Fluorescence Microscopy of Nanoscale Silver Oxide Thin Films *

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The experimental conditions for photoactivated intermittent fluorescence from nanoscale silver oxide were studied with fluorescence microscopy. Strong fluorescence was observed from the Ag_2O particles with size of 10–20 nm excited with both blue and green light. We observed the saturation of photoexcitation with blue light and explained the experimental results using the model of agglomeration of silver atoms to form small clusters and the fluorescence of Ag_2 and Ag_3 clusters.

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The rapid development of computer technology and optical communication requires the novel materials for new type of optical data storage. Metal particles and clusters with nanometre size have attracted much attention in the previous decade as promising materials due to their unique optical and electronic properties. The fluorescence effect was first shown for Ag and Cu clusters at cryogenic temperatures.[1] The agglomeration of copper or silver atoms in a matrix of noble gas atoms to form small clusters may be accompanied by the emission of visible light. Spectral analysis reveals the intermediate formation of electronically excited atoms and dimers as the source of the chemiluminescence. A similar concept was introduced in the field of nuclear reactions by Bohr in 1936.[2]

Furthermore, AgBr microcrystals treated with reducing agents to form small silver clusters on their surface and have been examined with low-temperature optical and optically detected magnetic resonance methods.[3] Two closely related Ag clusters are observed to be spectroscopically active. One of the centres manifests itself by low-temperature emission bands centred at 550 and 640 nm and an absorption band centred at 442 nm. The other centre, which absorbs with central wavelength of 430 nm, acts as a surface hole trap that completely changes the nature of the AgBr donor acceptor recombination. These centres are only observable on crystals with (111) planes. Spectroscopic and theoretical considerations suggest that these spectroscopically prominent centres are silver dimers in two different surface configurations.

Optical spectroscopy is believed to be a powerful technique to study the electronic structure of small clusters. However, direct optical absorption measurements of free mass selected clusters is impossible since sufficiently large cluster densities are not available. Small silver clusters have been investigated in free beam experiments, using resonant two-photon ionization spectroscopy,[4,5] laser-induced fluorescence,[6] pump–probe[7,8] or photodepletion[9] techniques.

The absorption and fluorescence spectra of silver clusters isolated in an Ar matrix were measured by Rabin *et al.*[10] The authors found that the fluorescence of Ag_2 and Ag_3 clusters appear at wavelengths of 478, 463, and 453 nm and 369, 373, 420, 608, 618, 625, and 703 nm, respectively. They also reached a conclusion that the peak of fluorescence spectra moves to the infrared region when the number of silver atoms increases. For example, for Ag_n ($n > 4$) the emission peaks appear at 791 and 958 nm.[11] Felix *et al.* reported the first observation of the fluorescence of the silver tetramer in an argon matrix as well as the corresponding excitation spectrum.[12] The major fluorescence peak is situated at 458 nm (2.71 eV) with a bandwidth of only 20 nm (0.12 eV). The excitation spectrum is compared with ab initio calculations as well as to photodepletion measurements and is found to be in good agreement with both of them. Not only Ag but also silver oxide (Ag_2O) have been investigated for its large surface-enhanced Raman signals resulting from photoinduced Ag cluster formation.[13−15]

Recently, Peyser *et al.* reported intermittent fluorescence on Ag particles.[16] They observed that nanoscale silver oxide (Ag_2O) shows strong photoactivated emission for excitation wavelengths shorter than 520 nm. Using this effect, they wrote the data to the films with blue excitation. Then the stored data could be read with strong red fluorescence resulting from green (wavelengths longer than 520 nm) excitation.

In this Letter, the experimental conditions

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for photoactivated intermittent fluorescence from nanoscale silver oxide are studied with fluorescence microscopy. Strong fluorescence is observed from the Ag_2O particles with size of 10–20 nm excited with both blue and green light. We also observe the saturation of photoexcitation with blue light and explained the experimental results using the model of agglomeration of silver atoms to form small clusters and the fluorescence of Ag_2 and Ag_3 clusters.

In order to study the dynamic of photoactivated fluorescence from thin films of silver oxide nanoparticles, small Ag_2O particles (10–30 nm) were produced by the rapid oxidation of very thin Ag films. The thin Ag films were prepared in vacuum by thermally evaporating Ag on to glass. Then the films were put in the pure oxygen with a pressure of 10 Pa. Using the glow discharge method, the oxidation of Ag films was performed until the transmittance of the films reached 100%. Finally, the films of Ag_2O were annealed in the vacuum for half-hour at the temperature of 80°C. The photograph of the film (15 nm-thickness) taken with electron microscopy is shown in Fig. 1. From this photograph, we can estimate the average size of Ag_2O nanoparticles to be 10–20 nm. The presence of Ag_2O was confirmed by x-ray photoelectron spectroscopy (XPS).

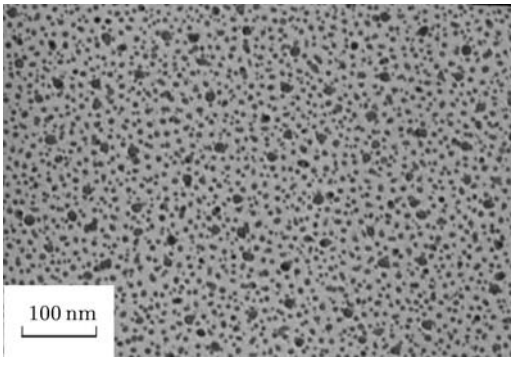

Fig. 1. Photograph of the Ag_2O film (15 nm-thickness) taken with an electron microscope.

The linear absorption of Ag_2O films was measured by using an Agilent 8453 UV-visible spectroscope, as shown in Fig. 2. It evaluates the absorption coefficient of $4.9 \times 10^4\,cm^{-1}$ for wavelength of 488 nm and $4.5 \times 10^4\,cm^{-1}$ for wavelength of 514 nm (Fig. 2).

Fluorescence microscopy of Ag_2O films was performed on an Olympus IX-70 inverted microscope. The photographs were taken with the ISO 400 film with 1-min exposures. The light-shielded Ag_2O samples were studied under mercury lamp excitation. The sample was nonfluorescent initially, but under blue excitation for several minutes, multicoloured (green and yellow) fluorescence slowly grows in, as shown in Fig. 3. The aperture image in Fig. 3 is about 180-μm wide. The average power of blue excitation (450 to 480 nm) is about 1 mW, and that of green excitation (510 to 550 nm) is about 8 mW. The intensity of blue excitation is about $4\,W/cm^2$ on the sample. Emission appeared from many small nanoparticle sites, and a blinking pattern of the emission was observed. Under green excitation, even brighter and more stable red fluorescence was observed. The photograph is shown in Fig. 4. Compared with the work of Peyser *et al.*[16] in which the excitation was performed at $\sim 35.8\,W/cm^2$, a much weaker excitation leads to the similar fluorescence pattern in our experiments. Another difference of our experiment in comparison with the result in Ref. [16] is that we did not observe the red fluorescence upon blue excitation. The possible reason is that the geometry and size of the Ag_2O nanoparticles are different in the two experiments. When blue light continued to illuminate the sample, the intensity of fluorescence did not increase anymore. This indicates that the photoexcitation reached the saturation.

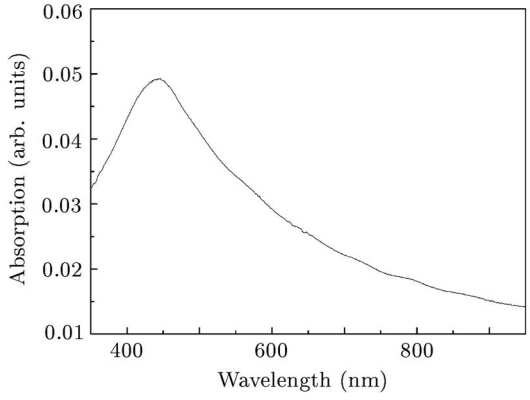

Fig. 2. Absorption spectrum for the Ag_2O film (15 nm-thickness) on glass substrates at room temperature.

Fig. 3. Photograph of the Ag_2O film with blue mercury lamp excitation.

With changing the thickness of Ag_2O films, we did

not observe any emission when the thickness > 30 nm even after strong blue excitation. This proves that only the films as thin as to support an inhomogeneous Ag layer exhibit fluorescence, so island formation must occur such that oxide growth is not self-passivating. We changed the thickness of Ag_2O films from 200 to 15 nm and found that not all Ag_2O nanoparticles can form Ag clusters, which exhibit strong photoactivated fluorescence. Only those Ag_2O nanoparticles with specific size can form such Ag clusters. Furthermore, we found that the fluorescence only appeared from the light-shielded Ag_2O samples. We concluded that Ag_2O nanoparticles are unstable under light illumination. A single nanoparticle of Ag_2O does not fluoresce under these (blue and green) excitations. Therefore, the fluorescence has no single nanoparticle behaviour. The emission appeared from many localized sites, each of which exhibited emission patterns characteristic of single Ag nanoclusters.

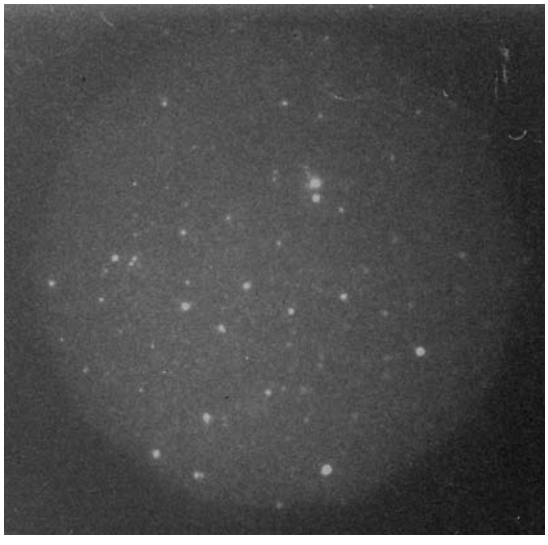

Fig. 4. Red fluorescence from the same region as in Fig. 3 but illuminated with green light.

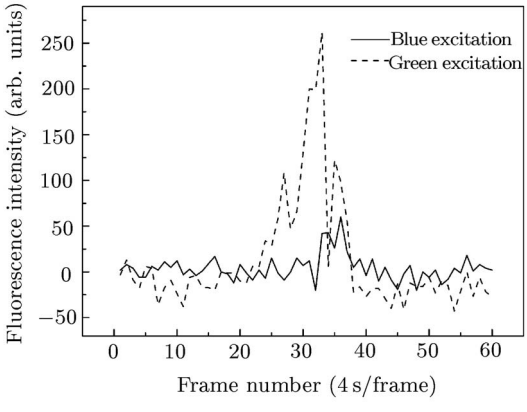

Fig. 5. Dynamics of the fluorescence from the Ag_2O film.

The photoactivated intermittent fluorescence from nanoscale silver oxide is too weak to be observed using a conventional fluorescence spectrophotometer. We studied the dynamics of the fluorescence using a fluorescence CCD technique. We replaced the eyepiece of the microscope with a highly sensitive CCD. The CCD can capture the dynamic process of the emission from silver oxide. The blinking traces are shown in Fig. 5. The solid line shows the blinking trace of fluorescence intensity in the Ag_2O film under blue excitation. The dashed line shows the corresponding process under green excitation. The intensity under green excitation is higher than that under blue excitation. The typical blinking time is about 20–40 s.

As mentioned above, the fluorescence of Ag_2 and Ag_3 clusters appears at wavelengths of 478, 463, and 453 nm and 369, 373, 420, 608, 618, 625, and 703 nm, respectively. These wavelengths are in agreement with the observed spectral dynamics in our experiments. We assume that the luminescent species are silver nanoclusters (Ag_2 and Ag_3 clusters, etc.) photochemically generated from the oxide.

Another assumption is that the photoactivated intermittent fluorescence from nanoscale silver oxide contains two steps: the first one is photochemically production of Ag atoms from Ag_2O, the second is agglomeration of silver atoms to form small clusters and the intermediate formation of electronically excited atoms, dimers, and trimers is the source of the chemiluminescence. In Ref. [1] the authors assumed that the agglomeration of Ag clusters was accompanied by light emission centred at 476 nm. They concluded that the coagulation of multiatomic ensembles causes the ejection of smaller, excited particles (M_2 or M) from an electronically excited intermediate state: $M_n + M_m \rightarrow M^*_{m+n} \rightarrow M_{m+n-1} + M^* \rightarrow M_{m+n-1} + M + h\nu$, where $h\nu$ is the energy of the emitted photon. For example, according to theoretical calculations,[17] the reaction $Ag_5 + Ag_3 \rightarrow Ag_8$ is associated with an energy gain of 5.2 eV, which could lead to the formation of an electronically excited Ag^*_8 species from which an excited Ag^* could be ejected.

We can use these two assumptions to explain the observed photoactivated intermittent fluorescent process from nanoscale silver oxide. Moreover, data are readily stored in and nondestructively read from these high-density nanoparticle films. This scheme can potentially store a plenty of information in a small space because it uses multiple colours and because the clusters, made up of only a few silver atoms, are so small. By using the correct distribution of particle sizes, these multi-colour emissions could allow storage of more than one bit of information in each data point. If the particles could be distributed in a three-dimensional matrix, they could provide a very dense storage medium that could be written and read in parallel.

In summary, we have investigated the photoactivated fluorescence of nanoscale silver oxide (Ag_2O) and observed strong emission for both blue (450 to 480 nm) and green (510 to 550 nm) excitation. The large-scale dynamic colour changes were observed. The fluorescence only appeared from the light-shielded Ag_2O samples. We also observed the saturation of photoexcitation with blue light and explained the experimental results using the model of agglomeration of silver atoms to form small clusters and the fluorescence of Ag_2 and Ag_3 clusters.

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