

BRIGHT WHITE LIGHT EMISSION FROM MESOPOROUS CARBON-SILICA COMPOSITES

S. Kawasaki¹, Y. Ishii¹, A. Matsumura¹ and Y. Ishikawa²

¹*Nagoya Institute of Technology, Nagoya 466-8555, Japan*

²*Japan Fine Ceramics Center, Nagoya 456-8587, Japan*

Abstract

Air-oxidized mesoporous carbon-silica composites show bright white light emission under low-energy ultraviolet irradiation. Like sunlight, the photoluminescence spectra of the air-oxidized nanocomposites almost cover the entire visible wavelength range.

Introduction

Fossil fuel depletion and low CO₂ emission demands have heightened the need for efficient lighting devices with low energy consumption. Light emitting diodes (LEDs) have attracted much attention to address this need. Multi-chip and single-chip methods are commonly used to generate LED-based white light. In the multi-chip method, white light is produced by combining light emitted by three individual red, green, and blue (RGB) LEDs. Since the spectrum of the multi-chip type “white light” is not very similar to that of sunlight, its color rendering property is low and its applications are rather limited. On the other hand, the single-chip method uses phosphor materials that convert monochromatic light from a blue or ultraviolet (UV) LED into a broad, white light spectrum. However, these phosphors typically include transition metals or rare earth elements that are expensive and/or environmentally toxic. Therefore, stable, efficient, inexpensive phosphor materials with high color rendering performance and low toxicity are strongly required.

In the present study, we report strong, white light emission from a mesoporous carbon-silica (SiO₂) nanocomposite system (MCS) under long-wavelength UV light irradiation. The nanocomposites consist of ordered cylindrical mesopores that form a homogeneous matrix of silica nanoparticles and amorphous carbon. MCSs may be promising candidates for phosphor materials used with LED because they contain neither expensive nor toxic elements.

Experimental

The starting mesoporous carbon-silica nanocomposite was synthesized through the tri-constituent co-assembly method[1]. For convenience, the obtained nanocomposite is designated as MCS-AM (as-made). The originally photoluminescence (PL) inactive MCS-AM was activated through an air oxidation process. MCS-AM was heated at various temperatures ranging within 400–600 °C in air for 6 h.

The heat-treated products are abbreviated as MCS-*x*, where *x* represents the oxidation temperature.

The obtained materials were characterized by transmission electron microscopy (TEM), FT-IR, X-ray diffraction (XRD), and N₂ adsorption-desorption isotherm measurements. PL and PL excitation (PLE) spectral measurements were performed at room temperature using a HORIBA SPEX Fluorolog-3 spectrometer equipped with a 450 W Xe-lamp.

Results and Discussion

While MCS-AM did not show luminescence, air-oxidized MCS-400, MCS-500, and MCS-600 exhibited strong, white light emission under UV light excitation. The emission intensity was so strong that the white light was clearly visible to the naked eye in daylight (not in the dark room) under very weak UV irradiation from a portable pen-type LED lighting device (370 nm). The PL spectra of air-oxidized MCSs excited at 370 nm are shown in Fig. 1. The spectra almost covered the entire visible light wavelength region. Therefore, MCSs show great potential in replacing the widely used fluorescent lighting devices.

As shown in Fig. 1, the most intense luminescence was observed for MCS-500, followed by MCS-600, and then MCS-400. The luminescent intensity of MCS-400 was much weaker than that of the other two samples (MCS-500 and MCS-600). However, the origin of this luminescence was essentially independent of the oxidation temperature because PL peak positions at about 413, 435, 462, 500, and 531 nm did not change upon oxidation. MCS-400 (dark gray) is much darker colored than MCS-500 (light brown) and MCS-600 (white), leading to a much lower transmittance. Differences in luminescent intensity are, thus, probably due to differences in light transmittance in the samples. However, these differences do not explain why the PL intensity of MCS-500 is higher than that of MCS-600.

Next, the population of the color centers of the three MCS samples was discussed. The PL peak shapes strongly depended on their oxidation temperature. The PL spectra could be divided into two large components, namely a blue luminescent band and a green-yellow luminescent band. The former band structure closely resembles PL spectra reported from defective silica materials, including silica gels, sol-gel derived mesoporous silica, amorphous silica nanoparticles, and silica nanowires. Although the detailed luminescent mechanisms of these materials are still not well understood, several possible mechanisms involving SiO₂ structural defect sites have been proposed to explain these PL phenomena. The PL properties of MCSs may originate from similar sites. However, in general, unlike MCSs, defective silica samples only display luminescence in the blue to green region (peak center: 400–500 nm). Therefore, the PL properties of MCSs, especially their green-yellow region emission component, cannot be explained exclusively by the SiO₂ defect mechanisms. Because all luminescent MCSs contain small amounts of carbon, their green-yellow luminescent center

might relate to the existence of carbon atoms. In order to compare the blue and green-yellow band intensities of the three MCSs, the MCS PL spectra were rescaled by normalizing the emission intensities at 425 nm that correspond to the blue component. It was found that the intensity ratio of green-yellow component to blue component gradually decreased with increasing oxidation temperature. This indicates that the population of the color centers related to the existence of carbon atoms decreases with increasing temperature. On the other hand, carbon removal increased the light transmittance of the samples. These two contrasting temperature effects granted MCS-500 with the highest PL intensity upon air oxidation.

Furthermore, the FT-IR intensity of the ACs mode corresponding to Si-O-C bonds may be related to the green-yellow PL intensity. This also suggests that the origin of the green-yellow PL emission is associated with the Si-O-C bonds. Unfortunately, the detailed chemical structure of the luminescent centers and their mechanisms are not well understood to this date. Further studies are needed to clarify the luminescence phenomena.

Conclusions

In this paper, we reported the white PL of air-oxidized mesoporous carbon-silica nanocomposites under long-wavelength UV light irradiation. The nanocomposite PL spectra were found to almost cover the entire visible wavelength range and their shape strongly depended on oxidation temperatures. The samples showed for the first time a green-yellow luminescence band. The carbon atoms present in the nanocomposites were shown to play a key role in producing the photoluminescence phenomena.

Acknowledgment

This work was partly supported by the Nippon Sheet Glass Foundation for Materials Science and the Engineering & Research Foundation for Materials Science. The authors sincerely thank Prof. Shigeru Okamoto for his help for the SAXS measurements.

References

[1] R. Liu, Y. Shi, Y. Wan, F. Zhang, D. Gu, Z. Chen, B. Tu, and D. Zhao, *J. Am. Chem. Soc.* **128** (2006) 11652.

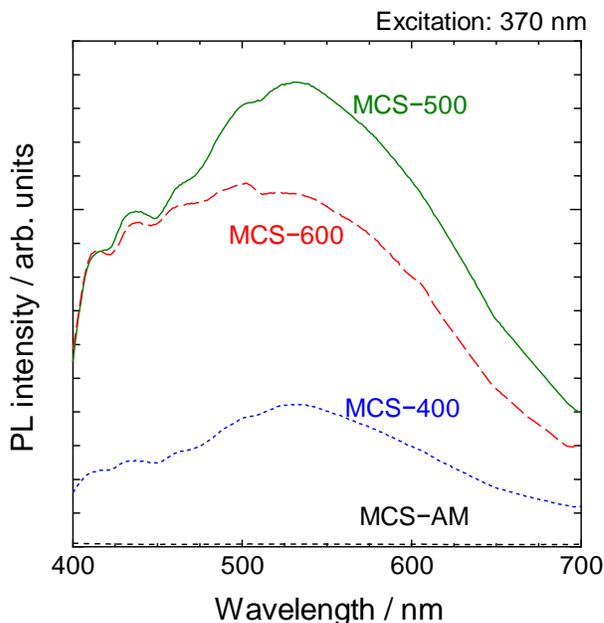


Fig. 1. Room temperature PL emission spectra of (a) MCS-400, (b) MCS-500, and (c) MCS-600 excited at 370 nm.