Effect of micro-/mesoporous structures on H₂O₂ sensing ability of YVO₄:Eu³⁺ phosphor particles

Kasumi MOTOMIYA¹, Manabu HAGIWARA¹ and Shinobu FUJIHARA¹,*

¹Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

YVO₄:Eu³⁺ phosphor particles are proposed as an H₂O₂ sensing material based on their turn-off luminescence. The YVO₄:Eu³⁺ particles having various surface microstructures were synthesized through liquid processes and their H₂O₂ sensing ability was evaluated by immersing them in an aqueous H₂O₂ solution with a constant volume at a fixed concentration. The microstructures were characterized in detail not only by electron microscopy but also by nitrogen adsorption to elucidate factors governing the H₂O₂ sensing ability. It was then indicated that micro-/mesoporous structures, which were introduced in the micrometer-scaled spherical particles during their synthesis by a biphasic sol–gel method, were a decisive factor for achieving the effective H₂O₂ sensing. The YVO₄:Eu³⁺ particles synthesized under the improved condition could show a 37% decrease of luminescence intensity after the H₂O₂ treatment.

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Key-words: Phosphor, Luminescence sensing, Hydrogen peroxide, Microspheres, Micropores, Mesopores, Adsorption

1. Introduction

Luminescence sensing is a technique for detecting or quantifying a certain kind of changes in physical or chemical environment using luminescent materials. In addition to traditional organic fluorescent dyes, inorganic phosphors,¹,² organic molecular crystals,³,⁴ and metal–organic frameworks⁵,⁶ have recently been studied as new materials for luminescence sensing. The sensing mechanism is based on changes of luminescent properties such as intensity, wavelength, and lifetime of emissions in accordance with external stimuli.

For inorganic phosphors, it is of prime importance to design and control the microstructure so that they can respond to physical or chemical changes effectively. We have developed a few rare-earth-activated inorganic phosphors such as CePO₄:Tb³⁺, CeO₂:Sm³⁺, and CaWO₄:Eu³⁺, which are chemically responsive to redox environment, by introducing a variety of particle structures through the hydrothermal synthesis.⁷⁻⁹ Most recently, YVO₄:Eu³⁺ has been synthesized as micro-/nano-structured particles by a biphasic sol–gel method where vanadium alkoxide and rare-earth chlorides were separately dissolved in an organic solvent and water, respectively.¹⁰ The resulting YVO₄:Eu³⁺ particles showed a decrease in luminescence intensity (called turn-off luminescence) when they were immersed in an aqueous H₂O₂ solution. The H₂O₂ response was suggested to be dependent on both the specific surface area and the pore size distribution of the particles. However, because the particles were polydispersed on a micrometer scale, the relationship between their nanoscale surface microstructure and the H₂O₂ responsivity has not yet been understood well.

In the present work, monodispersed YVO₄:Eu³⁺ microspheres were synthesized through a modified biphasic sol–gel method and their H₂O₂ response was examined in detail. Additionally, other kinds of YVO₄:Eu³⁺ particles having different surface microstructure were prepared and their turn-off luminescence was compared to each other. Experimental results demonstrate that the accessible interconnected micropores within the microspheres play a crucial role for adsorbing H₂O₂ molecules and accordingly quenching luminescence.

2. Experimental procedure

2.1 Synthesis of YVO₄:Eu³⁺ microspheres

The biphasic sol–gel synthesis of the monodispersed YVO₄:Eu³⁺ microspheres was carried out through a modification of the previously reported procedure.¹⁰ 1.00 mmol (187 µL of VO(OCl)₂H₃) (95.0%, Aldrich) was dissolved in 10 mL of ethanol, which was further added to 90 mL of xylene to obtain a 0.01 M organic solution. Separately, 38.0 mmol of YCl₃·6H₂O (99.9%, FUJIFILM Wako Pure
Chemical Corporation), 2.0 mmol of EuCl\(_3\)-6H\(_2\)O (99.95%, Kanto Chemical), and 40.0 mmol of HCOONa were dissolved together in 400 mL of deionized water. The pH value of the resultant aqueous solution was adjusted to 4.50 by using HCl (35.0–37.0%). A 70 mL aliquot of the aqueous solution was placed in a 1 L beaker, into which 70 mL of the organic solution was poured gently. The height of the aqueous (bottom) and the organic phase (top) was 1.5 and 0.7 cm, respectively. The resultant biphasic organic–aqueous reaction system was kept at a constant temperature of 50 °C for 6 h while stirring the bottom of the beaker at 100 rpm using a hot plate stirrer. Precipitates were then collected by suction filtration, washed with deionized water, and dried at 60 °C for a few hours. The dried powder was tinged with yellow, which was due to the coexistence of the (Y, Eu)V\(_2\)O\(_4\) particles and the amorphous V\(_2\)O\(_5\) gel.\(^{10,11}\) The yellow powder was washed with a 1.0 M aqueous NaOH solution under stirring for 5 h to remove the V\(_2\)O\(_5\) gel. The color of the powder was changed to white during the washing. Finally, the white powder was collected again by suction filtration, washed with deionized water, and dried at 60 °C for a few hours (MS1). Additionally, the MS1 sample was ground using a pestle and mortar with the addition of deionized water, and then ethanol. The resultant suspension was centrifuged at 10000 rpm for 10 min with deionized water and then ethanol. The nanoparticles thus obtained were dried at 60 °C for a few hours (NP1). Additionally, they were annealed at 500 °C for 2 h. The Eu\(^{3+}\) concentration in the SS sample was estimated to be stoichiometric 5 mol% from EDS.

2.3 Solid-state synthesis of YVO\(_4\):Eu\(^{3+}\) particles

The YVO\(_4\):Eu\(^{3+}\) powder (SS) was also synthesized by a conventional solid-state reaction method. Y\(_2\)O\(_3\) (99.99%, Wako), Eu\(_2\)O\(_3\) (99.9%, Wako), and V\(_2\)O\(_5\) (99.0%, Wako) were mixed using a pestle and mortar with the addition of acetone (Y: Eu: V = 0.95:0.05:1 in mol). The resultant mixture was dried at room temperature and heated at 1200 °C for 6 h in air. The Eu\(^{3+}\) concentration of the SS sample was confirmed to be stoichiometric 5 mol% from EDS.

2.4 H\(_2\)O\(_2\) treatment

A 100 ppm aqueous H\(_2\)O\(_2\) solution with \(pH = 5.8–6.1\) was prepared by adding 9.0 mL of a commercial 30 wt% aqueous H\(_2\)O\(_2\) solution (Wako) to 30 mL of deionized water. A 10 mL aliquot of the 100 ppm H\(_2\)O\(_2\) solution was used to examine the H\(_2\)O\(_2\) response of the YVO\(_4\):Eu\(^{3+}\) samples.

When the number of effective H\(_2\)O\(_2\) adsorption sites \(N_s\) on the YVO\(_4\):Eu\(^{3+}\) particles is smaller than the number of H\(_2\)O\(_2\) molecules \(N_m\), all the YVO\(_4\):Eu\(^{3+}\) particles can show the highest degree of turn-off luminescence in response to H\(_2\)O\(_2\). On the other hands, at \(N_s > N_m\), the degree of turn-off luminescence is reduced due to the presence of the non-adsorbed or the partly adsorbed YVO\(_4\):Eu\(^{3+}\) particles. We estimated experimentally the “\(N_s = N_m\)” point using the MS1 sample as the monodispersed particles having a specified large surface area. The MS1 sample, with its amounts varied between 10 and 280 mg, was added to each 10 mL aliquot of the 100 ppm H\(_2\)O\(_2\) solution and kept at room temperature for 1 h under stirring. The sample was then collected by suction filtration, washed with deionized water, and dried at 60 °C for 1 h. The turn-off luminescence of the sample was examined by measuring photoluminescence (PL) spectra before and after the H\(_2\)O\(_2\) treatment.

Next, to compare the H\(_2\)O\(_2\) sensing ability, the five samples (MS1, MS2, NP1, NP2, and SS) were added to each 10 mL aliquot of the 100 ppm H\(_2\)O\(_2\) solution and kept at room temperature for 1 h under stirring. The amount of the respective samples was set to fulfill the “\(N_s < N_m\)” condition. The treated samples were collected, washed, and dried and their turn-off luminescence was examined similarly. Note that luminescence intensity of the YVO\(_4\):Eu\(^{3+}\) samples did not change when they were treated simply with water.

2.5 Characterization

The crystalline phase of the samples was identified by X-ray diffraction (XRD; a D8 ADVANCE diffractometer, Bruker AXS) using Cu K\(_\alpha\) radiation. The crystallite size was calculated from the full width at half maximum of the XRD peak using the Scherrer’s equation with a shape factor of 0.9. The morphology of the samples was observed by field-emission scanning electron microscopy (FESEM; an S-4700 microscope, Hitachi). Conductive coating was applied to the samples with an osmium plasma coater. The EDS analysis was also performed using the FESEM. The microstructure of the samples was observed by field-emission transmission electron microscopy (FE-TEM; a Tecnai F20 microscope, FEI). A specimen for the FE-TEM observation was prepared by dispersing the particles in ethanol and drying onto a carbon coated copper grid. The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution of the samples were evaluated by using a nitrogen adsorption/desorption apparatus (BELSORP-mini II, MicrotracBEL). The hydrodynamic particle size distribution was measured by dynamic light scattering (DLS; a Partica LA-960 particle analyzer,
Horiba), where the powders were dispersed in deionized water with stirring. The refractive index of bulk YVO₄ (1.993) was used in the DLS analysis. PL spectra of the samples were measured at room temperature with a spectrofluorophotometer (FP-6500, JASCO) using a xenon lamp (150 W) as a light source. The samples were mounted on a silica glass plate having a square well 5 mm × 5 mm in dimension to regulate their amount in the PL measurement.

3. Results and discussion

3.1 Characterization of the YVO₄:Eu³⁺ particles

Figure 1 shows XRD patterns of the four samples of MS1 (the microspheres), MS2 (the pulverized microspheres), NP1 (the nanoparticles), and NP2 (the annealed nanoparticles). All peaks appearing in any of the patterns can be indexed to the tetragonal YVO₄ phase (ICDD 17-0341). The diffraction peaks of the MS2 sample are broader in width and lower in intensity than those of the MS1 sample because the crystallites were crushed and the crystallinity was reduced by the grinding treatment. The higher peak intensity observed for the NP2 sample than that for the MS1 and NP1 samples is due to the enhanced crystallinity after the annealing treatment at 500 °C. The crystallite size along the a-axis of (Y₃Eu)VO₄ is calculated to be 11.7, 8.3, 7.2, and 12.0 nm for MS1, MS2, NP1, and NP2, respectively, from the (200) peak using the Scherrer’s equation.

The morphology of the MS1, MS2, NP1, and NP2 samples was observed with FESEM as shown in Fig. 2. The MS1 sample is characterized as nearly monodispersed spherical particles 3.15 ± 0.19 μm in size with the coefficient of variation of 0.06. On the other hand, the MS2 sample is nanoparticulate and the micrometer-sized spherical particles are no longer observed. This implies that the YVO₄:Eu³⁺ microspheres comprise nanoparticles, which are connected loosely for aggregation. Both the NP1 and NP2 samples appear to be the accumulation of nano-sized powders, which need to be characterized further by FETEM.

In our previous study, we synthesized the micro-/nano-structured YVO₄:Eu³⁺ particles using the biphasic sol–gel method where the separated organic and aqueous solutions were kept still without stirring. They were defined as polydispersed secondary spherical particles, which were constructed of primary nanoparticles, with the size of 1.16 ± 0.22 μm and the coefficient of variation of 0.19. Accordingly, the smaller coefficient of variation (0.06) of the present MS1 sample was achieved by introducing the stirring in the biphasic sol–gel method. The influence of the stirring on the formation of the YVO₄:Eu³⁺ particles can be explained as follows. In the biphasic system, first, VO(OH)₂: dissolving in the organic phase to form VO₂(OH)²⁻:

\[
\text{VO(OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O} \rightarrow \text{VO}_2(\text{OH})_2^- + \text{H}^+ + 3\text{C}_2\text{H}_5\text{OH}
\]  

Fig. 1. XRD patterns of the four samples: MS1, MS2, NP1, and NP2.

Fig. 2. FESEM images of the MS1, MS2, NP1, and NP2 samples.
Then, the VO$_2$(OH)$_2$\textsuperscript{−} ions react with Y$^{3+}$ and Eu$^{3+}$ in the aqueous phase to form Y$_{1−x}$Eu$_x$VO$_4$:

\[
(1 - x)Y^{3+} + xEu^{3+} + VO_2(OH)_2^- \\
\rightarrow Y_{1−x}Eu_xVO_4 + 2H^+
\]  

(2)

When the biphasic solutions are kept still, the concentration of the VO$_2$(OH)$_2$\textsuperscript{−} ions is higher at near the interface and decreases gradually in a vertical direction. As a result, the nucleation frequency and the crystal growth rate of Y$_{1−x}$Eu$_x$VO$_4$ vary depending on the distance from the interface. On the other hand, when the bottom of the beaker is stirred, the VO$_2$(OH)$_2$\textsuperscript{−} ions can be dispersed in the aqueous phase and their concentration gradient is diminished. Under this circumstance, both the nucleation and the crystal growth proceed uniformly and then the monodispersed Y$_{1−x}$Eu$_x$VO$_4$ particles (MS1) can be obtained.

**Figure 3** shows FETEM images of the MS1, MS2, NP1, and NP2 samples. The MS1 sample is confirmed to be constructed of primary nanoparticles. The fine fringes observed in the images of the MS1 and MS2 samples indicate that the primary nanoparticles are the monocrystal and their size is comparable to the Scherrer crystallite size as mentioned above. The primary particles of the NP1 sample are observed to be almost spherical with the size around 5 nm. After annealing at 500 °C, the size of the primary particles is increased to approximately 12 nm as observed for the NP2 sample.

The surface microstructure of the samples was further examined by the N$_2$ adsorption experiment. **Figure 4** shows N$_2$ adsorption–desorption isotherms and pore size distribution curves of the MS1, MS2, NP1, and NP2 samples. The fitting analysis based on the BET equation revealed that specific surface areas of MS1, MS2, NP1, and NP2 were 176, 34.2, 131, and 57.8 m$^2$ g$^{-1}$, respectively.

The MS1 sample obtained by the biphasic sol–gel method has the largest specific surface area among the four samples. As shown in Fig. 4(a), the isotherm of the MS1 sample corresponds to the type IV in the IUPAC classification,\textsuperscript{14)} suggesting that it has both micropores and mesopores. The MS1 sample also shows the type H2(a) hysteresis loop in its isotherm, which is associated with an interconnected network of pores of different shapes.\textsuperscript{14,15)}

Note that the type H2(a) hysteresis is typical of porous adsorbents such as metal oxide gels and porous glasses. Surprisingly, the isotherm of the MS2 sample is drastically changed from that of MS1. Much lower adsorption volumes at relative pressures up to 0.9 indicate that the micropores and mesopores are lost by pulverizing the MS1 sample. Only macropores seem to survive as suggested by a rapid increase in the volume at higher relative pressures above 0.9.

The NP1 and NP2 samples also exhibit the type IV isotherms but their hysteresises are different from each other and also from that of the MS1 sample. The NP1 sample has the type H2(b) hysteresis,\textsuperscript{15)} which is due to the aggregation of the nanoparticles forming another network structure of pores, as compared to that of MS1. The aggregation state of the NP1 sample in water was estimated using DLS as shown in **Fig. 5**. The average particle size of the NP1 sample is as large as 8.28 µm. The pore network is supposed to be formed during drying the aggregated particles. The desorption pressures are reported to be
dependent on the size and spatial distribution of necks in the network of ink-bottle shaped pores. The H2(a) and the H2(b) hysteresis are explained by a narrow and a wide size distribution, respectively, of the pore necks. The NP2 sample has the type H1 hysteresis, which is caused by pores within aggregates of uniformly sized spherical particles. The pore size distribution of the samples was examined using the MP method for micropores [Fig. 4(b)] and the Barrett–Joyner–Halenda (BJH) method for mesopores [Fig. 4(c)]. The MS1 sample has a large number of micropores less than 2 nm in diameter, while the other three samples have very few micropores. The MS2 sample has also much fewer mesopores. Thus the grinding treatment of MS1 leads to the destruction of the porous structure and/or the closure of the open pores. The NP1 sample shows a wide range of the pore diameter between 2 and 40 nm due to the aggregation. Because of the particle growth, the interparticle space is broadened and the pore diameter is increased in the NP2 sample.

PL excitation and emission spectra of the MS1, MS2, NP1, and NP2 samples are shown and compared in Figure 6. Several sharp peaks are observed in both the excitation and the emission spectra, which are characteristic of the 4f–4f electronic transitions of Eu3+ doped in the YVO4 phase. Furthermore, strong and broad excitation bands ranging from 220 to 360 nm are also seen in the PL excitation spectra of all the samples. They are assigned to the overlapping absorption due to the O2− → V5+ charge transfer in the VO43− unit and the localized O2− → Eu3+ change transfer. The PL intensity of the MS2 sample is lower than that of the MS1 sample. This is because the crystallinity of the MS2 sample is lowered and the surface defects are generated after the grinding treatment. The NP1 sample exhibits the slightly lower PL intensity than the MS1 sample. This may be related to the lower Eu3+ concentration in the NP1 sample, as mentioned in the experimental section. In contrast, the NP2 sample has the much higher intensity compared to the other samples. This is due to the enhanced crystallinity and the decreased surface defects by the annealing treatment.

3.2 H2O2 treatment of the YVO4:Eu3+ particles

The H2O2-responsive turn-off luminescence was first examined for the MS1 sample to estimate \( N_e \) (the effective H2O2 adsorption sites) of the YVO4:Eu3+ particles. The pore size distribution of the samples was examined using the MP method for micropores [Fig. 4(b)] and the Barrett–Joyner–Halenda (BJH) method for mesopores [Fig. 4(c)]. The MS1 sample has a large number of micropores less than 2 nm in diameter, while the other three samples have very few micropores. The MS2 sample has also much fewer mesopores. Thus the grinding treatment of MS1 leads to the destruction of the porous structure and/or the closure of the open pores. The NP1 sample shows a wide range of the pore diameter between 2 and 40 nm due to the aggregation. Because of the particle growth, the interparticle space is broadened and the pore diameter is increased in the NP2 sample.

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Fig. 6. PL excitation and emission spectra of the MS1, MS2, NP1, and NP2 samples: an emission wavelength (\( \lambda_{\text{em}} \)) of 619.5 nm and an excitation wavelength (\( \lambda_{\text{ex}} \)) of 300 nm were used for measuring the excitation and the emission spectra, respectively.

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amount of the MS1 sample, which was varied between 10 and 280 mg, was converted to the total surface area using the measured specific surface area of 176 m² g⁻¹. In Fig. 7, the relative PL intensity, which was obtained by integrating the Eu³⁺ emissions between 500 and 750 nm, was plotted against the total surface area of the MS1 sample after the H₂O₂ treatment. Note that the intensity before the H₂O₂ treatment was taken as 100%. The intensity is decreased down to around 70% (turn-off luminescence) for the smallest surface area of 1.76 m² with 10 mg of the sample. This decrease is caused by the adsorption of the H₂O₂ molecules on the surface of the YVO₄:Eu³⁺ particles. The excitation energy is partly consumed by the photocatalytic decomposition of the adsorbed molecules. The degree of the turn-off luminescence is almost constant up to the total surface area of 41.5 m² (255 mg), thereby indicative of the “Nₛ < Nₘ” region. This result also confirms the high reproducibility of the turn-off luminescence, in contrast to our former study, when using the monodispersed MS1 sample. The degree of the turn-off luminescence starts to be decreased at 45.0 m² (255 mg) and the intensity becomes as high as 92% at 49.5 m² (280 mg). Therefore the “Nₛ = Nₘ” point is thought to lie between 41.5 and 45.0 m² for the YVO₄:Eu³⁺ particles. The relationship between the H₂O₂ sensing ability and the structure of the YVO₄:Eu³⁺ particles was examined by measuring PL spectra before and after immersing them in the 100 ppm H₂O₂ solution. Figure 8 shows the relative PL intensity (integrated between 500 and 750 nm) of the five samples, MS1, MS2, NP1, NP2, and SS, after the H₂O₂ treatment. The intensity before the H₂O₂ treatment of the respective samples was taken as 100% severally. The samples of MS1, MS2, and NP1 undergo appreciable turn-off luminescence with degrees of 31, 21, and 18%, respectively. On the other hand, the NP2 sample is not responsive to H₂O₂. The SS sample is completely unresponsive. According to the N₂ adsorption experiment, the SS sample was not porous and had the specific surface area as low as 0.8 m² g⁻¹. The much lower ability of the H₂O₂ adsorption therefore accounts for the unresponsive SS sample.

The above observation indicates that the monodispersed YVO₄:Eu³⁺ microspheres (MS1) obtained by the biphasic sol–gel method have the highest H₂O₂-sensing ability based on the turn-off luminescence. We also synthesized other YVO₄:Eu³⁺ samples with different Eu³⁺ concentrations (4.4, 12.1, or 18.4 mol % according to the EDS analysis) by the biphasic sol–gel method and confirmed that they showed almost the same turn-off luminescence. The difference in the H₂O₂-sensing ability among the YVO₄:Eu³⁺ particles is explained in the following. First, the H₂O₂-sensing ability does not necessarily depend on the specific surface area of the particles. This is true when comparing the degree of the turn-off luminescence of the three samples: MS2 (34.2 m² g⁻¹) > NP1 (131 m² g⁻¹) > NP2 (57.8 m² g⁻¹). Also the large amount of the mesopores is not effective for the turn-off luminescence, as in the case of the NP1 and NP2 samples. The factor for determining the H₂O₂-sensing ability is therefore the presence of the small-sized pores, especially the micropores. The H₂O₂ molecules adsorbed on the wall of the small pores would not be desorbed after drying at 60 °C for 1 h and would continue to work as a luminescence killer. To confirm this assumption, the relative PL intensity of the H₂O₂-treated MS1 sample was monitored for prolonged drying time up to 136.5 h. A result shown in Fig. 9 reveals that it takes 21.5 h to recover the PL intensity to 90%. A further recovery to 96% is observed after a much longer drying time of 136.5 h. Thus the H₂O₂ molecules once adsorbed in the small pores are hardly desorbed.

The present MS1 sample has the particle size of 3.15 ± 0.19 μm. This is somewhat larger than the size of the redox-
responsive CePO₄:Tb³⁺ (800 nm), CeO₂:Sm³⁺ (711 nm), or CaWO₄:Eu³⁺ microspheres (1.5 μm) reported so far. The degree of the turn-off luminescence in these microspheres was as high as 80% against the aqueous solutions of redox reagents. A final attempt was then made to decrease the size of the present MS1 sample, aiming at improving the turn-off luminescence property. A smaller MS1 sample (denoted as MS1′) was synthesized through the biphasic sol–gel method with a minor modification. Actually, 26.7 mmol of CH₃COONa was used as the additive, instead of 40.0 mmol of HCOONa, in preparing the aqueous solution. Monodispersed YVO₄:Eu³⁺ microspheres (MS1′) could then be obtained, as shown in Fig. 10, with the smaller particle size of 1.40 ± 0.03 μm. Although a BET specific surface area of the MS1′ sample, which was measured to be 131 m² g⁻¹, was slightly smaller than that of MS1, both the samples showed the similar adsorption–desorption isotherms, the pore size distribution curves, and hence the micro-/mesoporous structure. The MS1′ sample was proven to be more responsive to H₂O₂ with an improved degree of the turn-off luminescence of 37%.

4. Conclusions

The YVO₄:Eu³⁺ phosphor particles were synthesized and their H₂O₂ sensing ability was evaluated. The different synthetic procedures resulted in the evolution of the different surface microstructures of the particles as characterized by the nitrogen adsorption measurement as well as the electron microscopy observation. It was demonstrated that the micro-/mesoporous structures were more important than the specific surface areas for the effective adsorption of H₂O₂ and the subsequent turn-off luminescence. The monodispersed YVO₄:Eu³⁺ microspheres synthesized by the modified and optimized biphasic sol–gel method showed the highest degree of the turn-off luminescence (37%) due to the presence of a large number of the micropores.

Acknowledgment This study was supported by JSPS KAKENHI Grant Number 17K06801.

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