turquoise phase (Figures 5a and 3c), the absorption spectrum for this sample was intensified in the UV

![Figure 5](https://dx.doi.org/10.1021/acsomega.9b03882)
region. The UV absorption of Cu compounds usually was in the visible region and changed to the UV region with quantum confinement effect enhancement. In addition, UV absorption of the sample was observed because of the direct-charge transfer transition of $O^{2-} \rightarrow Fe^{3+}$ 3d of $\alpha$-Fe$_2$O$_3$ in the turquoise phase-ablated species. However, in Figure 5a, the same spectrum accomplished on the vein phase-ablated species was seen; for the vein phase-ablated species containing the core—double-shell particles, there is a strong absorption region including 250–360 nm corresponding to the direct-charge transfer transition of $O^{2-} \rightarrow Fe^{3+}$ 3d of $\alpha$-Fe$_2$O$_3$. Another strong absorption in the visible region due to an indirect transition of Fe$^{3+}$ 3d $\rightarrow$ 3d was seen. Furthermore, because of the presence of the jarosite phase, UV absorption for the vein phase-ablated species sample was strong and broad.

Figure 5b depicts the PL spectra of both laser-generated nanostructures from the 10 min laser ablation of the turquoise mineral in ethanol (vein and turquoise) and the target (vein and turquoise phases) before ablation. All samples were excited at 270 nm at room temperature. The emission band centered at 370 nm (3.35 eV) is observed in the vein phase-ablated species prepared from laser ablation of the vein phase of the turquoise stone. This luminescence is due to electron transition within $\alpha$-Fe$_2$O$_3$ and can be observed even with the bare eye at room temperature. The emission band centered at 364 nm (3.41 eV) is observed in the turquoise phase-ablated species, which indicated the copper compound emission in these ablated species. The presence of these compounds was previously illustrated using the FESEM image in combination EDX analysis (Figures 3c and S5a). The presence of $\alpha$-Fe$_2$O$_3$ can intensify the emission band in the UV region. The UV emission peak in 364 nm for the turquoise phase-ablated species was related to the recombination of electron–hole pairs in free excitons. These PL properties of the suspension were in agreement with the PL emission of Cu compounds and also $\alpha$-Fe$_2$O$_3$ emission bands in the UV region. The blue emission band of the sample (led to show the blue color of these compounds) is seen, as shown in Figure S4, when this sample was excited at 430 nm at room temperature. The PL spectrum of the turquoise phase-ablated species in Figure S4 showed the emission band located in 462 nm (led to the blue color emission) and 492 nm related to cyan color (a deep greenish-blue color) emission and also a weak peak in 504 nm corresponding to green color emission of these turquoise phase-ablated species. Intriguingly, the full width at half maximum (FWHM) of the emission spectra for both nanostructures synthesized from laser ablation of the vein and the turquoise phase of the target (i.e., vein phase and turquoise phases after LP-PLA) is narrower than the nonablated samples (i.e., vein and turquoise phases before LP-PLA). Basically, when the size of the nanostructures is less than 30 nm, the PL phenomenon is observed because of the quantum confinement effect. For the bulk material, the PL spectra are not observable because of the forbidden optical transition. In the current study, the effect of the size of the turquoise phase-ablated species and the core—double-shell NPs needs to be considered. Furthermore, the narrower spectrum in the turquoise phase-ablated species and core—double-shell NPs indicates higher uniformity of these nanostructure emission energies and thus higher size uniformity of these nanostructures compared to the untreated turquoise and vein-phase structures.

**CONCLUSIONS**

In conclusion, the presented work describes a suitable one-pot, one-step, “green” synthesis route for the selective laser synthesis of high-purity core—double-shell magnetic NPs and AIP nanosheets from the selective laser ablation of the mineral turquoise target in the ethanol environment. HRTEM and SAED analyses show that these core—double-shell NPs are composed of the hematite core and quartz inner shell and jarosite outer shell. Regarding the TEM images, the mean diameter of the hematite core is measured as 27 nm, while the mean quartz shell thickness is 9 nm. However, the nanosheet formation has been confirmed using FESEM images with a lateral size of 30–210 ± 6 nm. UV–vis–NIR absorption for core—double-shell NPs shows strong absorption in the UV region (250–360 nm) because of $\alpha$-Fe$_2$O$_3$ and jarosite and phases, while turquoise phase-ablated species have a peak located at 270 nm related to the presence of Cu compounds in the turquoise phase. The PL emission of core—double-shell NPs at 370 nm is due to the electronic transition within the iron oxide ($\alpha$-Fe$_2$O$_3$), while for the turquoise phase-ablated species, it is located at 364 nm and related to the presence of Cu compounds and $\alpha$-Fe$_2$O$_3$ phases in the turquoise phase.

**METHODS**

**LP-PLA Conditions and Sample Preparation.** A Ce:Nd:YAG laser with a fundamental wavelength of 1064 nm, the repetition rate of 10 Hz, and pulse duration of 10 ns with Gaussian beam distribution, pulse energy of 350 mJ/pulse (178.3 J/cm$^2$), with the irradiation time of 10 min were used for laser synthesis experiments. The turquoise target used in our experiment was obtained from the Nishapur (Iran). This target is composed of two phases of different colors on the surface, and the light brown veins were surrounded by the turquoise phase surface. The laser was made to irradiate from the top of the cylindrical container to the target at the bottom of the container to avoid reflections through the glass walls. Pure ethanol (Merck, 99%) filling up to 0.01 m height on the top of the target surface was used as a liquid environment for laser ablation experiments. The laser ablation experiments were performed in two steps. In the first step, the laser beam was directed on the vein of the turquoise surface and the related suspension was collected and dripped to Si wafer followed by drying for morphological and structural characterization. In the second step, the laser beam was conducted on the turquoise surface, and as performed in the first stage, the relevant solution was collected and dripped to the Si wafer followed by drying for morphological and structural characterization.**

**Instrumentation.** UV–vis–NIR spectroscopy was carried out on the separated supernatant of the ablation product, with a T80+ model spectrometer manufactured by PG Instruments Ltd. (United Kingdom), PL emission was recorded using PL spectroscopy (Gilden Photonics, Scotland), and XRD patterns were obtained using a Phillips X’pert MPD powder diffractometer with radiation of Co Kα (wavelength = 0.179 nm, Netherlands). The morphology of the nanostructures was characterized using a field-emission scanning electron microscope (FESEM, MIRA3TESCAN-XMU, Czech Republic). HRTEM images and SAED patterns were taken using FEI Titan 80–300 LB (200 kV, America).
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03882.

EDX analysis of the turquoise and vein phases before laser ablation, EDX mapping of the turquoise phase after laser ablation, further FESEM images of the vein phase after laser ablation, synthesized products with size distribution histograms, SAED of core−double-shell NPs, and PL property of turquoise-ablated species (PDF)

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Notes
The authors declare no competing financial interest.

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