Pulsed-laser Irradiation to Suspended Carbon Particles in Aqueous Silver Nitrate Solution

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When carbon suspended in water was irradiated repetitively by pulsed laser at 532 nm, the carbon particles were gradually consumed, being accompanied with morphology change. Transmission electron microscopy (TEM) showed formation of seemingly entangled long fibrils and/or thin shells from the particles. In the copresence of silver ions, characteristic plasmon absorption peak appeared and formation of nanosized silver particles was evidenced by TEM. Under the typical fluence of $125 \, mJ \cdot cm^{-2} \cdot pulse^{-1}$, the quantum yield of silver reduction was 10^{-3}.

Pulsed-laser irradiation to colloidal particles in water has been extensively studied, owing to its physicochemical interest as well as its potential usage in nanotechnology. However, such studies have not been widely performed for suspended carbon.[1–3] Recently, we reported[4] that when carbon suspended in water was irradiated by pulsed Nd:YAG laser at 532 nm, the carbon particles were consumed, being accompanied with gas evolution, audible sound, and diffuse white-light emission. In scanning electron microscopic (SEM) images, the recovered carbon particles appeared to have been connected with each other forming agglomerates to larger extents with the increase of laser fluence above ca. $60 \, mJ \cdot cm^{-2} \cdot pulse^{-1}$. We proposed to employ the pulsed-laser irradiation technique for activating the surface of carbon particles, for inducing reduction reactions and fabricating integrated materials with carbon. In the present paper, we will describe the peculiar morphology of the irradiated carbon particles observed by transmission electron microscopy (TEM) and also the formation of colloidal silver in the presence of silver ions.

Carbon particles (spherical carbon black particles with a primary average diameter of 66 nm (Tokai Carbon Co., Ltd., Tokablack #7050)) were suspended by mixing them with deionized water or with aqueous silver nitrate solution and were then dispersed through ultrasonic agitation for 300 s just before the irradiation. The prepared carbon suspension of $8 \, cm^3$ in a cylindrical cell of $2.5 \, cm^2$ cross section and 3 cm depth was irradiated through the top opening with a Nd:YAG laser (Spectra-Physics, GCR-170: repetition rate of 10 Hz, nominal pulse length of 7 ns, and beam cross section of $0.8 \, cm^2$) at 532 nm while being agitated with a magnetic stirrer. The typical carbon and silver nitrate concentrations were both 2×10^{-3} $mol \cdot dm^{-3}$, which implied that most of the input laser photons were consumed inside of the cell.

The carbon suspended either in water or aqueous silver nitrate solution showed a rather flat extinction spectrum from 250 to 900 nm before irradiation (Figure 1a at $t = 0$ s), as
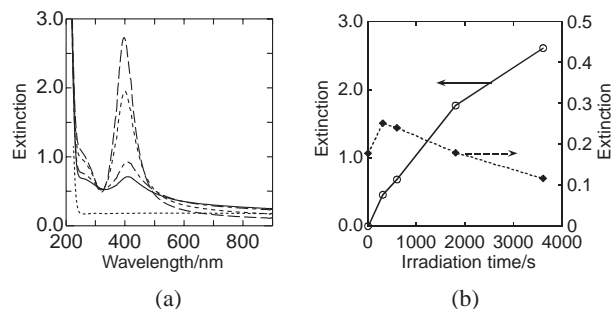

Figure 1. (a) Change of extinction spectra with the irradiation of the aqueous silver nitrate solution with suspended carbon. Irradiation time: 0 (dot), 300 (solid), 600 (dot dash), 1800 (short dash), and 3600 s (dash). Experimental conditions: Initial $AgNO_3$ and C concentrations, $2.0 \times 10^{-3} \, mol \cdot dm^{-3}$, respectively. Laser fluence, $125 \, mJ \cdot cm^{-2} \cdot pulse^{-1}$. (b) Time evolution of the extinction values at the surface plasmon peak (○) and at 900 nm (◆) corresponding to the suspended carbon. Data are taken from (a).

measured with a UV–vis spectrometer (JASCO, V-550).

When the suspended carbon was irradiated repetitively, the extinction gradually decreased as had been discussed in the previous paper[4] owing to the consumption of carbon. When the carbon suspended in aqueous silver nitrate solution was irradiated, a new extinction peak at around 400 nm grew almost linearly to the irradiation time and then gradually saturated as shown in Figure 1a, where the extinction (defined as $\log(I_0/I)$) spectra were measured for the solution diluted to 1/3 in a 1 cm optical cell. The peak was identified as the surface plasmon absorption of the mostly spherical colloidal silver by comparing the spectrum with those of typical colloidal silvers.[5–7] In the absence of suspended carbon, production of similar peak was negligibly small.

We plotted the extinction of the plasmon peak in Figure 1b as a measure of the amount of produced colloidal silver, after subtracting the possible contribution from the suspended carbon that was assumed to possess the same extinction as that at 900 nm. In general, the extinction spectrum of spherical silver particles does not extend up to 900 nm. The extinction at 900 nm increased in the initial stage probably owing to the increased dispersion of the original carbon particles under the laser irradiation as had been previously discussed[4] and then gradually decreased owing to consumption. We plotted the extinction at 900 nm also in Figure 1b as the measure of the suspended carbon amount. The gradual saturation found in the colloidal silver seems to be caused by the consumption of the suspended carbon.

The mass balance of silver was demonstrated at the irradiation time $t = 300$ s. The inductively coupled plasma atomic emission spectrometry (ICP) measurement for the filtrate from the irradiated solution through a 25-nm pore size filter showed that the solution contained 7.8×10^{18} silver ions. The remaining filter cake, after being treated by concentric nitric acid and analyzed by ICP, showed that the irradiated solution contained 9.1×10^{17} silver atoms. The sum of the ions and atoms corresponded to about 90% of the 9.7×10^{18} silver ions contained in the initial solution, showing a good mass balance. The yield of silver atoms at $t = 300$ s was thus 9.4%. On the other hand, at $t = 300$ s, the plasmon peak located at 409 nm, which corresponds to the mean particle diameter of 29.8 nm and extinction cross section of 3.13×10^{-11} cm^2, if the study by Evanoff and Chumanov[6] is applied to the present case. From the extinction value of the peak shown in Figures 1a and 1b, the total amount of the produced silver atoms in the irradiated solution was evaluated to be 6.6×10^{17} atoms via simple calculation using the above particle diameter and cross section. The obtained value was in rough agreement with the amount of silver atoms estimated from the ICP analysis of the filter cake, 9.1×10^{17}. At $t = 300$ s, the quantum yield of silver production against the absorbed laser photon (7.6×10^{20}) was then estimated to be 1.2×10^{-3} from the ICP analysis and 0.9×10^{-3} from the plasmon peak analysis. Thus, the quantum yield was in the order of 10^{-3}.

The recovered solid materials were characterized by TEM (JASCO, JEM-2010F) at 200-kV acceleration voltage. For the measurements, several drops of the solution with suspended carbon was deposited on a collodion–gold grid (200 mesh) and allowed to dry at 100 °C for 600 s.

Compared to our previous SEM,[4] the present TEM gave a more detailed view of the irradiated carbon particles as shown in Figures 2b and 2c. It was found that the morphology became quite different by the irradiation under the typical 125 mJ·cm^{-2}·pulse^{-1} fluence. The particles hardly retained their original shape, and the remaining material appeared to be made of entangled long fibrils and/or of thin shells. On the other hand, from the irradiation to suspended carbon in aqueous silver nitrate solution, formation of a large number of small, mostly spherical particles together with the remaining entangled long fibrils and/or thin shells of carbon was observed as shown in Figures 2d and 2e. The selected area electron diffraction image indicated that the particles mainly consisted of polycrystalline silver. However, it was not certain whether any strong interaction between the silver particles and the remaining carbon existed in the solution.

Concerning the reaction mechanism, some reductive species such as atomic carbon and hydrogen produced through the gas shift reaction, $C + H_2O \rightarrow CO + H_2$, are expected to exist[1–4] at the high temperature attained under the pulsed-laser irradiation. Thermionic emission is also one possibility to induce the morphology change and the reduction, consulting that efficient thermionic emission was reported in the case of gold colloids.[8] We will also take into account the study[9] on the irradiation of colloidal gold in the presence of silver ions to yield colloidal
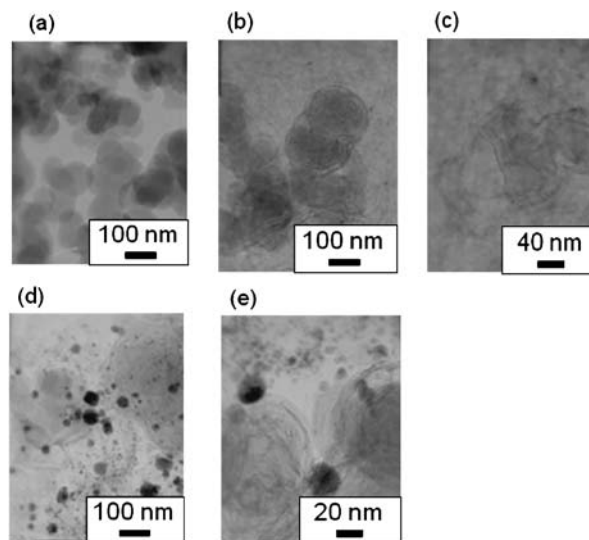

Figure 2. TEM images of recovered solid materials before and after the irradiation. (a) Before irradiation in water with C of 2.0×10^{-3} mol dm^{-3}. (b), (c) After irradiation of 600 s in water with initial C of 2.0×10^{-3} mol·dm^{-3}, at different magnifications and different positions on the TEM grid. Laser fluence, 125 mJ·cm^{-2}·pulse^{-1}. (d), (e) After irradiation of 300 s in aqueous silver nitrate solution with carbon suspension, at different magnifications and different positions on the TEM grid. Initial AgNO$_3$ and C concentrations, 2.0×10^{-3} mol dm^{-3}, respectively. Laser fluence: 125 mJ·cm^{-2}·pulse^{-1}.

gold–silver alloy. The detailed investigation of the mechanism is left to future.

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