

Ultraviolet Extinction and Visible Transparency by Ivy Nanoparticles

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Abstract Though much research has been conducted for nanoparticles, naturally occurring nanoparticles have not yet been well explored for their diverse properties and potential applications. This paper reports the optical absorption and scattering properties of nanoparticles secreted by English ivy. Both experimental and theoretical studies have been conducted. Strong ultraviolet extinction and excellent visible transparency are observed, compared to the inorganic TiO₂ and ZnO nanoparticles at similar concentrations. The contributions of absorption and scattering to the total extinction are quantified by simulation of the Mie scattering theory.

Keywords Ivy nanoparticle · Optical absorption · Light scattering

Introduction

Optical properties of naturally occurring organic nanoparticles have not been well explored. Their potential applications are largely unknown. This may be due to two reasons. First, research in the field of natural organic nanoparticles is new to material science. Although natural nanostructures with biological functions have been found for many years [1, 2], natural organic nanoparticles have not been investigated for material properties such as

mechanical and optical properties until recent years [3]. Second, most attention is attached to artificial organic nanoparticles [4, 5]. These nanoparticles formed of organic molecules and polymers offer variable optical properties due to the abundant alternative components. However, in the case of biological applications, organic nanoparticles formed in nature are also a promising alternative due to their compatibility and non-toxicity. Natural nanoparticles can be used as the functional materials just as the artificial nanoparticles. Optical absorption and light scattering are the two main optical properties that induce the extinction effect. Optical absorption and light scattering of materials have many applications. Nanoparticles with ultraviolet extinction properties have the potential to be used in sunscreen. The ingredients of modern sunscreens usually contain organic compounds [6], inorganic nanoparticles [7] and organic nanoparticles [8]. The inorganic nanoparticles (such as ZnO and TiO₂) and organic nanoparticles can reflect, absorb and scatter the solar light. Though inorganic nanoparticles have been widely used in cosmetic products, there are still concerns about the toxicity of these inorganic materials. TiO₂ has been reported to induce DNA [9, 10] and RNA [11] damage through the process of chemical oxidation. Considering these situations, if nature-derived harmless organic nanoparticles have strong ultraviolet absorption, they will be a potential promising alternative for sunscreen. In this paper, we reported the optical absorption and light scattering of ivy nanoparticles. These nanoparticles were isolated by two approaches, size exclusion chromatography and filtration. Optical absorption and light scattering properties of these samples were characterized. The advantages of these nanoparticles in their application to sunscreen compared to inorganic nanoparticles were also demonstrated.

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Experiments

Fresh-grown rootlets of English ivy were collected around the University of Tennessee, Knoxville Campus, before attaching themselves to solid surfaces. The collected rootlets were meshed using tweezers in 5-ml clean tube containing 500 μl of 20-nm-filtered water after washing them three times with ddH₂O. The solution was then centrifuged at 3000 RPM for 5 min, and the supernatant was collected. Two-thirds of the solution was dialyzed overnight at 4 degrees with ddH₂O through a cellulose membrane (Sigma–Aldrich, D9277) allowing free pass of chemicals less than 12,500 Daltons. Size exclusion chromatography and high-performance liquid chromatography (SEC–HPLC) was used to isolate the nanoparticles from the solution. This technology can separate the nanoparticles in solution based on their sizes [12]. The Varian HPLC system consists of three components including Varian Prostar 210, the Varian Prostar 335 detector and the Varian Prostar 430 autosampler. Next, 200 μl of dialysis solution was loaded to the column (Phenomenex[®] BIOSEP-SEC-S3000 column with an attached Security Guard[®] cartridge system). The running speed of the mobile phase was set to 0.5 ml/min, and the back pressure of the column was 580 psi. Samples were collected depending on the retention time. These samples we investigated in this study were named SEC-1, SEC-2 and SEC-3 with the time sequence. Filtration was another method used to reveal the optical properties of ivy nanoparticles. The dialyzed solution was filtered through the Millipore membrane (220-nm Nylon filters). This solution was marked as D220D1. Half of this solution was filtered again through 20-nm filters. The filtered solution was marked as D20D1. Furthermore, a portion of each solution was diluted into 1/3 concentrations. The diluted solutions were named D220D2 and D20D2, respectively. The non-dialysis solutions were also prepared and named ND220 and ND20, respectively.

The morphologies of the ivy nanoparticles were observed by Agilent 5500 atomic force microscope (Agilent Technologies, Santa Clara, CA). The instrument was operated at room temperature (20°C) using Picoview[™] in AC mode, which means little or no contact between the tip and the sample.

Dynamic light scattering (DLS) measurements were performed by a Brookhaven Instruments BI-200SM goniometer equipped with a PCI BI-9000AT digital correlator. The operating wavelength is 633 nm. The detector is located at the scattering angle of 90°.

The ultraviolet and visible (UV–Vis) extinction (absorption and scattering) spectra were measured by the Thermo Scientific Evolution 600 UV-Visible spectrophotometers. The optical length of the quartz cuvette is 10 mm.

Results and Discussion

Dry ivy nanoparticles were first imaged using an AFM, as shown in Fig. 1. The average diameter of ivy nanoparticles is 68.3 nm. This value is similar to that of the previous measurements [3]. The sizes of nanoparticles are not uniform in AFM image. Furthermore, size distributions of the ivy nanoparticles were observed in the samples of SEC-1, SEC-2, D220D1 and ND220 by dynamic light scattering (DLS) measurement. No size distribution was found in the sample of SEC-3. This effect is believed to be due to the low concentration of ivy nanoparticles in SEC-3. The nanoparticles in solutions are the polydisperse system. The sizes of nanoparticles display the large ranges from tens of nanometers to several hundred nanoparticles. The average diameters of particles are 117.4 nm for SEC-1, 131.6 nm for SEC-2, 97.8 nm for D220D1 and 112.3 nm for ND220. It is worth to note, in principle, DLS gives the hydrodynamic sizes of the particles. The hydrodynamic sizes are usually greater than the sizes of dry particles obtained by AFM [13, 14]. This is due to the polydispersity of the nanoparticles [14]. Large particles scatter a significant amount of light so that the diameters given by DLS intensity distributions will be greater than that obtained by AFM even if there are only a few large particles [14] Fig. 2.

The extinction spectra of samples from the SEC technology and the filtration are shown in Fig. 3a and b, respectively. The extinction spectra of ivy nanoparticles using the filtration method are obtained by subtracting the extinction spectra of samples filtered using 20-nm filters

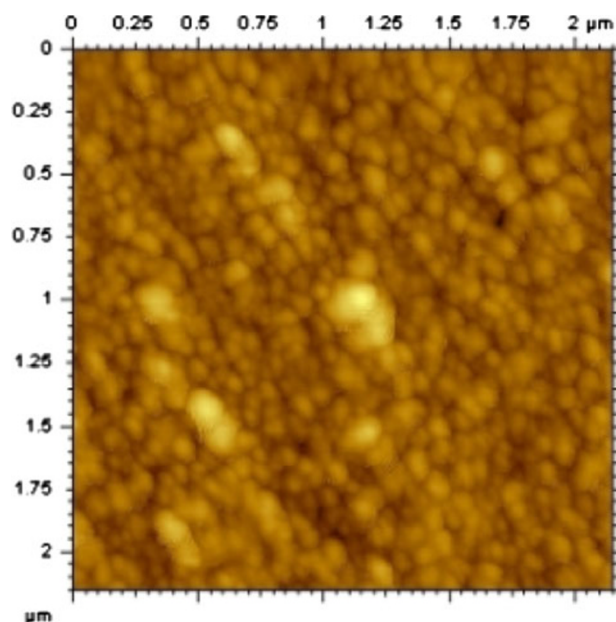


Fig. 1 The morphologies of ivy nanoparticles observed by AFM

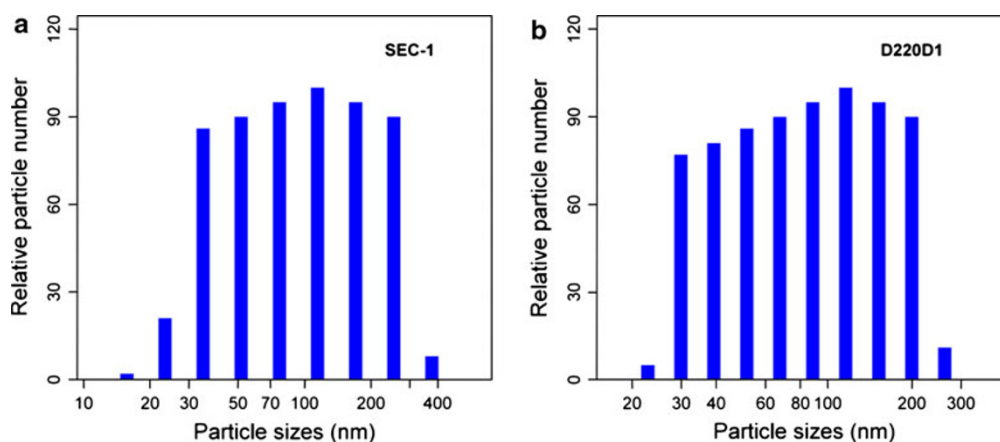


Fig. 2 Size distributions of ivy nanoparticles in water (SEC-1 and D220D1) obtained by dynamic light scattering

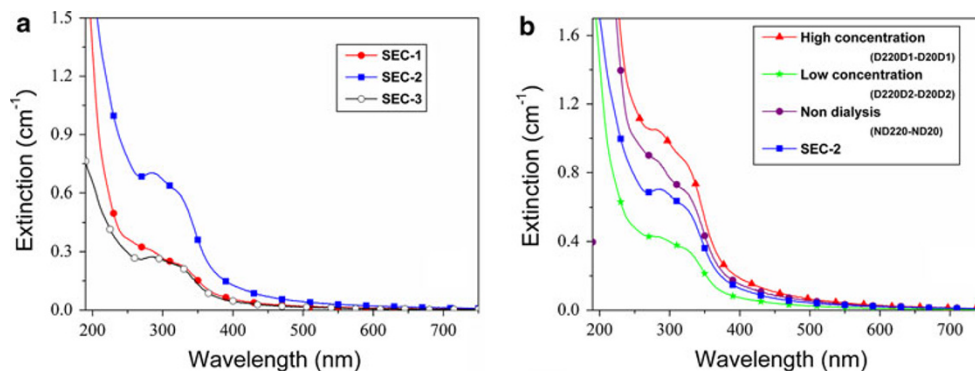
from those filtered by 220-nm filters. For example, the curve in Fig. 3b with the symbol of high concentration denotes the difference between the extinction spectra found in D220D1 and D20D1. The spectrum characteristics of those samples from the SEC technology and the filtration are approximately consistent. These phenomena including the DLS results mean that the SEC and the filtration are the effective direct and indirect methods to investigate the optical properties of ivy nanoparticles. These nanoparticles display strong ultraviolet and weak visible light extinction and, interestingly, a sharp transition edge from the ultraviolet to the visible range. A significant extinction band and a shoulder can be found around the wavelengths of 280 nm and 325 nm for all the samples, respectively.

To illustrate the content of the solution, the original spectra are shown before subtraction in Fig. 4. The extinction band and the shoulder are at the same positions not only for the samples filtered through the 220-nm filters but also the ones filtered through the 20-nm filters. This similarity implies that the components in the solutions are similar to that of the ivy nanoparticles. In addition, the non-dialysis samples show differences when compared to the dialysis samples in the original absorption spectra in Fig. 4. This may be due to the dialysis process in which some

protein or other molecules less than 12,500 Daltons are filtered out. The ingredients of ivy nanoparticles have been analyzed by this research team. Proteins have been confirmed as the dominant compounds of the ivy nanoparticles [15]. The absorption peak at the wavelength of 280 nm is the characteristic for many proteins [16]. In general, three of the amino acid side chains (Trp, Tyr and Phe) contribute significantly to the UV absorption of a protein at 280 nm. Those amino acids are believed to form ivy nanoparticles, but the actual types of proteins and amino acids are still under investigation. Furthermore, the concentration of ivy nanoparticles in the sample of high concentration (D220D1-D20D1) was measured to be 4.92 $\mu\text{g/ml}$ by the Bradford protein assay [17].

Scattering (just as the Tyndall effects shown in DLS experiments) also makes considerable contribution to the total extinction besides the absorption. Herein, we simulated extinction behaviors of the ivy nanoparticles by the Mie scattering theory with the help of the software MieTab 8.38 [18, 19]. While the refractive index of most organic compounds is between 1.3 and 1.73 [20], the refractive index of ivy nanoparticle was set to 1.5. The refractive index of water from 280 nm to 400 nm was from the reported data [21]. The extinction coefficients were

Fig. 3 UV-Vis extinction spectra of ivy nanoparticles in the samples prepared by **a** size exclusion chromatography technology and **b** the filtration. High concentration (Low concentration, Non-dialysis) represents the difference between the extinction spectra found in D220D1 (D220D2, ND220) and D20D1 (D20D2, ND20)



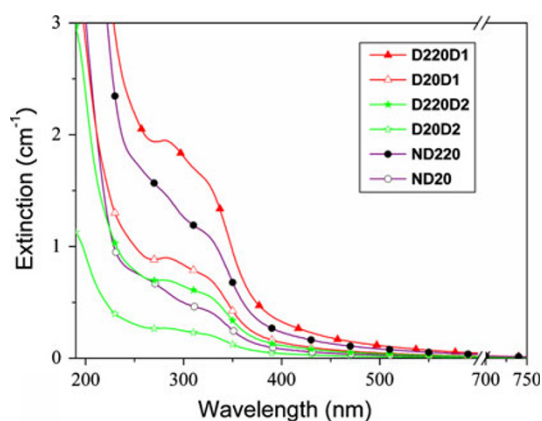


Fig. 4 Original extinction spectra of the filtered samples

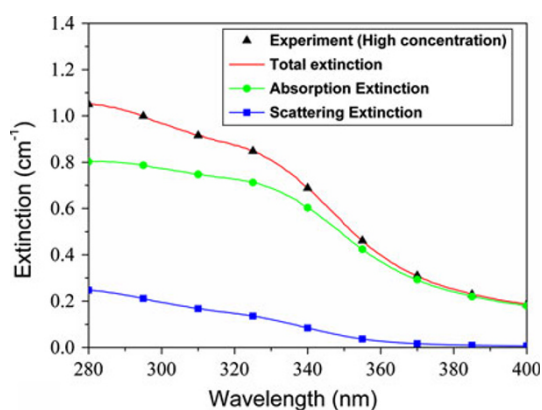
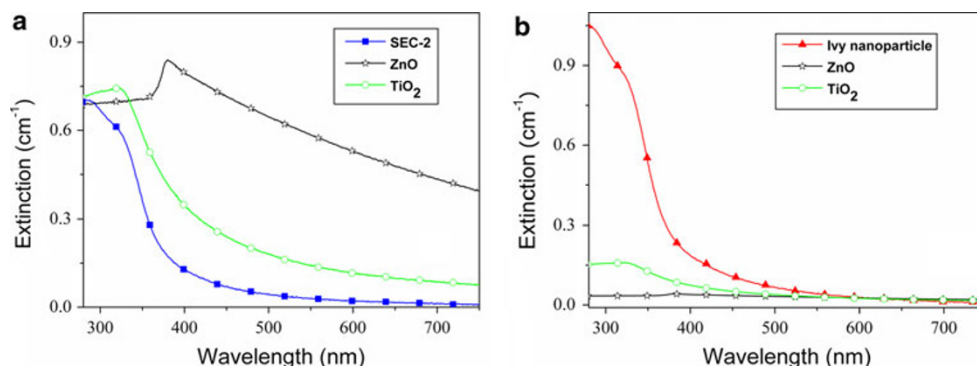


Fig. 5 Fitting curves considering scattering and absorption extinction. Experimental result is from the curve of high concentration in Fig. 3b

adjusted to fit the experimental results. The fitting curve of the total extinction, scattering and absorption curves are shown in Fig. 5. From these results, the scattering effect is found to contribute to the extinction, although this contribution is much smaller than that of the absorption. The absorption and scattering make ivy nanoparticles display strong ultraviolet extinction behavior. This behavior offers some potential applications such as sunscreen.

Fig. 6 Comparison of the UV–Vis extinction spectra of TiO₂, ZnO nanoparticles and ivy nanoparticles. **a** the relative UV–Vis extinction characteristics with the same extinction value at 280 nm. **b** the extinction behaviors at the same concentration (4.92 μg/ml)



The characteristics of extinction spectra of ivy nanoparticle make a great advantage in the sunscreen application for blocking the ultraviolet light and maintaining the high visible transparency. Ivy nanoparticles can use their optical absorption and scattering properties to eliminate the ultraviolet light, just as inorganic nanoparticles such as ZnO and TiO₂ do in sunscreen [7]. In order to illustrate the relative ultraviolet–visible extinction characteristics, solutions of ZnO nanoparticles (NanoAmor, 99.9%, 90–200 nm) and TiO₂ nanoparticles (NanoAmor, Rutile, 99%, 50 nm) were adjusted to be the same extinction value as SEC-2 at 280 nm. This wavelength is the beginning of UV-B (280–320 nm). Sunscreens protect from both UV-B and UV-A (320–400 nm) irradiation. In Fig. 6a, the ivy nanoparticles display a sharper edge from the ultraviolet range to the visible range. Herein, the concentrations of TiO₂ and ZnO suspensions are 23 μg/ml and 100 μg/ml, respectively. After this, the extinction spectra of the above TiO₂ and ZnO suspensions were roughly converted to the spectra with the concentration of 4.92 μg/ml, as shown in Fig. 6b. The ivy nanoparticles (high concentration) exhibit a much stronger ultraviolet absorption and sharper decrease near the visible range. Due to the non-toxicity and strong extinction property, ivy nanoparticles are a promising material for sunscreen application.

Natural or biological nanoparticles have not been investigated in detail for their material properties. In this study, we investigate these type nanoparticles as the functional materials just like usual inorganic and organic nanoparticles. The ivy nanoparticles are not monodisperse in solutions. This effect is due to the biological process of the nanoparticle formation. Nanoparticles from the original tiny ones to the mature ones all exit in the rootlets of ivy. The SEC technology isolated the nanoparticles from the mixed solutions including molecules, but it did not give us uniform size of nanoparticles. The effective methods to obtain the monodisperse ivy nanoparticles are in the future investigation. The modifications of ivy nanoparticles to improve the optical properties are expected. Recently, in order to increase refractive index of organic polymers,

surface modification methods, such as deep UV modification and ion-beam implantation, have been reported [22, 23]. If similar modifications are applied to ivy nanoparticles, the refractive index mismatch between ivy nanoparticles and the medium will become larger. This effect can increase the light scattering of ivy nanoparticles and, furthermore, benefit the extinction.

Conclusions

In conclusion, ivy nanoparticles have been isolated by the SEC technology and the filtration methods. Optical absorption and scattering properties of these nanoparticles have been characterized. The extinction spectra of the ivy nanoparticles display strong ultraviolet and weak visible extinction with a sharp transition edge. Compared to inorganic nanoparticles, ivy nanoparticles can be used in ultraviolet protection due to their optical properties and harmless nature.

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