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Novel one-step synthesis of silica nanoparticles from sugarbeet bagasse by laser ablation and their effects on the growth of freshwater algae culture

Nalan Oya San[a,b,c], Canan Kurşungöz[c], Yasin Tümtaş[c], Öncay Yaşa[c], Bülend Ortaç[c,*], Turgay Tekinay[a,b,**]

[a] Polatlı Science and Literature Faculty, Biology Department, Gazi University, Ankara 06900, Turkey
[b] Life Sciences Application and Research Center, Gazi University, Ankara 06830, Turkey
[c] UNAM Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey

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ABSTRACT

Scientific research involving nanotechnology has grown exponentially and has led to the development of engineered nanoparticles (NPs). Silica NPs have been used in numerous scientific and technological applications over the past decade, necessitating the development of efficient methods for their synthesis. Recent studies have explored the potential of laser ablation as a convenient way to prepare metal and oxide NPs. Due to its high silica content, low cost, and widespread availability, sugarbeet bagasse is highly suitable as a raw material for producing silica NPs via laser ablation. In this study, two different NP production methods were investigated: laser ablation and NaOH treatment. We developed a novel, one-step method to produce silica NPs from sugarbeet bagasse using laser ablation, and we characterized the silica NPs using environmental scanning electron microscopy (ESEM), energy dispersive spectrometry (EDS), dynamic light scattering (DLS), transmission electron microscopy (TEM), attenuated total reflectance-Fourier transform infrared spectroscopy (ATR–FTIR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. EDS analysis and XPS confirmed the presence of silica NPs. The NPs produced by laser ablation were smaller (38–190 nm) than those produced by NaOH treatment (531–825 nm). Finally, we demonstrated positive effects of silica NPs produced from laser ablation on the growth of microalgae, and thus, our novel method may be beneficial as an environmentally friendly procedure to produce NPs.

1. Introduction

Silica is beneficial to many plants (Ding, Ma, Shui, Wan, & Li, 2005). It is well known that certain plants, including grasses (*Poaceae*), rice (*Oryza sativa*), sugarbeet (*Beta vulgaris*), and horsetail (*Equisetum*), contain high levels of biogenic silica (Sun & Gong, 2001). In particular, sugarbeet is an attractive source of biogenic silica because the silica content of this plant is mainly concentrated in bagasse. Sugarbeet bagasse is produced in large quantities as an agro-industrial byproduct and is often used as boiler fuel for generating steam during the processing of sugar.

In recent years, there has been an increasing trend toward the more efficient use of agro-industrial by-products for animal nutrition, fuel, and fermentative products. Several processes and products using sugarbeet bagasse as the raw material have been reported, particularly in pulp and paper production; it is also used as a feedstock in fermentation processes (Alves, Felipe, Silva, Silva, & Prata, 1998; Pandey, Soccol, Nigam, & Soccol, 2000). However, sugarbeet bagasse can also be processed to produce high-purity silica, exceeding 99% purity and primarily bearing K_2O, and MgO as impurities (Affandi, Setyawan, Winardi, Purwanto, & Balgis, 2009). As such, bagasse is an economically viable raw material for silica nanoparticle (NP) production.

Nanoparticles are frequently used in several nanotechnological applications. In particular, silica NPs are widely used in drugs, cosmetics, printer toners, varnishes, and food preservatives (Baek & An, 2011; Bagwe, Hilliard, & Tan, 2006; Hua et al., 2009; Lin, Huang, Zhou, & Ma, 2006). In addition, the use of silica NPs has recently been extended to the biomedical and biotechnological

* Corresponding author. Tel.: +90 312 290 3526; fax: +90 312 266 4365.
** Corresponding author at: Polatlı Science and Literature Faculty, Biology Department, Gazi University, Ankara 06900, Turkey. Tel.: +90 312 484 62 70; fax: +90 312 484 6271.
E-mail addresses: ortac@unam.bilkent.edu.tr (B. Ortaç), ttekinay@gazi.edu.tr (T. Tekinay).

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fields (Clément et al., 2013; Trewyn, Giri, Slowing, & Lin, 2007). Such trends necessitate the development of eco-friendly processes for the production of NPs. As a result, the focus of NP synthesis has shifted away from physical and chemical processes toward 'green' chemistry and bioprocesses (Gonzalez-Arellano, Balu, Luque, & Macquarrie, 2010; Tolaymat et al., 2010; Zhao & Zhu, 2009).

To date, many approaches have been developed for silica NP synthesis. Generally, silica precursors, such as silicon alkoxides, are used as the silicon source, and NPs are generated by hydrolysis and subsequent polycondensation (Cadby & Tolbert, 2005; Molenkamp, Watanabe, Miyata, & Tolbert, 2004; Suzuki, Kiba, & Yamauchi, 2011). Such chemical processes are energy intensive and thus expensive. In addition, they are usually associated with high temperatures, strong acidities, and high pressures that render NP synthesis ecologically hazardous (Bansal, Ahmad, & Sastry, 2006). Considering the increasing demand for silica NPs in new applications (Lee, Park, Singha, & Kim, 2013), current approaches for silica NP synthesis may be unsustainable and cost prohibitive in the near future. Therefore, it is highly desirable to identify alternative approaches to reduce production costs.

Most NP synthesis techniques, such as physical vapor deposition (Yousefi & Muhamad, 2010), precipitation (Yang & Hu, 2010), solvothermal/hydrothermal methods (Wang, Shi, Qi, & Liu, 2010), and sol–gel methods (e.g., sol–gel combustion), are expensive and complex and offer only limited control over particle size and size uniformity. In recent years, pulsed-laser ablation of solids in solution has attracted interest due to its versatility and low cost (Alkis, Oruç, Ortaç, Koşger, & Okyay, 2012; Amendola & Meneghett, 2009; Wu, Dickinson, & Lele, 2012). Sajti, Sattari, Chichkov, and Barcikowski (2010) demonstrated recently the bulk synthesis of NPs by laser ablation, yielding ceramic NPs on a scale of several grams. Their study indicates the potential feasibility of laser ablation for large-scale synthesis applications.

Based on the available literature (Affandi et al., 2009), we hypothesized that sugarbeet bagasse, which is inherently rich in silica, can be used to synthesize silica NPs. In this study, we describe for the first time the use of laser ablation for the synthesis of silica NPs from agro-industrial byproducts. It is also important to investigate the effects of nanomaterial exposure on the aquatic environment. Green algae are known to be sensitive to many chemicals. They have been considered indicators of the bioactivity of industrial wastes, and they vary in their responses to a variety of toxicants. Their ecological position at the base of most aquatic food webs and their essential roles in nutrient cycling and oxygen production are critical to many ecosystems. Therefore, we examined how silica NPs impact the growth of a freshwater green algae species that is among the most widespread of all algae: *Chlorella vulgaris*. Our results may aid the development of environmentally friendly and economically attractive alternatives to current NP production methods.

2. Materials and methods

2.1. Nanoparticle production

Sugarbeet bagasse was obtained from the Ankara Sugar Factory, Etimesgut, Ankara, Turkey. Two separate treatments were adopted to extract silica from the bagasse samples. In the first approach, bagasse ash was obtained by calcining sugarbeet bagasse at 500 °C for 12 h. One gram of bagasse ash was then treated with concentrated $HCl:HNO_3 = 1:3$ (v/v) at 35 °C for 2 h and oven-dried at 60 °C. Then, 50 mL of water was added to the residue, and the solution was alkalized to a pH of 13–14 with concentrated NaOH. Following overnight incubation, the alkaline solution was neutralized with HCl. For the second approach, the raw sugarbeet bagasse sample was used directly as the laser ablation target, without any purification or cleaning procedure. The generation of NPs from sugarbeet bagasse was achieved with a commercial nanosecond pulsed Nd:YLF laser (Empower Q-Switched Laser, Spectra Physics) operating at 527 nm with a pulse duration of 100 ns and an average output power of 16 W at a pulse repetition rate of 1 kHz, corresponding to a pulse energy of 16 mJ. Raw bagasse was placed in a glass vessel containing 25 mL of pure deionized water. The laser beam was focused on the target using a plano-convex lens with a focal length of 50 mm; the depth of the liquid layer above the target was approximately 5 mm. Laser ablation was carried out for ~5 min by scanning the laser beam over the target surface. The formation of NPs in water was observed visually during laser ablation, as samples had changed in color to light yellow by the end of the irradiation. In addition to producing silica NPs, laser irradiation damaged the fibrous structure of the sugarbeet bagasse. Therefore, samples were filtered with a 0.22 μm filter to remove the fibers from the NP solution.

2.2. Nanoparticle characterization

The morphology and elemental composition of raw bagasse was measured by an environmental scanning electron microscope with EDS (ESEM, Quanta 200 FEG, FEI Instruments, USA). The particle size and distribution of particles dispersed in distilled water were measured using dynamic light scattering (DLS) (Malvern Instruments Ltd., Malvern, UK). The stability of the silica NPs was measured from the zeta potential of the solution (NanoZS, Malvern Instruments Ltd., Malvern, UK). The morphology of silica NPs was also analyzed using a FEI Tecnai G2 F30 transmission electron microscope (TEM) connected to a high resolution imaging system. NP samples were prepared by drying a total of 2 μL of the laser ablated mixture on carbon coated copper grids at room temperature.

Fourier transform infrared spectroscopy (ATR/FTIR) analysis was performed using a Nicolet 6700 (Thermo Fisher Scientific, USA) ATR–FTIR spectrometer. Spectra were obtained within the 4000–500 cm^{-1} range with a resolution of 4 cm^{-1} (Bruker, Vertex 70 with Hyperion Scanning Microscope, Germany). The samples (100 μL) were placed in the attenuated total reflectance (ATR, ZnSe) analyzer and analyzed.

X-ray photoelectron spectroscopy (XPS) (Kα-Monochromated high performance) (Thermo, USA) measurements were performed in an ultra-high vacuum (UHV) with a conventional X-ray source (Mg-Kα).

Raman spectra were acquired at room temperature by using a Witec Alpha300S + Raman Module (Witec, Germany). A solid-state 532 nm wavelength laser was used for excitation. Raman measurements of single spectra were taken at 50× magnification and with 2.03 s integration times.

2.3. Effects of silica nanoparticles on C. vulgaris growth

The alga *C. vulgaris* was obtained from a culture collection at Gazi University Life Sciences Application and Research Center and sub-cultured in the laboratory. *C. vulgaris* was cultivated in sterilized Tap medium (Tris–acetate–phosphate) under an illumination intensity of 4000 lux. The temperature in the air-conditioned growth chamber was maintained at 25 °C. We exposed silica NPs produced from two different treatments to algal cultures. The algal density of three replicates was then calculated by measuring the optical density (OD) at a wavelength of 750 nm with a UV–vis spectrophotometer (Shimadzu, UV-1201V, Japan). Medium without NPs inoculated with alga was used as the control. Every day,

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