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Single-wall carbon nanotube colloids in polar solvents

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Stable single-wall carbon nanotube (SWCNT) colloids in polar solvents, such as water, ethanol, acetone and DMF, have been prepared and the third-order optical nonlinearity of the SWCNTs measured using the femtosecond optical Kerr effect.

Owing to their novel structural, electronic and mechanical properties, single-wall carbon nanotubes (SWNTs) are likely to possess many potential applications.[1,2] However, it is difficult to study their chemical behavior and properties because of their insolubility in solvents. Chen *et al*.[3,4] obtained an SWCNT derivative which was soluble in organic solvents obtained from shortened SWCNTs[5] and studied the solution-phase EPR of such SWCNTs.[6] Liu *et al*.[7] successfully deposited individual short SWCNT segments on chemically functionalized nanolithographic templates from a 0.1 mg ml^{-1} carboxylated SWCNT suspension of DMF. Here, we report the preparation of stable SWCNT colloids by dispersing carboxylated SWCNTs in several polar solvents, which will facilitate the study of chemical properties and the engineering of electronic devices based upon SWCNTs. The third-order optical nonlinearity of colloidal SWCNTs in DMF was measured. The high third-order optical nonlinearity susceptibility obtained indicate potential applications of SWCNTs in optical information processes.

SWCNTs were produced by the dc arc-discharge method[8] and purified to > 90%.[9] The SWCNTs had a diameter of *ca*. 1.3 nm and existed as SWCNT bundles both in the raw-soot and purified samples. The SWCNT bundles had a diameter of 20–30 nm in the raw-soot and 50–60 nm in the purified sample with lengths of > 10 μm.[9] The preparation of aqueous colloids was carried out by dissolving 100 mg purified SWCNTs in 120 ml 98% H_2SO_4–70% HNO_3 (3 : 1) and subjecting to ultrasonication for 8 h. The obtained solution was diluted with deionized water to 500 ml and left to stand over night. After decanting the solution, 50 ml of deionized water was added to the residue which was allowed to stand for one day. After discarding the supernatant, 25 ml of deionized water was added to the residue to form a colloidal solution of SWCNTs in water. The pH value of the colloidal solution was *ca*. 3 for a concentration of 1.77 mg ml^{-1}. The colloid solution remained very stable for > 1 year.

In order to remove the residual acids, the colloid solution was passed through a PTFE membrane disc Filter (Gelman, 1 μm pore size) under vacuum followed by washing several times with deionized water. The SWCNTs on the membrane disc were readily dispersed in water, ethanol, acetone and DMF after ultrasonication for a few minutes to form black colloids in the absence of surfactants. The saturated concentration of SWCNTs in water, ethanol, acetone and DMF were 1.16, 0.5, 1.06 and 2.0 mg ml^{-1}, respectively, and the pH value of the colloid solution of SWCNTs in water was 5.5.

In our experiments, the saturated concentration of SWCNTs in water largely depended on the acidity of the solution. At pH < 1.5, SWCNTs in water precipitate in 1 or 2 h after standing while pH at 2.4, 1.97 mg SWCNTs can be dispersed in 1 ml of water to form a stable colloid. At a pH of 5.5 the saturated concentration of SWCNTs is reduced to 1.16 mg ml^{-1}. Thus, the pH range 2–3 is favorable for the formation and existence of stable colloids of SWCNTs in water.

The observation of stable colloids suggests the presence of carboxylic groups at open ends of the SWCNTs, which was verified by the characteristic stretching band ($\nu_{C=O}$) at 1710 cm^{-1} in the FTIR spectrum.[4] The structure of the SWCNTs was established by Raman spectroscopy. As shown in Fig. 1, no obvious change occurs in the Raman spectra of SWCNTs before or after treatment with mixed acids except for a decreasing peak ratio G : D, which implied that the SWCNTs were shortened after acid treatment. Compared to Liu's results for relatively longer nanotubes,[5] it can be anticipiated that SWCNTs should exist in a non-aggregated state in the various colloid solutions.

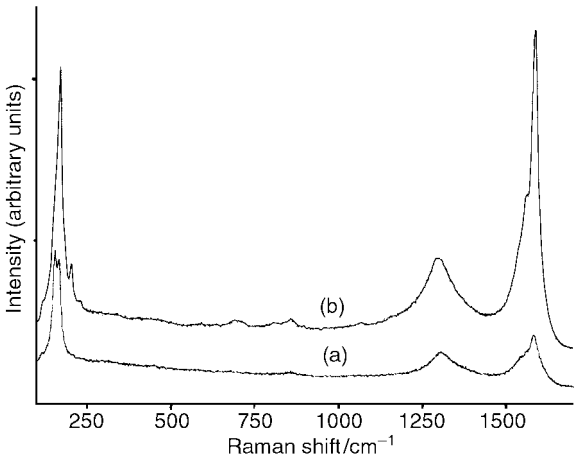

Fig. 1 Raman spectra of purified (b) and carboxylated (a) SWCNTs at 783 nm.

The tube length distribution of SWCNTs in solvents can be approximately estimated by the hydrodynamic radius *via* laser-scattering characterization. SWCNTs in water have a hydrodynamic radius in the range 23–300 nm with a mean of 81.1 nm (Fig. 2). In other words, the length of the SWCNTs ranges from 50 to 600 nm with a mean of *ca*. 160 nm. The length distribution is shorter than that reported by Liu *et al*.[5]

The successful preparation of the colloids made it possible to measure the third-order optical nonlinearity of the SWCNTs. Nonlinear optics (NLO) measurements were performed using the femtosecond optical Kerr technique[10] with a Ti:sapphire laser (Mira 900F, Coherent Co. Ltd., USA). The operating wavelength was centered at 820 nm, where the sample shows no absorption. In our experiments, three SWCNTs colloid solutions of 0.33, 0.22 or 0.13 mg ml^{-1}, in DMF were used and the sample cell thickness was 1 mm. The zero delay point was determined with a BBO crystal (0.3 mm thick) and the pulse duration was set at 120 fs.

The ultrafast NLO response of the SWCNT colloids is shown in Fig. 3 together with that for the reference sample of CS_2 under the same conditions. The instantaneous response proves that the NLO signal is attributed to conjugated π-electrons. The

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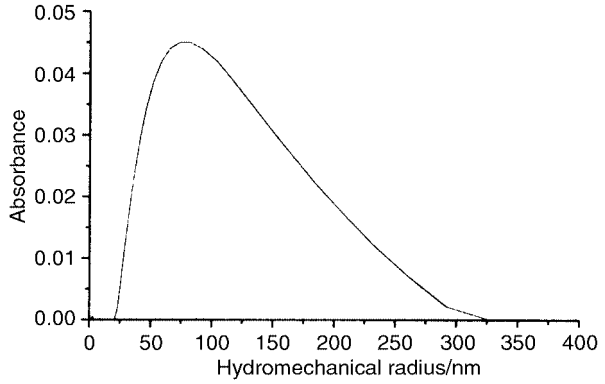

Fig. 2 Hydrodynamic radius distribution of an aqueous colloid of SWCNT measured using 514.5 nm laser-scattering.

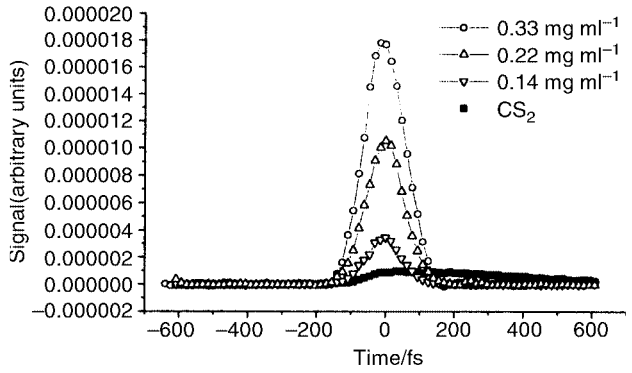

Fig. 3 Ultrafast OKE signals of SWCNT colloids in DMF together with a reference sample of CS_2.

signal caused by colloids at different concentrations indicates a square dependence of the signal on the concentration. The third-order optical nonlinearity susceptibility, $\chi^{(3)}$, of the colloid at a given concentration can be calculated[11] and a value of 4×10^{-13} esu was obtained for the 0.33 mg ml^{-1} SWCNT colloid in DMF. In this measurement, the contribution of DMF (*ca.* 1×10^{-14} esu) is reasonably neglected as the $\chi^{(3)}$ value for DMF is nearly ten times smaller than that of CS_2[12] (1×10^{-13} esu).[13] Furthermore, the magnitude of the second-order hyperpolarizabilities, γ_c, for each carbon atom can be calculated as 7.7×10^{-33} esu, which is much higher than those of C_{60} and multiwall carbon nanotubes,[14] and close to the value expected from theoretical calculation.[15] This is a remarkably large non-resonant and instantaneous NLO response for π-conjugated molecules, which indicates that SCWNTs may be useful as nonlinear optical materials.

In conclusion, stable SWCNTs colloid solutions in polar solvents, such as water, ethanol, acetone and DMF, have been prepared with purified SWCNTs and using a sulfuric acid–nitric acid mixture. This opens the possibility for template assembly or functionalization of SWCNTs in polar solvents. For colloids of SWCNTs in DMF, the third-order optical non-linearity of SWCNTs was measured and a large nonresonant and instantaneous NLO response was obtained, indicating the potential applications of SWCNTs in optical information process.

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