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To cite this article: Takahiro Fukuda *et al* 2007 *New J. Phys.* **9** 321

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Dissociation of carbon dioxide and creation of carbon particles and films at room temperature

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Abstract. As fluids approach their gas–liquid critical points, the physical properties such as the specific heat and compressibility diverge due to the formation of large molecular clusters. Incident light cannot penetrate near-critical fluids because of the large clusters, a phenomenon known as critical opalescence. In this paper, we irradiate near-critical carbon dioxide ($ncCO_2$), the critical temperature and pressure of which are $31.0°C$ and $7.38\,MPa$, with a laser beam of 213, 266, 355 and 532 nm wavelength and show that CO_2 is dissociated and particles are produced when the system is set so close to the critical point that critical opalescence occurs in the case of 213 and 266 nm wavelength, whereas no particles are produced when the temperature is made to deviate from the critical value. We also apply a dc electric field to $ncCO_2$ during irradiation with a laser beam of 213 and 266 nm wavelength and find that particles are formed on both anode and cathode. As the intensity of the electric field increases, films are formed on the electrodes. Electron diffraction patterns and energy-dispersive x-ray, Auger electron, x-ray photoelectron and Raman spectroscopic analyses show that the particles and films are composed of amorphous carbon.

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Contents

1. Introduction

As fluids approach their gas–liquid critical points, the physical properties such as the specific heat and compressibility diverge due to the formation of large molecular clusters [1]. Incident light cannot penetrate near-critical fluids because of the large clusters, a phenomenon known as critical opalescence. The relaxation time of molecular diffusion increases and the fluctuations of the local temperature, pressure and density become significant. In terms of non-equilibrium transport phenomena, the temperature, pressure and density perturbations propagate quickly as acoustic waves due to low thermal diffusivity and high compressibility, which is known as the piston effect [2]–[7], and strong buoyancy convection is driven due to low thermal diffusivity and high temperature coefficient of volume expansion [8]–[13].

Critical fluids have also been recognized as useful fluids from a technological point of view and they are, therefore, often used in nanotechnology as well as chemical, electrical and environmental sciences and engineering. Reactions are encouraged [14]–[17], chemicals are extracted [18]–[21], semiconductors are washed and cleaned [22, 23] and nanomaterials and nanostructures can be produced [24]–[26] efficiently utilizing super-critical fluids such as super-critical carbon dioxide (scCO$_2$), which has both gas- and liquid-like characteristics.

When nanostructures such as fullerenes and carbon nanotubes are produced by laser ablation, a laser of 532–1064 nm wavelength irradiates carbon substrates, which are placed in an inert gas such as helium or argon [27, 28]. The ambient temperature and pressure are in general set, respectively, at over 1000°C and at lower than or equal to 0.1 MPa.

In this paper, we irradiate near-critical carbon dioxide (ncCO$_2$), the critical temperature and pressure of which are 31.0°C and 7.38 MPa [29], with a laser beam of 213, 266, 355 and 532 nm wavelength, supposing that the chance of photons hitting CO$_2$ molecules increases dramatically as the fluid approaches the critical point due to critical opalescence. We show that CO$_2$ is dissociated and particles are produced when the system is so close to the critical point that critical opalescence occurs in the case of irradiation with laser beams of 213 and 266 nm wavelength, whereas no particles are produced when the temperature is made to deviate from the critical value. We also apply a dc electric field to ncCO$_2$ during irradiation with a laser beam and find that particles are formed on both anode and cathode. As the intensity of the electric field increases, films are formed on the electrodes. Although quite a few CO$_2$ dissociation methodologies have been developed [30]–[35], the operation temperature is,

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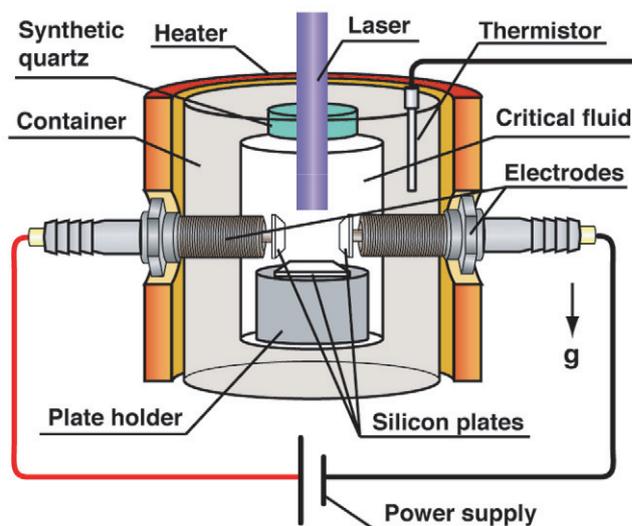
Figure 1. Outline of experimental system. $ncCO_2$ is confined in an aluminium cylindrical container. A laser beam of 213, 266, 355 and 523 nm wavelength is used to irradiate the $ncCO_2$. A silicon plate is placed at the central part of the container in each experiment to collect any by-products. Electrodes are also installed in the container so that a dc electric field can be applied in the horizontal direction during laser irradiation.

generally speaking, high. The present method of CO_2 dissociation, therefore, may be unique in terms of being at room temperature and, what is more, carbon particles and films are produced during the operation. We suppose that the dissociation of molecules in a fluid and formation of particles via the interactions between UV photons and large molecular clusters under critical opalescence conditions may be universal chemico-physical phenomena. We explain the experimental apparatus and procedure in section 2. We discuss the experimental results in section 3 and finally summarize what we obtained in this study in section 4.

2. Experimental details

The outline of our experimental system is shown in figure 1. $ncCO_2$ was confined in a cylindrical container made of aluminium. The inner and outer diameters and the inner and outer heights of the container were, respectively, 22 and 60 mm and 45 and 72 mm. A synthetic quartz glass, the diameter and thickness of which were 20 and 5 mm, was mounted at the top of the container for the introduction of the laser beam. Fluid, the amount of which corresponded to the critical density, was introduced into the container. A thermistor (SZL-64, Takara Thermistor Co. Ltd) was set in the container wall and the temperature of the fluid was controlled by a heater installed around the container and a temperature controller (C541, Technol Seven Co. Ltd). The temperature deviation from the critical temperature was changed from 0.01 to 1.00 K. In each experiment, 50 000 pulses of a laser beam were irradiated from a neodymium doped yttrium/aluminium/garnet (Nd : YAG) laser (Brilliant Quantel Ltd Co.) into the $ncCO_2$. The wavelength of the laser beam was changed as follows: 213, 266, 355 and 532 nm. The diameter
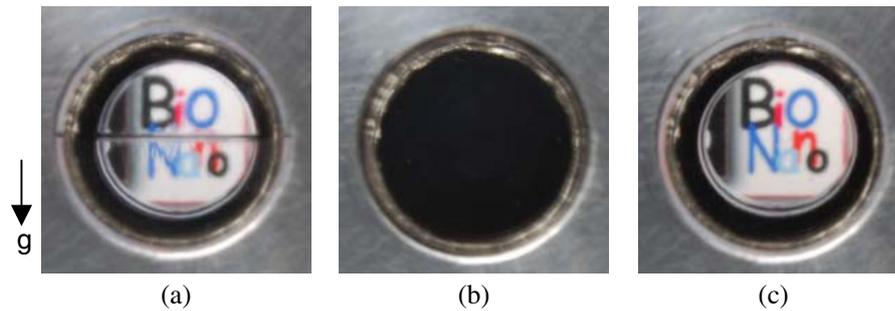
Figure 2. Carbon dioxide under sub-critical, near-critical and super-critical conditions. (a) Sub-critical CO_2, the temperature is 28.0°C; (b) ncCO_2, 31.1°C; (c) scCO_2, 35.0°C. The present experimental system can create critical opalescence.

and average energy flux of the laser beam were 10 mm and 1.3 mW mm^{-2}. The duration of each laser pulse and the frequency of the pulse generations were 4.3 ns and 10 Hz. The beam was not focused on any particular spot. A silicon plate or transmission electron microscope (TEM) grid was placed at the central part of the container in each experiment to collect any by-products. Aluminium electrodes, which were covered with silicon plates of 5 mm width × 5 mm depth × 1 mm thickness, were installed in the cylindrical container, so that a dc electric field could be applied in the horizontal direction during laser irradiation experiments (see figure 1). After each experiment, the critical fluid was released gradually controlled by a valve switch and the surfaces of the silicon plate, TEM grid and electrodes were examined by scanning electron microscope (SEM) (JSM7400F, JEOL) and TEM (JEM2200FS, JEOL). We also analysed the components and structures of the materials collected on the silicon plate, TEM grid and electrodes by the electron diffraction method (JEM2200FS, JEOL), energy-dispersive x-ray spectroscopy (EDS) (JED2300-F and JED2200-T, JEOL), Auger electron spectroscopy (AES) (PHI700, ULVAC-PHI Inc. and JAMP-7810, JEOL), x-ray photoelectron spectroscopy (XPS) (AXIS-His, Kratos Analytical Inc.) and laser Raman spectroscopy (LabRAM, HR-800, HOLIBA JOBIN YVON S.A.S.).

3. Results and discussion

3.1. Critical opalescence

First of all, let us show the photographs of CO_2 confined in the container under sub-critical, near-critical and super-critical conditions in figure 2, where the container is placed horizontally and another synthetic quartz glass is mounted at the bottom of the container for visualization. CO_2 is not transparent under near-critical conditions due to the formation of large molecular clusters, whereas it is transparent under both sub-critical and super-critical conditions. We measured the transmission spectrum of a deuterium/tungsten/halogen light (DH2000-DUV, Ocean Optics Inc.) passing through ncCO_2. The light source provides a 190–1700 nm range. The transmission spectrum was measured by a spectrometer (USB2000, Ocean Optics Inc.). The detectable spectrum range is 200–1100 nm. The raw spectrum of the incident light is shown in figure 3(a) and the transmission spectrum is shown in figure 3(b). As the system approaches

(a)   (b)
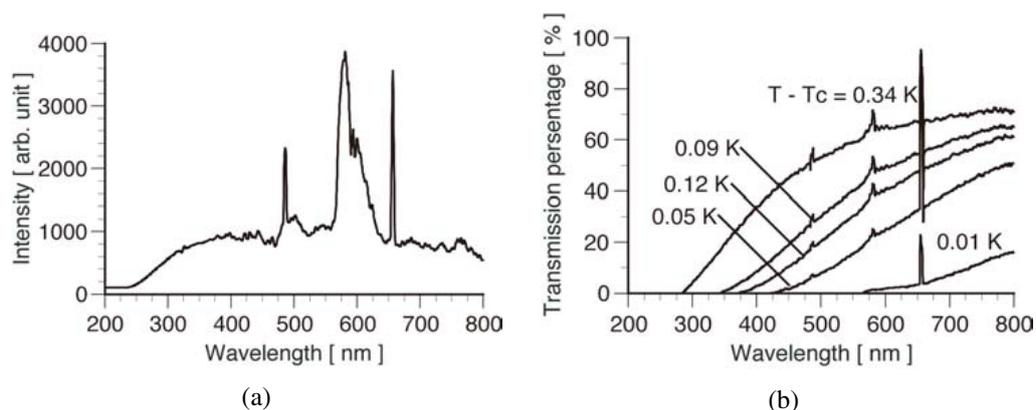
Figure 3. Transmission spectrum. (a) Raw spectrum of the incident light from a deuterium/tungsten/halogen lamp. (b) Transmission spectrum of the incident light. As the system temperature approaches the critical temperature, the amount of absorption or scattering by molecular clusters in $ncCO_2$ increases and the cutoff wavelength shifts towards a longer wavelength region.

the critical point, the amount of transmitted light decreases and the cutoff wavelength shifts towards a longer wavelength region. The result of this preliminary experiment shows that our experimental system creates critical opalescence properly.

3.2. Irradiation of a UV laser into $ncCO_2$

We irradiated $ncCO_2$ with a laser beam of 213, 266, 355 and 532 nm wavelength and found that particles were created after irradiation of a laser beam of 213 and 266 nm wavelength when the temperature was set so close to the critical temperature that critical opalescence occurred (see the SEM and TEM images in figures 4(a) and (b)), whereas no particles were observed on the silicon plate in the case of a laser beam of 355 and 532 nm wavelength. Particles were produced and collected by the silicon plate and some particles accumulated to form three-dimensional architectural structures. The number and diameter of the particles produced in $ncCO_2$ were very similar in both 213 and 266 nm cases. As the temperature was made to deviate from the critical value, particles were not produced even in the case of a laser beam of 213 and 266 nm wavelength. In this case, the plate was hit by the laser beam since critical opalescence did not occur and web-like structures made of silicon were produced. EDS and AES analyses show that the particles, which were produced in the $ncCO_2$ and collected by the silicon plate, are mainly made of carbon (see figures 4(c) and (d)). According to the electron diffraction pattern shown in figure 4(b), there are no clear crystalline structures in the particle. The Raman spectrum of a particle is shown in figure 4(e). The spectrum shows the D and G peaks, located approximately at 1380 and 1600 cm^{-1}, respectively. The rightward shift of the G peak from the 1575 cm^{-1} location for graphite points to increased disorder [36]. According to [37] for UV Raman in mostly sp^2 bonded amorphous carbon, the G peak position increases with growing sp^3 content, reaching values similar to those seen here. Comparing the G peak location and the peak intensity ratio, $I(D)/I(G)$, with the amorphization trajectories appearing in [37, 38] places the sp^3 fraction of the present sample above 20%. Although the D peak is shallow, it is clearly present in the spectrum. Taking into account the wavelength employed here for the Raman spectroscopic analysis, i.e. 325 nm, we suppose that the present sp^2 bonds are
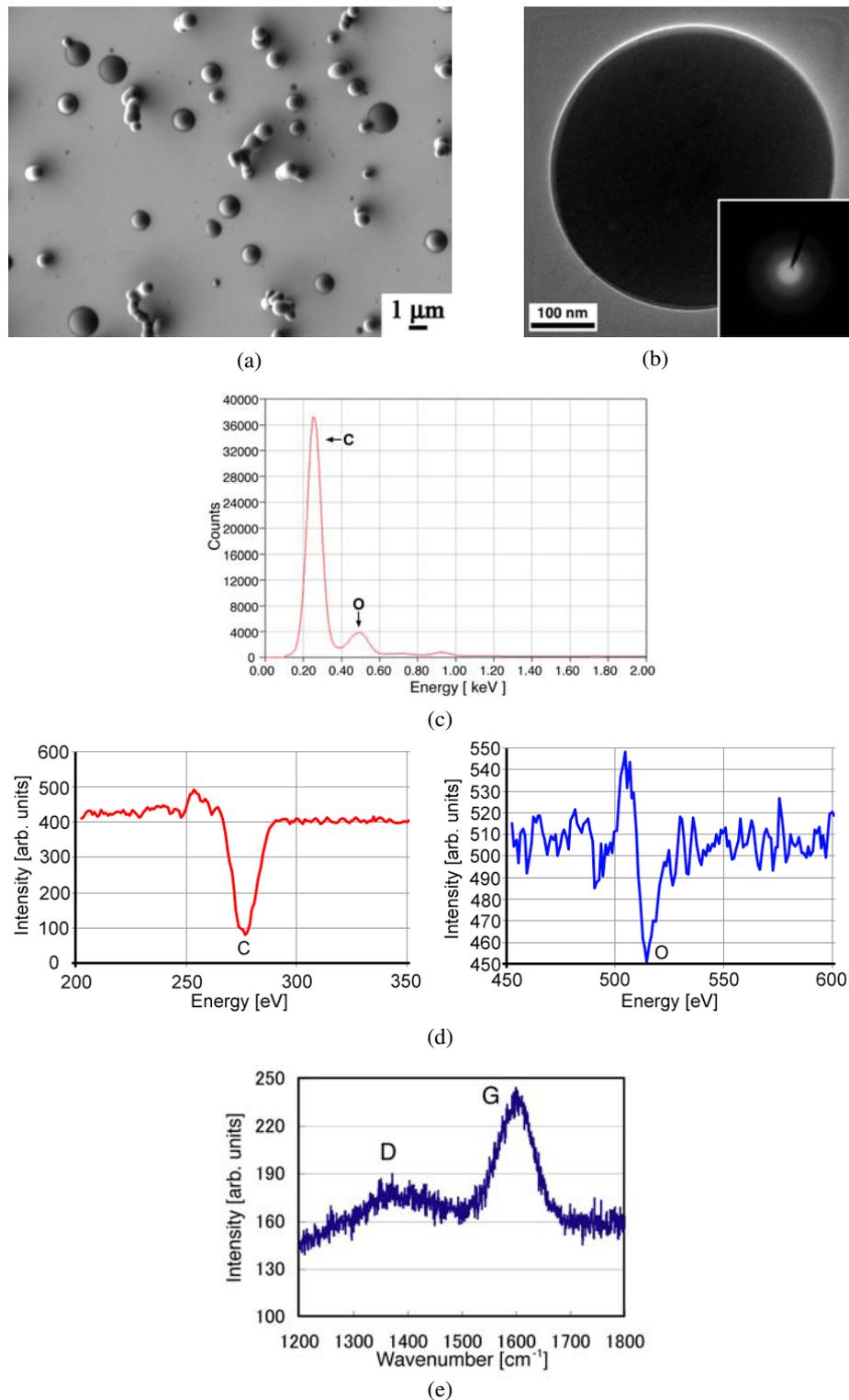
Figure 4. SEM and TEM images, electron diffraction pattern, EDS and AES analyses and Raman spectrum of particles created in ncCO$_2$ after 50 000 pulses of laser irradiation. The temperature was set at 31.0 °C. The wavelength of the laser beam was 266 nm. (a) SEM image, (b) TEM image and electron diffraction pattern, (c) EDS analysis, (d) AES analysis and (e) Raman spectrum.
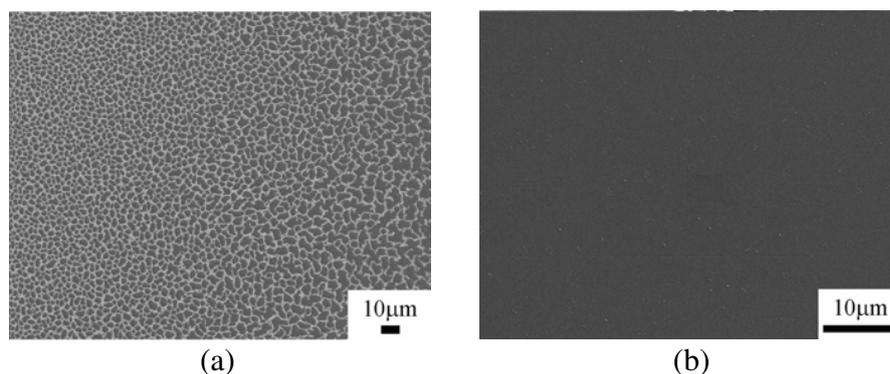
Figure 5. SEM images of films formed on anodes in a dc electric field. The wavelength of the laser beam was 266 nm. (a) The intensity of the electric field was $0.3\,\mathrm{kV\,mm^{-1}}$. A film composed of small domains was formed on the anode. (b) $0.8\,\mathrm{kV\,mm^{-1}}$. The anode was completely covered with film. The same structures were formed on the cathode in both 0.3 and $0.8\,\mathrm{kV\,mm^{-1}}$ cases.

not in graphitic six-fold rings, but in disordered forms, since the D peak is absent in UV in the case of graphitic order [39]. Based on the Raman spectrum and the lack of any crystalline diffraction pattern, we suppose that the produced structures are disordered carbon containing sp^2 hybridized bonds, as well as a substantial amount of sp^3 bonding.

3.3. Application of an external dc electric field

We applied dc electric fields of 0.3 and $0.8\,\mathrm{kV\,mm^{-1}}$ during the laser irradiation (see figure 1). In this case, particles were produced in the $ncCO_2$ and attracted to both anode and cathode. In the case of $0.3\,\mathrm{kV\,mm^{-1}}$, films, which were composed of small domains, were formed on both electrodes (see figure 5(a)), whereas in the case of $0.8\,\mathrm{kV\,mm^{-1}}$, both anode and cathode were completely covered with films (figure 5(b)). In both 0.3 and $0.8\,\mathrm{kV\,mm^{-1}}$ cases, no particles were found on the silicon plate set at the central part of the container. In other words, particles, which were produced in the $ncCO_2$, were collected very efficiently by the electrodes. EDS, AES and XPS analyses of the film show that the film is mostly composed of carbon and that oxygen is bonded to carbon at the surface of the film [40]–[42] (see figures 6(a)–(d)). The Raman spectrum of the film is very similar to that of the particles (see figures 4(e) and 6(e)). In other words, the film structures are disordered carbon containing sp^2 hybridized bonds, as well as a substantial amount of sp^3 bonding.

3.4. Important features in summary

Let us summarize the important features obtained through the above experiments. (i) No particles were created in $ncCO_2$ without any laser irradiation even when critical opalescence occurred. (ii) Particles and films were created by irradiating $ncCO_2$ with a laser beam of 213 and 266 nm in wavelength when critical opalescence occurred. The number and diameter of the particles were the same in both 213 and 266 nm cases. (iii) No particles were created in the case of 355 and 532 nm wavelength even when critical opalescence occurred. (iv) No particles were formed even in the case of 213 and 266 nm wavelength
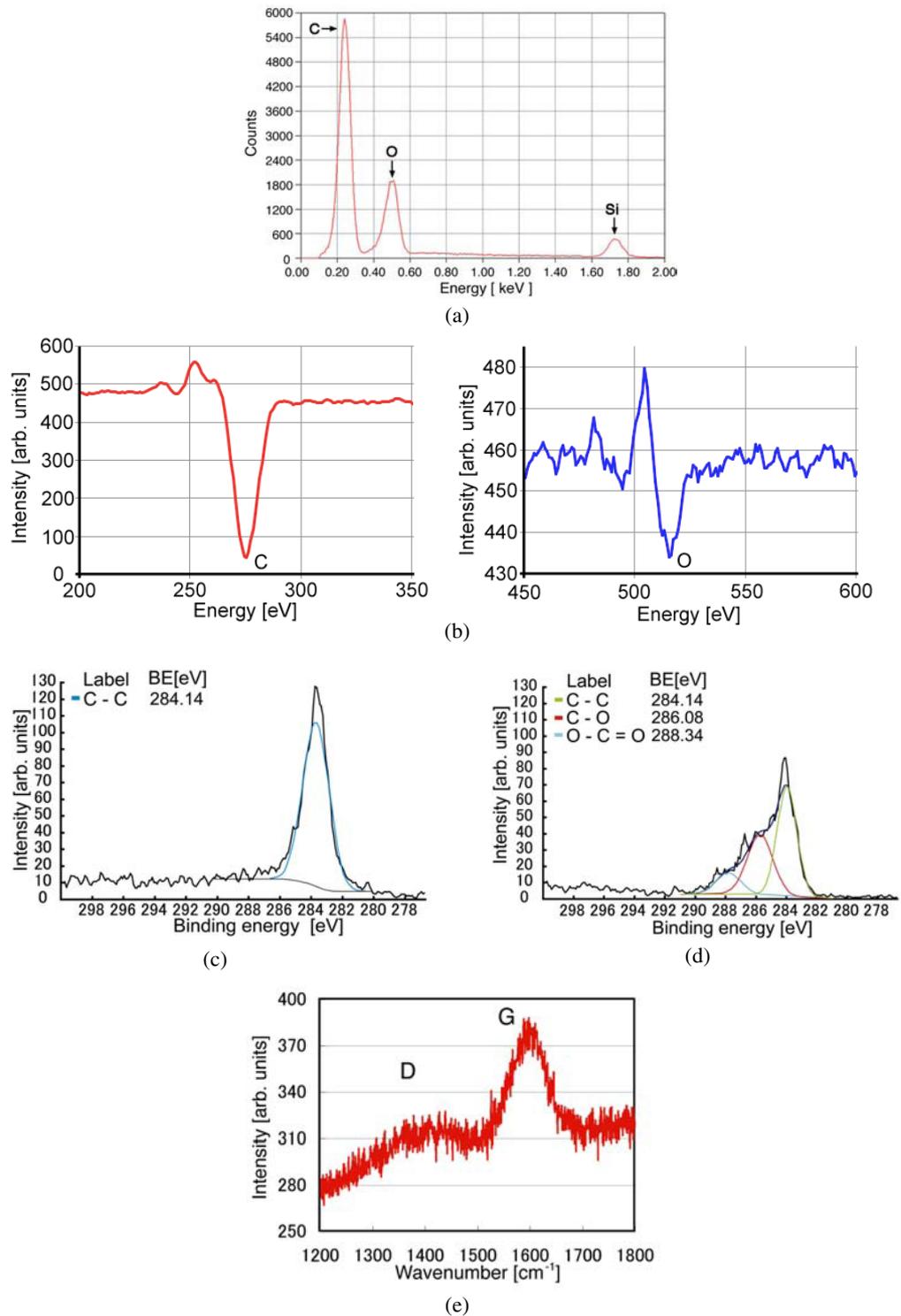
Figure 6. EDS, AES and XPS analyses, and Raman spectrum of the film corresponding to figure 5(b). (a) EDS analysis, (b) AES analysis, (c) XPS analysis inside the film, (d) XPS analysis near the surface of the film and (e) Raman spectrum.

when the temperature was made to deviate from the critical value. (v) Particles and films were mainly composed of amorphous carbon. Oxygen was bonded to carbon at the surface of the films.

The above experimental facts teach us that the large, flexible molecular clusters of CO_2, which are formed only under near-critical conditions, and the irradiation of photons of short wavelengths are essential for CO_2 dissociation. The dissociation energies of $CO_2 \rightarrow CO + O$ and $CO \rightarrow C + O$ are, respectively, 5.45 and 11.40 eV [43, 44]. Since the photon energies of 266 and 355 nm in wavelength are 4.66 and 3.49 eV, it is supposed that three-photon absorption may be occurring in the flexible fractal molecular clusters, which are created under near-critical conditions. Multi-photon absorption cannot occur in fluids under normal conditions since they are transparent even under UV photon irradiation, while in the case of near-critical fluids, multi-photon absorption can occur, thanks to the formation of large molecular clusters. According to our experiments using different fluids, ethane and benzene are also dissociated and carbon particles are created under near-critical conditions via the interactions between UV photons of 266 nm wavelength and large molecular clusters (see supplementary data). What is more, a binary fluid system such as a hexane/methanol binary system, in which critical opalescence occurs under 0.1 MPa, is dissociated and carbon particles are formed under near-critical conditions after irradiation with a laser beam of 266 nm wavelength (see supplementary data). It is therefore supposed that the dissociation of molecules in fluids and formation of particles via the interactions between UV photons and large molecular clusters under critical opalescence conditions may be universal chemico-physical phenomena. As we mentioned, quite a few CO_2 dissociation methodologies have been developed, but the operation temperature is, generally speaking, high. Therefore, the present method may be unique in being a room temperature operation and, what is more, carbon particles and films are created. We suppose that UV lasers of higher energy fluxes and higher pulse frequencies will be more effective for the dissociation of molecules and formation of particles and films. The number of carbon particles and films may increase with an increase in the laser energy flux and pulse frequency since the number of photons irradiated per unit time is increased and the probability of photons interacting with fluid molecules increases. Catalysts mixed in $ncCO_2$ may encourage the particle formation process and change the particles' structures.

4. Conclusions

We found that CO_2 is dissociated and particles are created by irradiating $ncCO_2$ with a UV laser of 213 and 266 nm wavelength. The SEM and TEM images, electron diffraction patterns and EDS, AES, XPS and Raman spectroscopic analyses showed that the particles are made up of amorphous carbon. Particles were collected more efficiently by electrodes by applying a dc electric field. Films were formed on the electrodes as the intensity of the external dc electric field was increased. New methods of dissociating carbon dioxide at room temperature may be opened up based on the present result. We suppose that the dissociation of molecules in fluids and formation of particles via the interactions between UV photons and large molecular clusters under critical opalescence conditions may be universal chemico-physical phenomena.

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