Laser-enhanced Dispersion of Multiwalled Carbon Nanotubes in Acetonitrile

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Laser irradiation effect on the dispersibility of multiwalled carbon nanotubes (MWCNTs) has been investigated by UV–vis spectroscopy. Absorbance growth indicated increased dispersion in acetonitrile. Dispersibility depended on the irradiation time and power density. Even under high fluence irradiation the morphology scarcely changed under SEM observation, while the Raman spectrum measurement was indicative of the surface change.

Carbon nanotubes (CNTs) and carbon nanofibers have great scope in industrial applications.[1–3] However, low dispersion and stacked bundles complicate nanocomposite and nanohybrid production, thus leading to restriction of its applications. Therefore, development of an effective dispersion method is desired. A number of strategies like sonication,[4] acid-treated surface modification,[5] surfactant use,[6] and amylase encapsulation[7] have been developed to increase the concentration of dispersed carbon nanoparticles. However, these methods have some disadvantages, e.g., sonication causes shrinkage,[4] surface modification alters physical properties of CNTs like conductance[8] and band gap energy, and surfactant addition limits the subsequent fabrication. In this letter we present a simple method to raise the concentration of MWCNTs in organic solvents on laser irradiation. Laser ablation is applied to disperse the organic molecules in water.[9] Good dispersion is attained by adjusting the laser power density.

A mass of 10 mg of MWCNTs (ILJIN Nanotec CM-95, diameter 10–30 nm, length 10–20 µm) was dispersed in 40 mL of hexane, toluene, or acetonitrile solvent (Wako Pure Chemicals, S grade) and sonicated for 1 min. The dispersions were irradiated by the fundamental of a Nd:YAG laser (Spectra Physics, Quanta-Ray INDI 40, rep rate 20 Hz) while stirring and then centrifuged for 5 min at 10000 rpm to remove aggregates and entangled carbon nanotubes. The resulting supernatant was analyzed by UV–vis spectroscopy (Shimadzu, UV2000) to assess the dispersibility. Field emission scanning electron microscopy FE-SEM (Hitachi, S-4100) was used to check the morphology changes. Raman spectra were obtained using RAMAN RXN Systems excited at 532 nm.

We first compared the dispersibility of MWCNTs in hexane, toluene, and acetonitrile solvents. The absorbance of MWCNTs in acetonitrile at 500 nm after laser irradiation was more than twice compared to that of the other solvents. Similar to the case of sonication of CNTs in nonpolar organic solvents,[10] polar organic solvents tend to disperse MWCNTs. Solvent dependence of dispersibility may indicate that laser-induced dipole of MWCNTs is stabilized in polar solvents to exist as a monomer or small bundles. It is interesting to compare the results where pre-polymer-coated CNTs dispersed in *N*,*N*-dimethylformamide were flocculated by laser irradiation.[11]

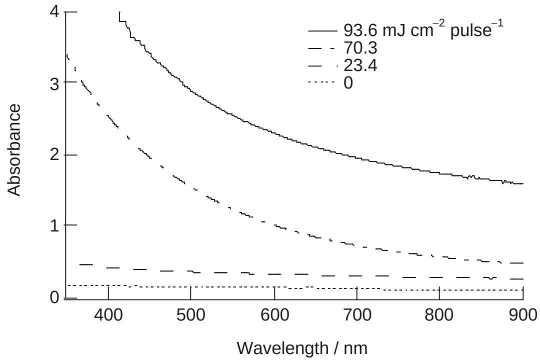

Figure 1. Absorption spectra of MWCNTs dispersed in acetonitrile.

Absorption spectra measured after 18000 pulses of the 1064 nm YAG fundamental at different fluences, shown in Figure 1, demonstrate that the absorbance increases with the fluence. At 500 nm, for the samples irradiated at 23.4, 70.3, and 93.6 mJ cm^{-2} pulse^{-1} fluence their absorbance increased by 2.4, 10.4, and 19.4 times, respectively, compared to that of a nonirradiated sample. Figure 2 shows the laser irradiation time dependence of dispersibility of MWCNTs at 23.4 mJ cm^{-2} pulse^{-1}. Prolonged irradiation resulted in better dispersibility, even at lower fluence. High-density laser irradiation may cause undesired ablation. Ma et al.[12] observed changes in morphology of block-type CNTs after continuous CO$_2$ laser irradiation under an Ar atmosphere. Depending on the laser

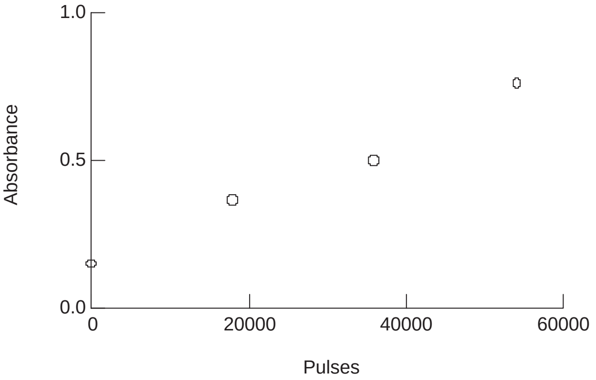

Figure 2. Laser pulse dependence of the dispersibility of MWCNTs irradiated at 23.4 mJ cm^{-2} pulse^{-1}.

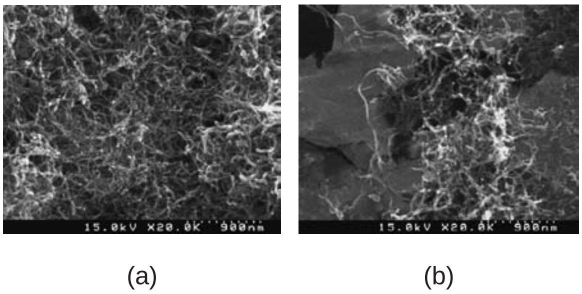

Figure 3. SEM micrographs of MWCNTs. (a) Preirradiation and (b) postirradiation (18000 pulses) at 93.6 mJ cm^{-2} pulse^{-1}.

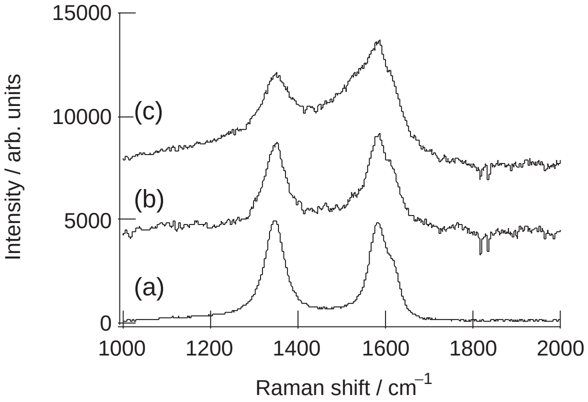

Figure 4. Raman spectra of MWCNTs. (a) Preirradiation and postirradiation (18000 pulses) at (b) 70.3 and (c) 93.6 mJ cm^{-2} pulse^{-1}.

power and irradiation time, the nanoparticles sintered and C_n cluster formation occurred.

SEM micrographs were taken (Figure 3) to confirm that the absorbance increase was due to the dispersion of MWCNTs, and not the collapsed amorphous carbon. Sample drops were placed on the sample holder and the solvent was evaporated. After repeating this sample-application and solvent-evaporation process, SEM images were captured. Figure 3a shows MWCNTs before irradiation. Upon sonication, the bundles were considerably loosened compared to the as-received dry sample (not shown). While owing to solvent evaporation MWCNTs were aggregated, MWCNTs were well loosened, as shown in Figure 3b. Significant morphology change was not observed. The solvent may help dissipate the excess heat leading to graphene structure decomposition under the present laser density.

Figure 4 shows Raman spectra of pre- and post-laser-irradiated MWCNTs, the same samples used in SEM measurements. In the first-order spectra, three typical peaks[13] were observed around 1350 (D), 1580 (G), and 1620 (D′) cm^{-1}. Peak analysis was conducted by applying the Lorentzian function for the D and G bands and the Gaussian function for the D′ band.[13] No peak shift was caused by the laser irradiation, while the band widths increased especially in Figure 4c. Relative intensity of the D band to the G band (I_D/I_G) decreased from 1.2 to 1.0 after irradiation at 70.3 mJ cm^{-2} pulse^{-1}. The D band is the characteristic feature of disordered carbon. A slight decrease in the I_D/I_G ratio may imply the removal of the amorphous carbon layer or curing effect of the structural defect. At 93.6 mJ cm^{-2} pulse^{-1}, however, it is impossible to fit the peak shape around 1580 cm^{-1} by two functions. Apparently a shoulder peak is discernible in lower frequency regions of the G band. It may be due to the destruction effects as observed in electron irradiation.[14] Deposition of amorphous carbon would result in the red-shifted peak. In the case of single-walled carbon nanotubes (SWCNTs), photoluminescence is observable only when the tubes are individually dispersed.[15] If not, electronically excited bundled-SWCNTs are nonradiatively quenched. In the present case photoexcited MWCNT aggregates will be quenched similarly. Partial excitation energy will be used to break up the aggregates. This is one of the reasons for the enhanced dispersion.

We have introduced a simple method to increase the dispersibility of MWCNTs in acetonitrile by laser irradiation. This method will be applicable to the synthesis of composite materials.

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