



Existence of nanoparticles in azurite and malachite pigments – Raman spectroscopy and X-ray diffraction studies



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ABSTRACT

The lightness of the color of mineral pigments changes with its particle size. We investigated the Raman spectra of azurite pigments of several particle-size groups, ranging from ~5 to ~110 μm. The line-widths of the phonon modes ~400 cm⁻¹ of azurite powders were found to increase as the particle sizes get smaller. Similar phenomena were also observed for the malachite pigments. The broadening of phonon modes implies the existence of nanoparticles in the pigment powder. Scanning Electron Microscopy (SEM) measurements confirm the existence of more nanoparticles in the finer particle-size groups. These results were assured by X-ray diffraction (XRD) measurements as well. Even further, we could determine the average size of azurite particles simply by comparing the line-width of the Raman mode ~400 cm⁻¹ of the unknown with that of the known particle-size groups. Non-destructive estimation of typical sizes of mineral pigments using Raman spectroscopy could be useful in cultural-heritage conservation science.

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1. Introduction

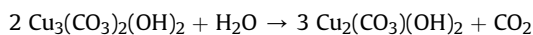
The application of scientific methods for analyzing the pigments on traditional paintings is now well established. Raman spectroscopy, for example, is one of the useful tools in characterizing archaeological materials, such as traditional paintings and building decorations. With the recent advent of handheld Raman instruments with relatively good resolution, the usage of the Raman spectroscopy in art and archaeology is even greater than ever [1]. Up to now, most of the Raman studies have focused on identifying the material of the pigments. However, the lightness of mineral pigments such as azurite, malachite, or cinnabar depends on its average particle size. As the average particle size of those pigments gets smaller, the color gets brighter [2]. Therefore, simple identification of the pigment material is not enough to restore and conserve the painting heritages properly. Nondestructive finding of the average particle size of the pigments in the paintings should be essential.

We report the existence of nanoparticles in natural mineral

pigments of micro-grains and the line-widths of some Raman modes of a particular mineral pigment can be used in assessing the typical size of the mineral pigment. We have measured the Raman spectra of azurite and malachite pigments of several particle-size groups, and investigated the effect of nanoparticles residing in those groups. The results were assured by X-ray diffraction (XRD) experiments on both azurite and malachite pigments.

Azurite is monoclinic in crystal structure, and it is Cu₃(CO₃)₂(OH)₂ in chemical formulae. It has been used as a blue colored pigment from ancient, as found in cave paintings at Dun Huang in Western China and wall paintings in Central China from the Tang and Song dynasties, and also in Japan. It was also the most important blue pigment in European painting throughout the middle ages and Renaissance [3].

Malachite is also a copper carbonate hydroxide mineral, with the formula Cu₂CO₃(OH)₂ and also monoclinic in crystal structure. Malachite has long been used as a green pigment in the East [4]. It is often found together with azurite. In fact, azurite is unstable in open air and can transform into malachite, by replacing some the carbon dioxide (CO₂) units with water (H₂O):



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Therefore, it would be reasonable to investigate both azurite and malachite pigments together and compare their results.

2. Experimental

Natural azurite and malachite pigments of different particle sizes were purchased from commercial vendors in Japan (Kiya) and China (Yiwen Art & Craft). The Kiya product number 7, 9, 11, 13, 15, and Baek are denoted as “Azurite 7, 9, 11, 13, 15, and 17” in the case of azurite pigments. The higher product number corresponds to the finer particle-size group, and the finest particle-size group, called “Baek” is numbered as 17 in this paper.

We measured Raman spectra of the pigment samples using a Horiba Jobin Yvon micro-Raman spectrometer (LabRam ARAMIS) with 532 nm excitation source, $\times 10$ lens of microscope focusing beam-diameter of 2.6 μm , 1800 groove/mm-reflective grating with a focal length of 450 mm, and Peltier-cooled CCD of 1024×256 array. The spectral resolution was found to be about 2.5 cm^{-1} with mercury line of 546 nm, which means that two peaks separated less than 2.5 cm^{-1} cannot be resolved into separate peaks. However, depending on the number of data points, the changes in the peak position and the line-width can be measured within the 0.1 cm^{-1} precision from the Lorentzian fitting of the Raman peaks.

As the excitation laser is highly polarized, the intensity of Raman modes of azurite changes very much depending on the crystal direction of the individual azurite particle. Furthermore, particles of even a particular particle-size group are different in size from spot to spot in the pigment sample. In order to obtain the representative spectrum of a specific particle-size group of azurite, random selection of measuring sites should be ensured. The Raman mapping technique could be exploited to obtain a large number of spectra from particles randomly distributing in the pigment sample.

The pigment of each particular particle-size group was spread evenly over adhesive tape, which is attached to a slide glass. Then the slide glass was fixed on the motorized x-y stage. 13×13 spots separated by 120 μm of the sample surface were measured. Spectra from impurities were removed and ~ 40 spectra were chosen for analysis of each sample. Spectral range of $300\text{--}480 \text{ cm}^{-1}$ was truncated, and the baseline was subtracted, then the most intense peak $\sim 400 \text{ cm}^{-1}$ was used to normalize each spectrum. Finally, all the spectra were averaged to represent the spectrum of a specific particle-size group. By this way, each representative spectrum of six particle-size groups and of the unknown particle-size group (Azurite X) was obtained. Mercury lines were used in calibrating the wavenumbers of the Raman spectra for each measurement.

It is known that strong laser power used in Raman measurements can change the physical and even chemical state of the pigments. For example, strong laser power can blacken the azurite by altering it into the copper oxide (tenorite). Mattei et al. [5] studied the laser-induced degradation of azurite as a function of the particle size. They found that the temperature of the particles decreases as the size increases, and azurite degrades into tenorite only below the critical value of 25 μm . The typical particle sizes of product number 13, 15, 17 are smaller than 25 μm . Therefore, extreme care was taken when measuring the Raman spectra of the azurite and malachite samples. To avoid heat degradation of the material and to get optimal measurement condition, the finest size group (product number 17) was examined varying the laser power and irradiation time. All the Raman measurements were done with the optimal conditions; laser power less than $\sim 0.1 \text{ mW}/\mu\text{m}^2$ and excitation time of 10 s with multiple averaging. No trace of tenorite was found even in the finest size group after the Raman measurements.

Raman spectra of azurite and malachite have been reported previously. Frost et al. [6] extensively studied the Raman spectra of

azurite and malachite at both 298 K and 77 K. In the high wavenumber range (above $\sim 700 \text{ cm}^{-1}$), most of the Raman and IR modes are from the hydroxyl group and carbonate group in azurite and malachite crystal structure. They found many lattice modes below 600 cm^{-1} , including the characteristic Cu-O mode at $\sim 400 \text{ cm}^{-1}$ for azurite and $\sim 433 \text{ cm}^{-1}$ for malachite.

In our Raman study, the intense peak near 400 cm^{-1} of azurite is utilized in fitting in order to look for possible particle-size effect on the peak shift and peak broadening. Fitting the peak near 400 cm^{-1} with several Lorentzian peaks gives values of the peak position and the full-width-at-the-half-maximum (FWHM) values significant down to $\sim 0.1 \text{ cm}^{-1}$ in our Raman measurements. For the case of malachite, we used the strong peak near 433 cm^{-1} in searching the particle size effect.

The results of Raman spectroscopy were confirmed by X-ray diffraction (XRD) measurements. All the XRD measurements were performed using Rigaku X-ray diffractometer (MiniFlex II). Powder samples were packed evenly in glass holders. The Cu $K\alpha$ line was used with a scan rate of $0.02^\circ/\text{step}$ and $10^\circ/\text{min}$. The XRD peaks at 2 theta of $\sim 46.5^\circ$ of azurite powder groups and $\sim 24^\circ$ of malachite powder groups showing the asymmetric broadening were used to support the results of Raman measurements on the particle-size effects of the azurite and malachite pigments.

In order to verify the existence of nanoparticles, Scanning Electron Microscopy (SEM) measurements were performed by using a Jeol SEM (JSM-6700F) with $\times 20,000$ magnification.

The particle size which represents each particle-size group was obtained by a Malvern particle size analyzer (Mastersizer 2000) utilizing laser diffraction with powders being dispersed in water by a dispersant unit (Hydro 2000S).

3. Results and discussion

Fig. 1-(a) shows the optical images of some particle-size groups of azurite pigments. It shows that particles even in one particle-size group distribute non-uniformly. Generally, particle sizes distribute lognormally. In this case, the geometric mean size of a particle-size group is taken as the typical particle size, which is denoted by the diameter of a sphere equivalent in volume with the particle. Fig. 1-(b) presents the lognormal distributions of azurite powders of six kinds of particle-size groups; each particle-size group is divided into one hundred sections of equal “length” of the x-axis in the logarithmic scale over $0.01\text{--}10,000 \mu\text{m}$. The volume fraction of particles belonging to each section shows a normal distribution on the logarithmic scale of the particle size.

Hatch et al. [7] carried out an experimental study of finely divided particle-size groups, of which the geometric mean of diameters range from ~ 1 to $\sim 70 \mu\text{m}$. For the study, crystalline materials like quartz and calcite were processed through crushing, grinding, sieving, dispersing and levigation in water, which is the same method used for inorganic ore pigments like azurite, malachite, or cinnabar are graded into several particle-size groups. The geometric mean size is equal to the median size corresponding to 50% cumulative fraction of the total particles on the base of size frequency. With his succeeding study [8], Hatch showed a graphical method to derive the geometric mean and geometric standard deviation of the particle size using linear fitting of logarithmic probability curve which satisfies the relation;

$$\sigma_g = 84.13 \text{ percent size}/50 \text{ percent size}, \quad (1)$$

where, σ_g means geometric standard deviation and converted these results to the geometric mean based on volume fraction in total volume.

Fig. 1-(c) presents the logarithmic probability curves of the six

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