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Fabrication of Gold Nanoparticle-Doped Zeolite L Crystals and Characterization by Optical Microscopy: Laser Ablation- and Crystallization Inclusion-Based Approach

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This letter reports the optical microscopy characterization of gold nanoparticle-doped zeolite L crystals prepared by applying two key techniques: laser ablation and crystallization inclusion. The former allowed the stable formation of Au NPs in the synthesis gel, while the latter permitted the encapsulation of Au NPs exceeding the pore openings of the zeolite crystals, still maintaining the crystal structure as a whole. The microscopy characterization was performed by exploiting single particle light scattering spectroscopy and imaging techniques which offered the Rayleigh scattering images of individual Au particles within the crystals and the scattering spectra ascribable to the surface plasmon resonance band of Au NPs embedded. This is a unique demonstration for the application of laser ablation-induced NPs in solution to practical use for fabricating a nanocomposite material. Furthermore, the present results revealed that the dark field microscopy is capable of visualizing metal nanoparticles as small as 40 nm diameter confined in the light scattering crystalline medium.

Noble metal nanoparticles (NPs) have attracted considerable attention due to their characteristic localized surface plasmon resonances which find potential applications in biosensing,[1,2] Raman scattering enhancement,[3,4] and many other fields.[5] The surface plasmon resonances have intriguing properties such as their spectral tunability within the visible and infrared wavelength regions. For instance, the scattering cross section of a subwavelength particle depends on the dielectric function of the particle material, the particle shape and volume, and the dielectric constant of the surrounding medium. Thus the investigation of optical properties of Ag and Au NPs with various sizes and shapes in different media is currently a key subject of research efforts.[6−8]

Incorporation of the metal NPs in suitable host materials such as glasses minimizes agglomeration, improves durability, and hence allows superior optical performance necessary for optical switching devices, shutters, and waveguides.[9−11] Additionally, supported Au clusters have gained wide attention because of their unique catalytic properties for reactions such as CO oxidation and NO reduction.[12,13] As a result, much effort has been devoted to the preparation of zeolites and mesoporous materials incorporated with metal clusters and NPs.[14−25] It was hoped that the crystalline structures of zeolites limits the migration of gold and the size of resultant clusters. However, the preparation of Au clusters or NPs in these materials is not feasible compared with the corresponding Ag- or Cu-loaded materials because of unstable nature of Au^{3+} ions without ligands, which makes difficult to incorporate by an ion-exchange method. An attempt to prepare Au metal particles by inserting Au species by sublimation of $AuCl_3$ into dehydrated zeolite A followed by the reduction procedures such as exposing to H_2S or H_2, and vacuum heating fell short of expectations because of the formation of various kind of stable species.[17] Besides, metal NPs are usually formed both inside and outside the pores and channels. Accordingly, an approach based upon an aspect different from traditional ion-exchange or sublimation-based impregnation method needs to be implemented.

In the present study, zeolite L crystals loaded with Au NPs were prepared on the basis of a crystallization inclusion method developed by Schulz−Ekloff and co-workers.[26] Previously, inclusion of dye molecules was observed when the dyes were added to the gel mixture of the hydrothermal synthesis of a molecular sieve, $AlPO_4$-5. This method allows the encapsulation of dyes exceeding the pore openings and thus a greater variety in the type of guest species. Besides, this method can immobilize guest species to prohibit agglomeration which has been a serious problem for CdS quantum dots prepared previously in zeolite Y.[27,28] One drawback of the method is a harsh experimental condition such as an extremely basic solution at a high temperature under which dyes or Au NPs have to survive. Our synthetic effort tailored the procedures appropriate for the fabrication of Au NP-loaded zeolite crystals through the use of stabilizer-free Au NPs produced in the synthesis gels by the laser ablation method. The characterization of the crystals was performed by applying single particle light scattering spectroscopy and imaging techniques.

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Zeolite L crystals loaded with Au NPs were synthesized based on a procedure for the zeolite L synthesis described in the literature.[29] The molar ratio of the synthesis gel is $Al_2O_3/SiO_2/K_2O/H_2O = 1:20:10:1030$. Aluminum sulfate octadecahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$, Aldrich) was used as the Al source and 40% colloidal silica (Ludox HS-40, Aldrich) was used as the Si source. A typical procedure for the preparation of synthesis gel is as follows. KOH (1.39 g) was dissolved in 16.32 g of doubly distilled water and 0.70 g of $Al_2(SO_4)_3 \cdot 18H_2O$ was added to this solution with vigorous stirring for 30 min. Then, 3.16 g of colloidal silica was added dropwise to the mixture and vigorously stirred overnight. The synthesis gel thus prepared was added with 4.0 mg of Au flakes (99.9%, Horikin) and subjected to a laser irradiation by a 1064 nm light beam from a pulsed Nd:YAG laser (10 Hz, 6 ns pulse width, 1 J/(cm^2 pulse)) for 2 h. The laser ablation of the Au flakes in the gel allowed the formation of Au NPs which developed a red color indicative of the characteristic surface plasmon resonance band (Supporting Information, Figure S1). After the laser irradiation, the gel was centrifuged for 10 min at 4000 rpm and the residual Au powders were discarded. The gel was redispersed in supernatant by stirring for 1 h. Gels with higher concentrations of Au NPs were prepared by repeated 2 h of laser irradiations for 2−4 times with newly added flakes. The synthesis gel was then transferred into a Teflon-lined autoclave and heated at 180 °C for 3 days under static condition. Zeolite crystals were collected by filtration and washed with copious amount of doubly distilled water. Finally, crystals with similar sizes were collected after a separation based on the sedimentation of crude crystals by passing them through a 1.5 m long water column. We assume that the laser irradiation causes the least damage to the synthesis gel because the 1064 nm laser light is unabsorbed by the gel which absorbs only at UV regions. Besides, a simultaneous multiphoton absorption is unlikely at the fluence employed. Indeed, zeolite L crystals prepared from a gel subjected to 8 h of the laser radiation is morphologically indistinguishable form those prepared from an intact gel.

For microscopy characterization, samples were prepared by spin-coating an aliquot of aqueous suspension of zeolite L crystals on a microscope coverslip and covered with a droplet of immersion oil. Light-scattering images and spectra were acquired on a setup[30−32] based on an inverted microscope (IX71, Olympus) equipped with a dark-field condenser (U-DCD or U-DCW, Olympus) and a 100 W halogen lamp (Supporting Information, Figure S2). Two types of objective lenses (100×, NA = 0.9 and 20×, NA = 0.4; Olympus) were employed to collect scattered light from both narrow (500 nm) and wide (20 μm) spatial area. The scattered light was introduced into a polychromator (MS128, ORIEL; grating, 77480, ORIEL) coupled with a CCD camera (DV420-OE, Andor) through a pinhole. For the calibration of light scattering spectra, we divided a scattered light intensity spectrum from a specimen by that from a frost plate (DFQ1−30C02−240, SIGMA) that has a uniform scattering efficiency. Transmission electron micrographs (TEM) were obtained with a JEOL JEM-3010 or JEM-3100FEF microscope operated at 300 keV and UV−vis extinction spectra were recorded on a Hitachi U-2010 spectrophotometer.

Examination of the crystal image, Figure 1a, reveals that a hexagonal cylinder shape is unequivocally attributed to a zeolite L (LTL[33]) structure. Practically no morphological difference was observed for crystals formed from a gel containing Au NPs from those prepared from a gel containing no Au NPs. The magnified image, Figure 1b, unambiguously suggests that Au NPs with 20−50 nm diameter are embedded in the zeolite crystals: ill-defined dark spots observed in the TEM image are indicative of particles located inside, not outside the crystals. Note that Au particles attached outside the crystals are also observed when prepared from gels with relatively high concentrations of Au NPs. The NPs have a broad size distribution and scattered randomly within a zeolite crystal (see Supporting Information, Figure S3). Two key techniques that have led to the incorporation of Au NPs into zeolite L crystals may deserve comments. One is the laser ablation technique to generate Au NPs in the synthesis gel. Previously, the laser ablation of Au and Ag flakes was found as a highly efficient way to produce NPs in pure water, acetone, and various alcohols.[34−36] The NPs produced in the gel are very stable represented by a surface plasmon resonance band with a peak at 523 nm (Supporting Information, Figure S1) while in water it is located at 516 nm. The size distribution of Au NPs in the gel was not measured because of unfeasible separation of the particles. In water, Au particles prepared were polydisperse with a diameter of 13 ± 9 nm (TEM). The other technique is the crystallization inclusion method originally developed for the synthesis of aluminophosphate molecular sieve, $AlPO_4$-5, doped with dyes such as porphyrins.[26] We demonstrated that this technique is applicable to the incorporation of NPs.

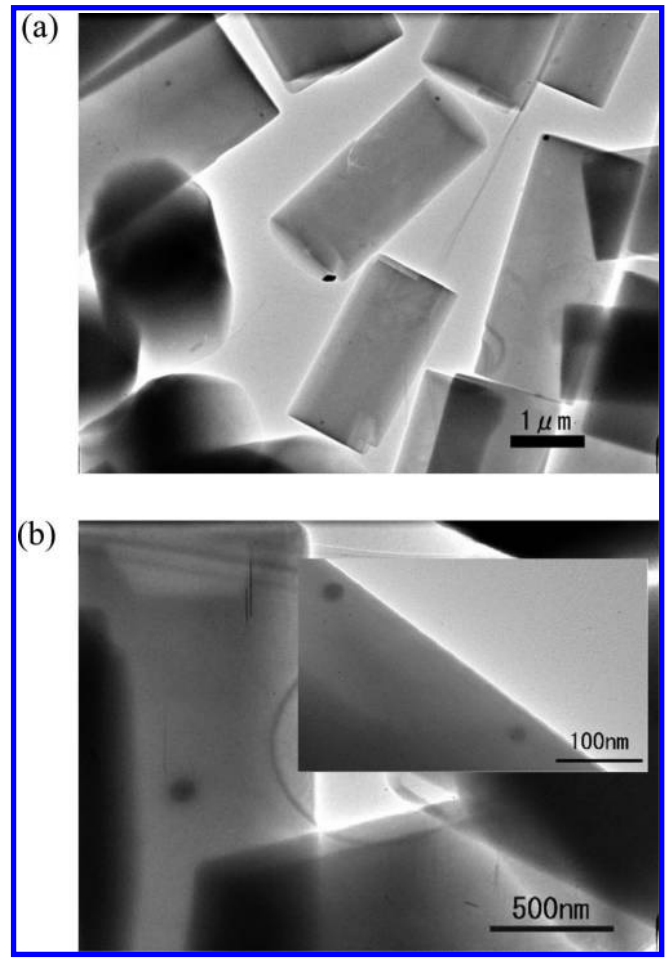

Figure 1. TEM micrographs of Au NP-doped zeolite L crystals synthesized in the present study. The image (a) shows that hexagonal cylindrical shape is retained in the presence of Au particles inside the crystals. Only a few large Au particles are seen in this image. The image (b) represents a magnified view showing the presence of 20−50 nm diameter dark spots ascribable to Au NPs. See Supporting Information Figure S2 for more magnified images.

Microscopy characterization of zeolite L crystals with a 100× magnification objective (pinhole diameter, 100 μm) under the

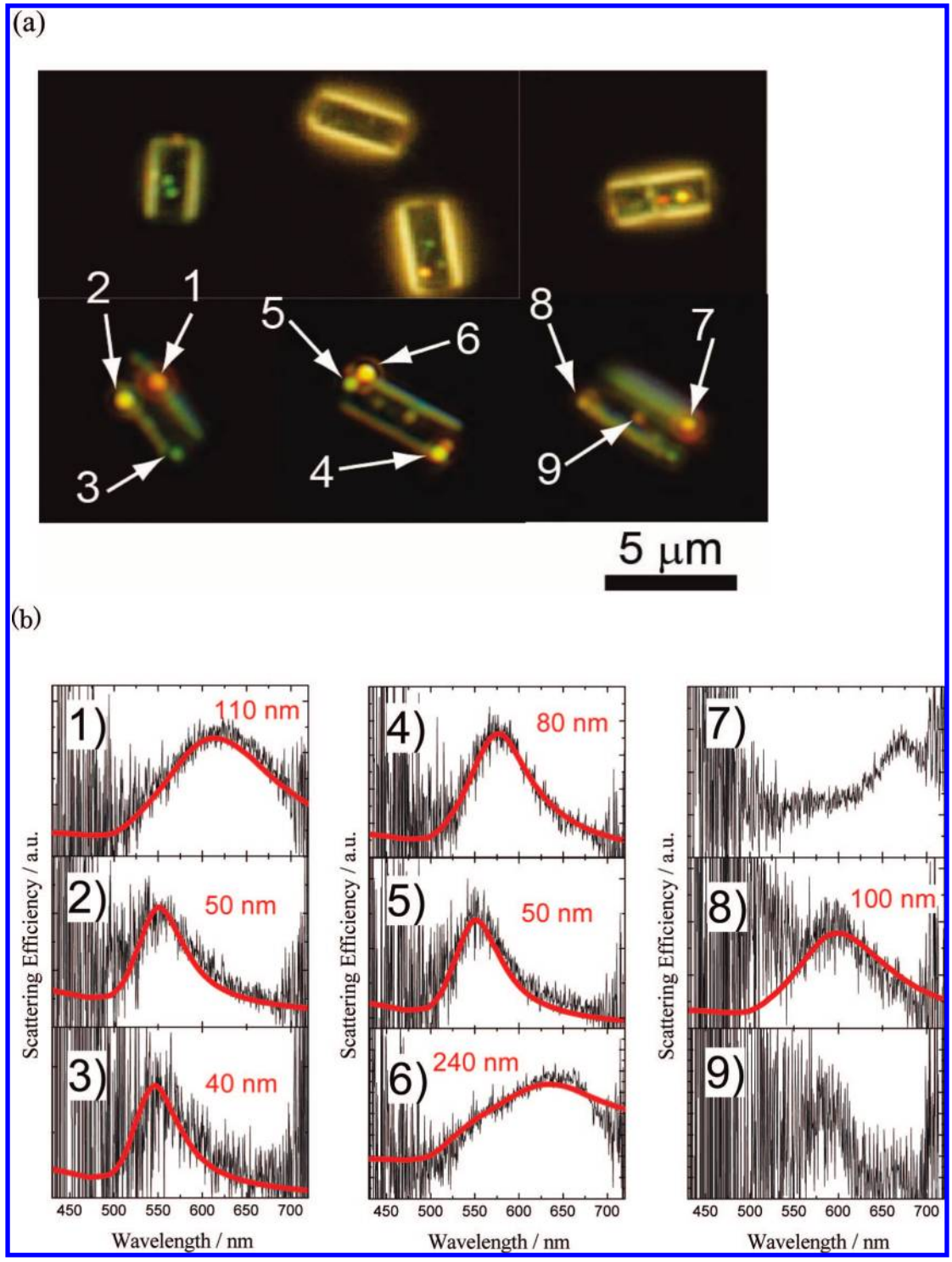

Figure 2. Dark-field light scattering images and spectra of Au NP-doped zeolite L crystals are shown. (a) Light-scattering images of seven representative zeolite crystals and (b) space-resolved light-scattering spectra of bright spots indicated as 1−9 in the crystals in panel a. The black curves 1−9 in panel b correspond to the light scattering spectra for the spots 1−9 in panel a, while the red curves represent calculated scattering spectra for single spherical Au NPs on the basis of Mie theory (ref 38). The experimental spectra were fitted by a particle diameter as an adjustable parameter, and the diameters obtained by the fitting are given in each graph. The fitting assuming a spherical particle failed for particle 7, and the fitting was not carried out for particle 9 because of a noisy spectrum. The 100× objective was employed with a pinhole diameter of 100 μm for the measurements.

dark field illumination revealed that a single zeolite crystal contains several bright spots with various colors, Figure 2a. The colored spots are indicative of strongly light scattering Au NPs. In a strict sense, it is difficult to distinguish microscopically whether they are located inside or outside. However, the image of the same crystal at different focus positions of the objective revealed that Au NPs are located at various depths, suggesting that some crystals are definitely buried inside (see Supporting Information, Figure S4). It was also the case that certain portion of the Au particles tends to occur near the edge of the zeolite crystals. The colors of the scattered light may correspond to the various sizes of Au particles, for instance, green is ca. 30−50 nm diameter, yellow is ca. 60−80 nm, and red is ca. 100 nm or larger according to the Mie theory of light scattering.[37] The

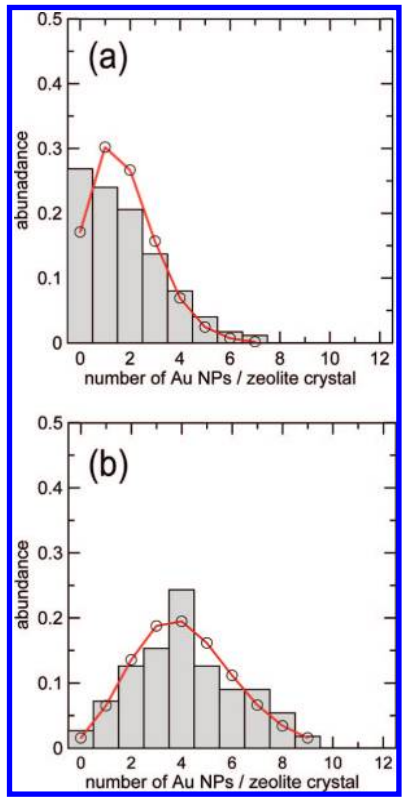

Figure 3. Plots of the number of Au NPs per zeolite crystal (occupancy) vs abundance for different laser ablation periods of the synthesis gels: 2 h (a) and 8 h (b). Bar charts represent the experimental results for 175 zeolite crystals and line plots show calculated curves based on the Poisson distribution law for the experimental average occupancies: 1.8 for (a) and 4.2 for (b).

present result may imply that Au NPs doped in the zeolite crystals are significantly larger in size than those prepared in pure water by the laser ablation, suggesting the formation of aggregates of the particles during the zeolite synthesis. The light scattering spectra of the bright spots are depicted in Figure 2b, 1−9.

For spots 2, 3, 4 and 5, the spectra exhibit a peak in 540−570 nm region, which can be assigned to the surface plasmon resonance band of Au NPs. Furthermore, their spectral shapes and peak positions are well reproduced by calculated spectra on the basis of Mie theory for spherical Au NPs with diameters of 40−80 nm.[38] For the calculation, the refractive index of the surrounding zeolite medium is set to 1.45[39] and that of Au particles was taken from the literature.[40] Thus, we have accomplished the spectroscopic characterization of single Au NPs in the zeolite crystals. In contrast to the spots given above, the spectra for spots 1, 6, 7 and 8 display a distinct peak at 600−620 nm, reminiscent of that of larger or aggregated particles.[41] At present, our dark field microscopy technique does not allow for the imaging of Au NPs smaller than 40 nm diameter. Given that a Rayleigh scattering intensity decreases as the sixth power of diameter, d, it can rapidly attenuate below the background level as the value of d is decreased, resulting in the difficulty in detecting much smaller particles that may exist. Introducing a much brighter illumination source such as the supecontinuum light generated by a photonic crystal fiber combined with a femtosecond laser source will be a great help to overcome this problem.[42,43] Such modification of our setup is now underway.

It is noteworthy that the number of Au NPs per zeolite crystal defined as an "occupancy" determined by the inspection of

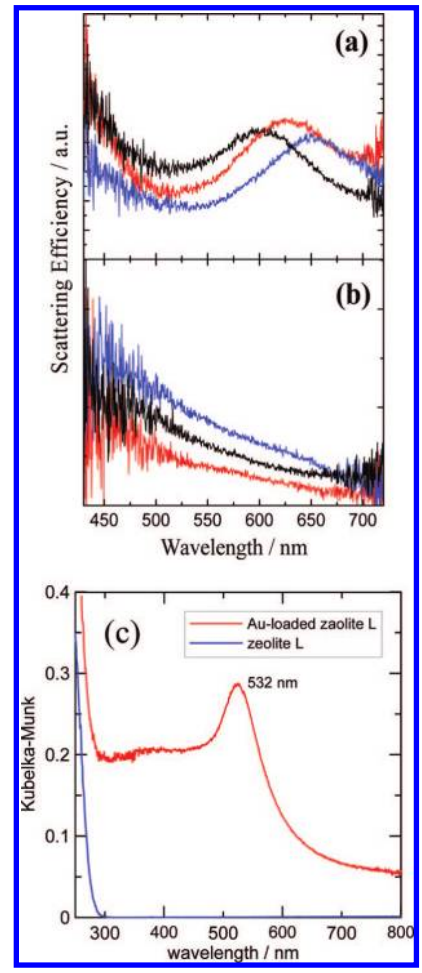

Figure 4. (a) Three representative light-scattering spectra of Au NP-doped zeolite L crystals, showing particle-to-particle difference in ensembled spectral signals. (b) The scattering spectra of empty zeolite L crystals, exhibiting typical wavelength dependence of nonabsorbing materials. (c) Absorption spectra of zeolite powders represented by the Kubelka−Munk remittance function for both zeolite L loaded with Au NPs and zeolite L without Au NPs.

optical microcopy images, is well represented by the Poisson distribution law as typically shown in Figure 3 for two sets of samples prepared from different concentrations of Au NPs. The greater value of an average occupancy is obtained for the sample with a higher concentration of Au NPs prepared by a prolonged laser irradiation of the synthesis gel. The uptake of Au NPs during the crystallization of zeolite L is reminiscent of the uptake of guest molecules by micelles scrutinized many years ago.[44]

Next, we measured the light scattering spectra of whole single zeolite crystals by employing the low magnification objective lens (20×) with a 300 μm pinhole in order to see the particle-to-particle difference in the spectra. Figure 4a shows examples of the spectra for three different crystals. Inspection of the spectra reveals that peak positions located at ca. 600−650 nm are basically assignable to the surface plasmon resonance band of doped Au NPs. A clear difference was observed for Au NP-doped crystals from those without Au NPs. An increase in the scattering intensity with decreasing wavelength can be due to the contribution of the Rayleigh scattering from the zeolite crystals (see Figure 4b). The peak position and spectral bandwidth varied from crystal to crystal and this could be due to the ensemble effect of various sizes, shapes, and aggregation states of Au NPs embedded in each zeolite crystal. For comparison with the scattering spectra, the powder absorption

spectra of zeolite L crystals both loaded and unloaded with Au NPs were measured and depicted in Figure 4c. The absorption peak position of Au-loaded zeolite L is located at 532 nm, an appreciably shorter wavelength than that of the scattering peak positions of the single crystals. This suggests that powder absorption spectra are advantageous to pick up signals from smaller Au particles doped in the zeolite crystals. Despite this, the light-scattering microscopy technique allowed the measurement of the spectra of single Au NPs as small as 40 nm in micrometer-sized zeolite crystals as well as those of a whole crystal. This will help examine the catalytic activities of this zeolite-Au NP composite under in situ conditions. Further investigation along this line is in progress.

In summary, we carried out the preparation of gold NP-loaded zeolite L crystals via unprecedented protocols and demonstrated their optical characterization to a single crystal level by microscope-based light scattering spectroscopy and imaging techniques. Such method can be useful for exploring nanocomposites and other mesoscopic complex systems in the absence of fluorophores, allowing in situ observation of chemical reactions. Improving a spatial resolution and detection limit down to particle sizes smaller than 40 nm is a task to be accomplished by the application of an intense illumination source and confocal light scattering detection. At the same time, the present preparation method of gold NP-doped zeolite L crystals is versatile and capable of synthesizing zeolite crystals doped with metal nanorods and semiconductor quantum dots, leading to advanced materials.

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Supporting Information Available: Extinction spectra of zeolite L synthesis gel containing Au nanoparticles, a schematic diagram for a dark-field light scattering microscopy-spectroscopy, magnified TEM images of Au NP-loaded zeolite L crystals, microscope images of Au NP-loaded zeolite L crystals captured at different focus position of a 100× objective with the axial resolution of 1 μm. This material is available free of charge via the Internet at http://pubs.acs.org.

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