# Photoluminescence Characteristics of Calcined Silica Gels Containing Carbonized Intermediates

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(Received October 2, 1995)

Photoluminescence was observed from the carbonization intermediates of acenaphthylene or 2-methyl-1,2'-naphthyl ketone in silica gels by an excitation wavelength of 337 nm. As the calcination temperature increased from 500 to 1000 ℃, the spectral line shape exhibiting two regions of maxima centered at 390 and 490 nm changed systematically. No photoluminescence was seen from the samples without calcination, nor from a clear gel calcined over 1050 ℃. SEM observations indicate uniform mixing of the intermediates in the silica matrix down to a few tens of nanometers.

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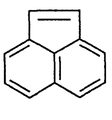
Nanometer sized pores in silica gels made by the sol-gel method are excellent matrices to disperse organic compounds or to make composites of silica with carbon materials. Previously, most optical studies of silica gels containing organic compounds have been conducted on the samples without calcination in order to preserve intrinsic properties of the mixed compounds.[1-3] In some cases, organic adsorbates were used as probes to study silica surfaces.[4-8] Other studies of silica with carbon materials were directed toward improvements of Vickers hardness and viscosity at high temperatures.[9-11]

Recently, a family of aromatic compounds were found to be graphitized at temperatures well below 1000 ℃.[12] Encouraged by this finding, we have investigated a possibility of incorporating carbonized intermediates of these aromatic compounds in silica gels. In particular, we focus our study on photoluminescence from the compounds prepared at various calcination temperatures.

To a solution containing tetramethoxysilane(TMOS) (1 mol), methanol (2.2 mol), water (10 mol) and N,N-dimethylformamide (1 mol) was added either acenaphthylene(AN, 1) or sulfonated 2-methyl-1,2'-naphthylketone(MNK, 2). In the case of AN (MNK), $NH_4OH$ ($H_2SO_4$) was used as a hydrolysis catalyst. After gelation, wet gels were dried at 60 ℃ for 3 weeks. The dry gels were calcined at the temperatures between 500 to 1000 ℃ in $N_2$ gas atmosphere.



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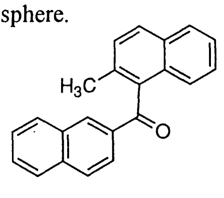

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Microstructures of uncoated samples was observed by FE-SEM with an acceleration voltage of 1 kV and a beam current of 10 μA. UV-VIS absorption spectra were taken by the powder reflection method using an integrating sphere.

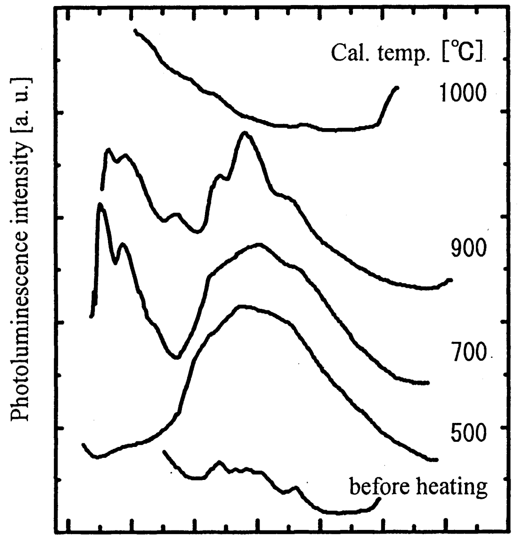

**Figure 1.** Photoluminescence spectra Ex : λ =337 nm The dry silica gels containing 1 wt% AN were calcined at the temperatures between 500 to 1000 ℃ in $N_2$ gas atmosphere.

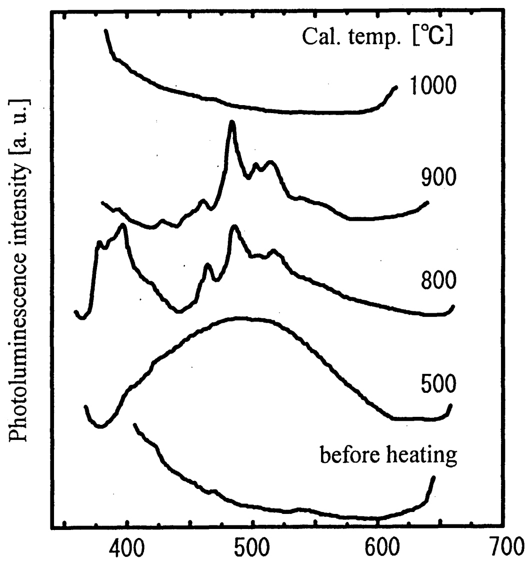

**Figure 2.** Photoluminescence spectra Ex : λ=337 nm The dry silica gels containing 0.01 wt% MNK were calcined at the temperatures between 500 to 1000 ℃ in $N_2$ gas atmosphere.

Photoluminescence spectra was obtained from a freshly cracked surface at an excitation wavelength of 337 nm.

Photoluminescence spectra of the samples containing 1 wt% AN and 0.01 wt% MNK are shown in figures 1 and 2, respectively. Both samples exhibit two regions of maximum intensities centered at 390 and 490 nm. As the calcination temperature increased, the peak intensities near 390 nm increased relative to those of 490 nm. At the same time, a number of sharp peaks becomes observable around 490 nm. For instance, at least seven independent peaks are necessary to fit these regions for both sample calcined at 800 and 900 ℃. While we cannot assign each peak presently, it is interesting to observe the dramatic line sharpening and the spectral shifts of these peaks with an increase in calcination temperatures.

The dry gels without heat treatment did not show photoluminescence in this region by the same excitation beam. Also, the samples that have been calcined at the temperature over 1050 ℃ did not show photoluminescence. At this temperature, the calcination intermediates were evaporated off completely from the silica gel. This suggests that the observed fluorescence is strongly correlated with the presence of calcination intermediates.

Figure 3 shows the UV-VIS absorbance spectra measured from the AN samples. The peaks at 225, 275, 320 and 340 nm are seen from all temperatures. The peaks at 225 and 275 nm have been attributed to E' center, oxygen vacancy, ozone molecules or non-bridging oxygen hole centers.[13] The peaks at 320 and 340 nm, however, cannot be explained by the peroxy-linkeage(Si-O-O-Si) defect[14] or chlorine molecules trapped in the glass[15] with the procedure employed by the present study. These peaks, however, appear at 1050 ℃ and are not in accord with the photoluminescence. It is not clear at this moment if a decrease in the slope of the apparent baselines with increasing temperature is correlated with the photoluminescence.

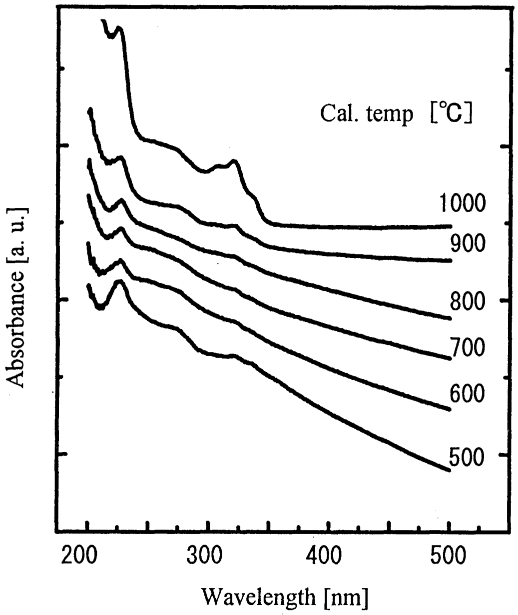

**Figure 3.** UV-VIS absorbance spectra measured from the calcined samples which were made of the starting mixtures containing 1 wt% AN.

Figure 4 is a SEM photograph of a sample calcined at 500 ℃, exhibiting nano-scaled pores which are characteristics of silica gels made by the sol-gel method. All samples show the same type of micropore structures as shown in this photograph. As the calcination temperature increases, the size of micropores becomes smaller. We could not observe any structure suggesting filling of pores by carbon aggregates or any texture due to coexisting phase separated materials. Thus, we estimate that a composite structure is developed at a nanometer level and is uniform over the entire gel.

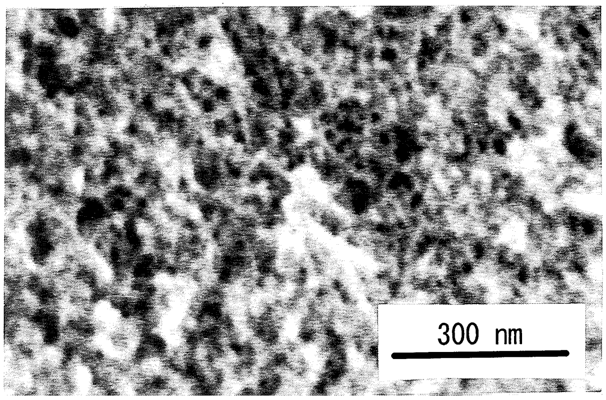

**Figure 4.** SEM photograph of the sample calcined at 500 ℃ for 10 minutes. The starting silica gel contained 0.05 wt% AN.

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