Stable Dispersions of Aromatic Hydrocarbon Colloidal Particles by Laser Ablation

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Introduction

Polycyclic aromatic hydrocarbons are a very interesting class of materials. They show a very broad range of very interesting properties like intensive colour, fluorescence, photoconductivity, semiconducting properties and a very special chemical and photochemical behaviour [1]. Therefore these materials are often used for pigments and dyes, fluorescent probes, etc. and they are promising materials for sensors, bioprobes, devices, and so on.

In the last few years research on different kinds of organic nanoparticles is steadily increasing. Even so, preparation methods for these particles are not very well established yet. Two different methods have been usually employed to prepare such particles. These are reprecipitation by adding a solution of the substance to a non-solvent and evaporation-condensation processes in vacuo. Only recently, laser ablation, has been used to prepare organic microcrystals in aqueous media [2, 3]. The use of surfactants was found to greatly enhance the performance of particle formation and the stability of the dispersions [4].

In this work we investigated the influence of different ionic and non-ionic surfactants and of laser fluence on the rate of particle formation.

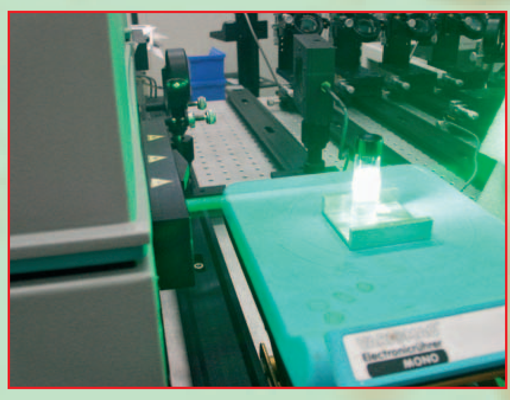

Figure 1: Laser ablation setup.

Figure 2: Micrograph of tetracene crystals before irradiation.

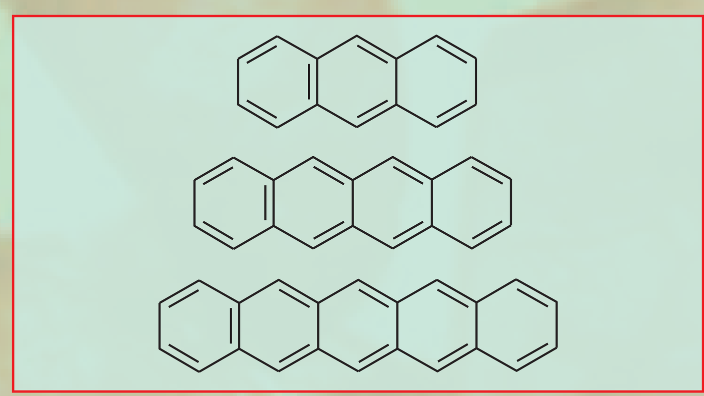

Figure 3: Structures of anthracene, tetracene, and pentacene.

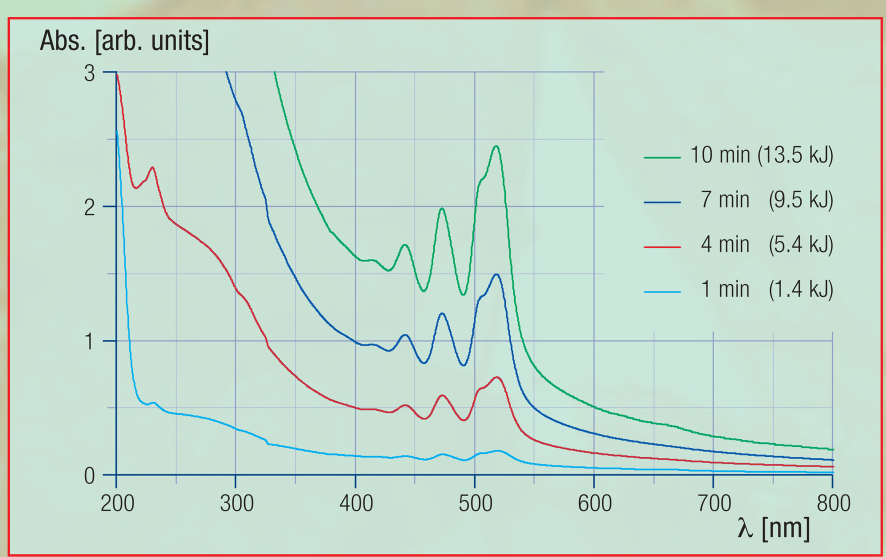

Figure 4: Absorption spectra of irradiated tetracene suspensions in 1 mM CTAB solution for different irradiation times (total energy input).

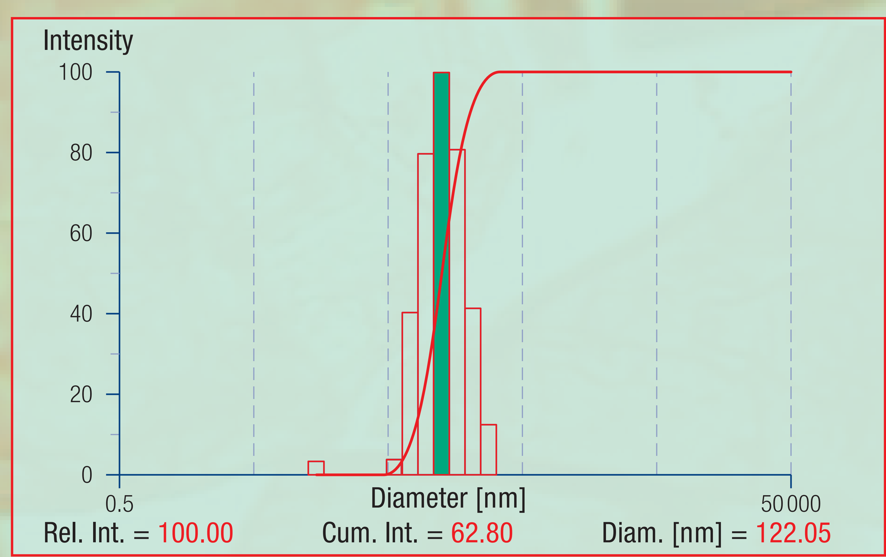

Figure 5: Typical result of PCS-measurements for particle sizing.

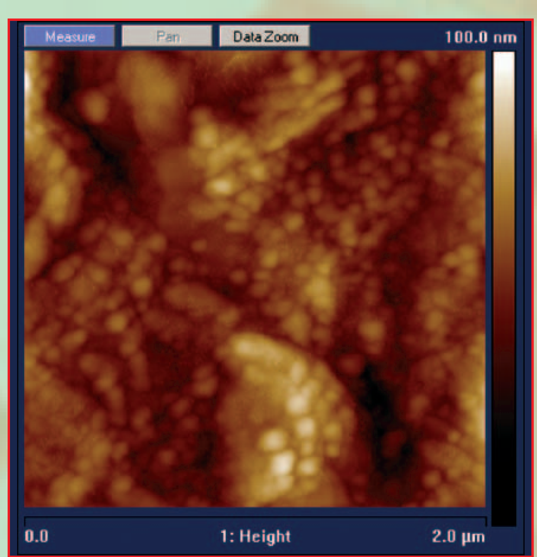

Figure 6: AFM image of colloidal pentacene particles produced by laser ablation in CTAB 1 mM.

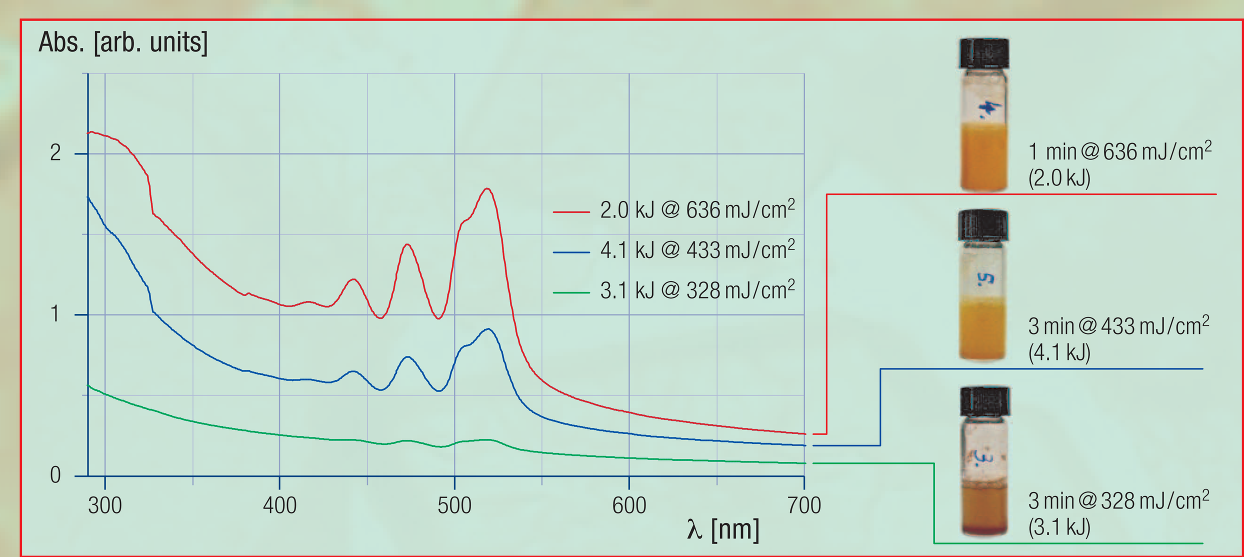

Figure 7: Absorption spectra of the samples of tetracene in 1 mM CTAB solution irradiated at different fluence.

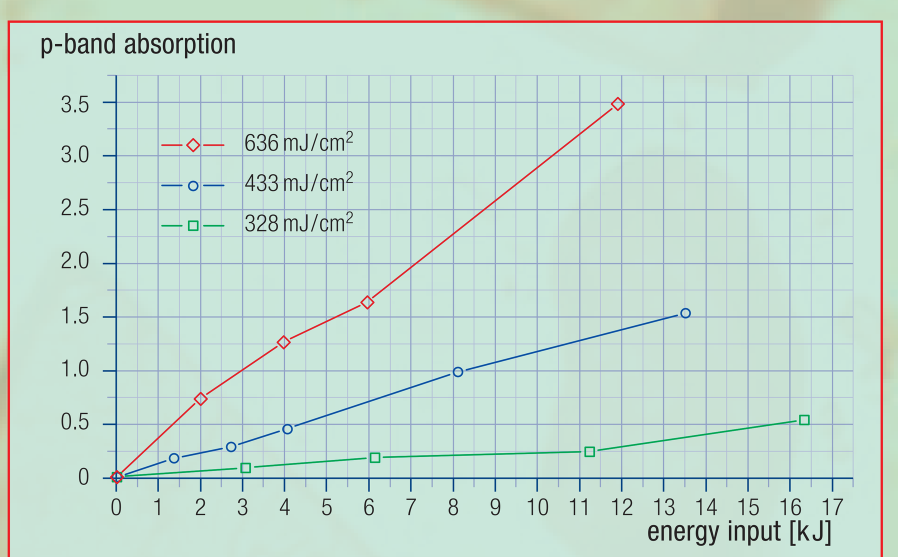

Figure 8: Pentacene p-band absorbance of dispersions in 1mM CTAB as function of laser energy input for different laser fluence.

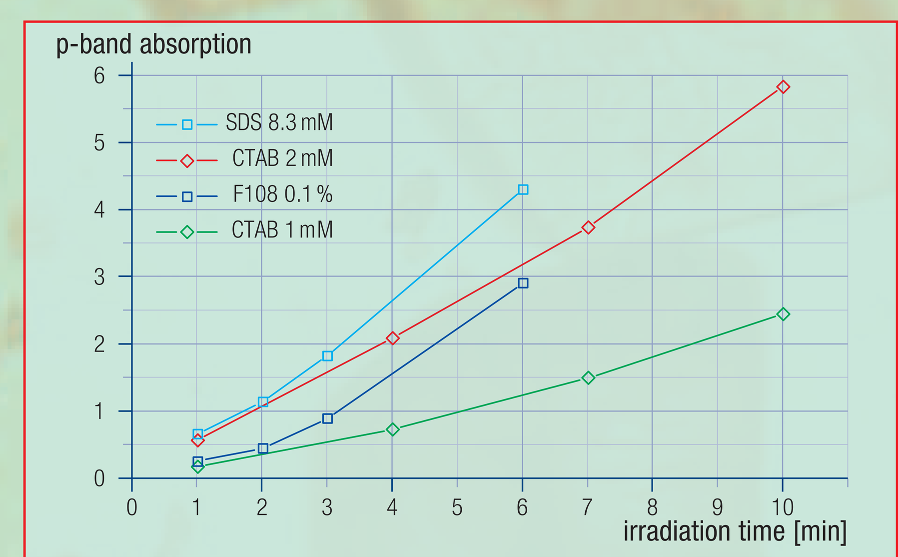

Figure 9: Tetracene p-band absorbance of dispersions irradiated at 433 mJ/cm² as function of irradiation time.

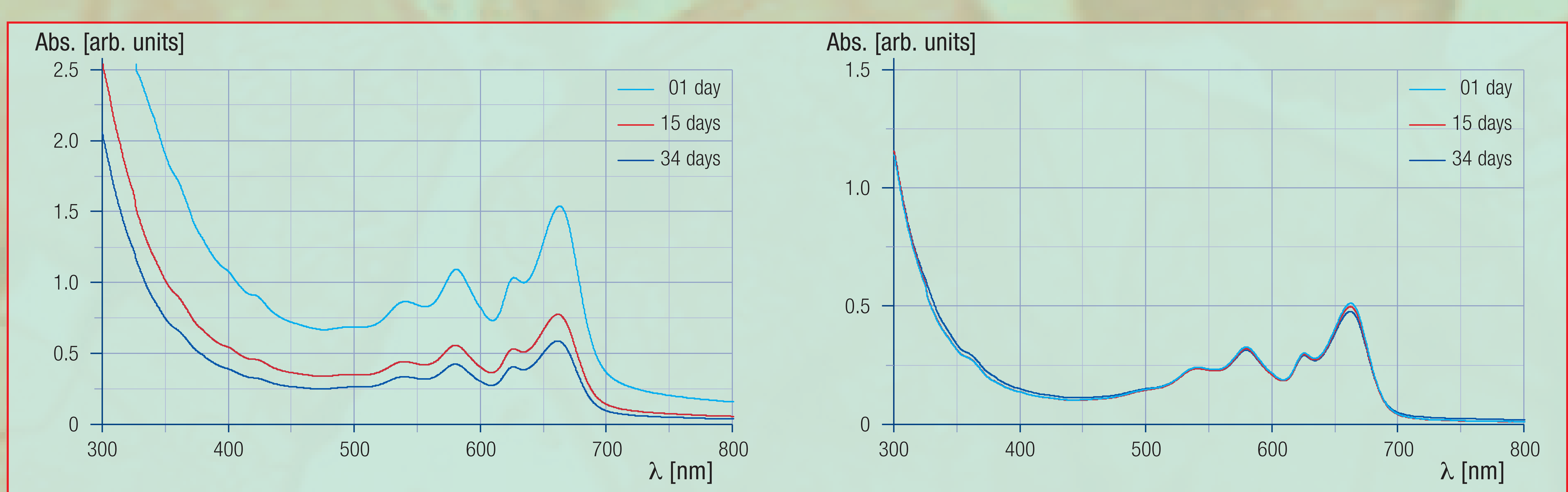

Figure 10: Long term stability of pentacene colloidal dispersions irradiated for 10 min at a fluence of 433 mJ/cm², a.) CTAB 1 mM; b.) SDS 8.3 mM (dil. 1:10).

Experimental

Micron sized crystals of polycyclic aromatic hydrocarbons were dispersed in a surfactant solution. The dispersions were irradiated in vials while stirring. The second harmonic output of a Nd:YAG laser (532 nm, 50 Hz, 9 ns fwhm) was applied as the irradiation source. The solutions were centrifuged in order to precipitate big crystals and the clear supernatants were used for further investigation. The experimental setup is shown in Figure 1.

Results

The increase of nanoparticle concentration in the supernatant with irradiation time was followed by UV-Vis spectroscopy (see Figure 4). The characteristic peaks of aromatic hydrocarbons are growing regularly with irradiation time for a given laser fluence. This laser fluence, is a key parameter in laser ablation of organic particles. As can be seen from the example in Figure 5 for aromatic hydrocarbons, fluence seems to bee even more important than the total amount of energy deposited on the sample. This total amount of energy corresponds to the number of photons emitted onto the sample. Formation of colloidal dispersions of organic hydrocarbons was only possible if a surfactant was added to the liquid phase in order to stabilize the formed nanoparticles and to prevent aggregation. Different types of surfactants (anionic, cationic, non-ionic) were used in these experiments. The results were a bit different, but all three types of surfactants were appropriate for this process if the were used in concentrations above their cmc (critical micellation concentration) values.

The obtained particles were characterized by AFM (atomic force microscopy), PCS (photon correlation spectroscopy) and zeta-potential measurements. The particles are mainly spherical with mean diameters of about 120 nm, what can be deduced from AFM images and PCS).

The produced dispersions are stabilized by steric interactions in the case of the non-ionic polymer-surfactant. In the case of anionic and cationic surfactant solutions the very high positive respectively high negative zeta-potentials show electrostatic stabilisation. Nevertheless we found significant differences in long term stability of the dispersion, depending on which surfactant is used for stabilisation.

Conclusion

Laser ablation is a very fast and simple method and is very useful for organic microcrystal preparation. Many parameters such as wavelength, fluence, pulse duration, surfactant type and concentration, temperature, and so on, can be used to tailor the properties of the obtained particles. Nanoparticles of polycyclic aromatic hydrocarbons were successfully prepared by the laser ablation technique. It was found that with these materials the use of surfactant solution is indispensable for nanoparticle dispersion preparation. The dispersions were very stable due to electrostatic or steric interactions if suitable surfactants were chosen.

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