Hierarchical Assembly of Atomically Precise Metal Clusters as a Luminescent Strain Sensor

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emergence of a new peak in the luminescence spectrum was observed during the course of mechanical stretching. This peak increased in intensity gradually with the degree of elongation or strain of the material. A mechanochromic luminescence response was further demonstrated with a writing experiment on a luminescent mat of the material, made by electrospinning.

KEYWORDS: protein-protected noble metal clusters, mechanochromic luminescence, hierarchical, bioinspired, aminoclay

INTRODUCTION

Metal nanoclusters (NCs), especially of gold and silver, protected with ligands have drawn attention due to their unique molecular properties such as dye-like absorption, characteristic emission, chirality, reactivity, and so forth. Among them, intense luminescence in the visible and NIR regions made these clusters very attractive in multiple areas of research. Protein-protected clusters (PPCs), a subclass of atomically precise clusters, have been grown within proteins.²⁻⁴ They are water-soluble and exhibit intense luminescence. Besides, they are comparatively more stable than other classes of ligand-protected NCs. The highest quantum yield (QY) of noble metal cluster systems till date have been known for PPCs.⁵ This has made PPCs to be used for a range of multidisciplinary applications, especially in sensing and biology.⁶ Different topics such as sensing of hazardous analytes, targeting and bioimaging, drug delivery, and therapeutic applications have been researched upon for more than a decade. Recently, cluster-conjugated hybrid materials are being pursued for improved performance.

Clays have been used from antiquity.^{7,8} In prehistoric times, clays were used to make bricks. They were used as bleaching materials and as soaps in ancient civilizations. Nowadays, they are used in our daily life in toothpastes, paints, pencils, different household ceramics, and so forth.⁹ Considerable

interest has been developed in clay materials due to their applications in catalysis,¹⁰ functional nanocomposites,^{11,12} separation,¹³ biomedicine,¹⁴ ferrofluids,¹⁵ and so forth. Despite these widespread applications, poor solubilities of common clays such as kaolinite, smectite, bentonites, and so forth, in water, limit their utilization in specific applications. Mann and co-workers synthesized a tailormade clay, coined as aminoclay, which is an aminopropyl-functionalized magnesium phyllosilicate clay.^{16–18} It has high water solubility and shows fascinating properties.^{19–22}

Nacre, the gold standard for biomimicry, also known as the mother of pearl is an example of a bioinspired structural material.^{23–26} Nacre mimics are nanocomposites made by assembling two-dimensional (2D) nanosheets to achieve a higher-order structure and high mechanical performance, similar to nacre.^{27–29} The unique combination of strength and toughness in these biomimetic hybrid materials made them fascinating light-weight structural components for the

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future.³⁰ Nacre mimics are obtained by intercalating a soft phase between the layers of a hard phase. Both the hard and soft phases contribute to the mechanical properties of the resultant hybrid material. Mimicking the characteristics of these natural materials is not an easy task.^{31–33} Clay materials, due to their unique 2D structure, have often been utilized as the hard phase in nacre mimics. Polymers, biomolecules, and a combination of both have been used as the soft phase. Although the systematic integration of hard and soft phases in a hierarchical fashion is a recent development, confinement of guest molecules in layered 2D matrices to form an organoinorganic hybrid is well established.³⁴ Multifunctional polymer-clay hydrogels were formed by "guest-molecule-directed self-assembly" of a nanocomposite.³⁵ Lipid templates helped to grow higher-order organoclay pipes by self-assembly.³⁶ Wrapping of biomolecules such as proteins, enzymes, DNAs, and so forth, by the aminoclay, was carried out to make functional hybrid materials for real-life use.^{37,38} The secondary structure of the entrapped biomolecules was retained during bioimmobilization.³⁹ Thus, there is reduced probability for losing the biological function in these hybrid materials. Their structural and chemical properties could be integrated to enhance their applications, and their thermal and chemical stability enhanced their scope in biocatalysis, biosensing, and biomedical devices.

Herein, we have made an attempt to incorporate optically active biomolecules between the layers of functionalized clay sheets to create a unique nacre mimic. Highly luminescent, stable, and BSA-protected Au₃₀ NC was used to intercalate in the aminoclay template. Water-soluble Au₃₀@BSA clusters attach to the aminoclay sheets through Coulombic interactions due to their opposite charges in solution and form a waterinsoluble hierarchical organo-inorganic hybrid material. The layered structure of the hybrid material was observed through field emission scanning electron microscopy (FESEM). Intercalation of the cluster between the layers of aminoclay sheets was identified from powder X-ray diffraction (pXRD). Gradual formation of larger aggregates in solution during the synergistic interaction of both the cluster and the aminoclay sheets was seen in dynamic light scattering (DLS) measurements. These cluster-attached clay sheets were also identified by transmission electron microscopy (TEM). Luminescence of Au₃₀@BSA was retained in the hybrid material. The material was cast into different shapes after the addition of polyvinyl alcohol (PVA) into it. This PVA-added hybrid material was highly ductile in nature. The material, shaped as a dog bone, could be stretched to 300% of its original length without failure. Moreover, the change in the luminescence of the cluster was observed when the material was stretched, indicating its inherent strain sensitivity. This sensitivity was enhanced and was evident in the form of changing luminescence of an electrospun mat, when it was used for writing. Combination of interesting optical and mechanical properties in a cluster-based hybrid material makes it an exciting material.

EXPERIMENTAL METHODS

Materials. Magnesium chloride and BSA (about 96% purity) at pH 6–7 were purchased from Sisco Research Laboratory. Tetrachloroauric acid trihydrate (HAuCl₄·3H₂O) was prepared inhouse starting from elemental gold. Sodium hydroxide pellets were purchased from a local supplier (Rankem, India). Milli-Q water with a resistivity of 18.2 MΩ·cm was used for synthesis. 3-Amino-

propyltriethoxysilane was purchased from Sigma-Aldrich. PVA (MW: 85,000–124,000) was purchased from S. D. Fine-Chem Limited. All the chemicals were used as received without further purification.

Synthesis of Au₃₀@BSA NC. About 25 mg of BSA was dissolved in 1 mL of Milli-Q water. Then, 1 mL of 6 mM HAuCl₄ aqueous solution was mixed with it and stirred vigorously for 5 min. Then, 100 μ L of 1 M NaOH solution was added to it. The reaction was stirred for 12 h. A brown colored solution was formed, indicating the formation of Au₃₀@BSA, which showed bright red luminescence.

Synthesis of Aminoclay. The aminoclay was synthesized by a method reported earlier.^{17,18} An organosilane precursor-like 3-aminopropyltriethoxysilane (1.3 mL, 5.85 mmol) was used at room temperature to prepare the amine-functionalized nanoclay. A solution of magnesium chloride (0.84 g, 3.62 mmol) in ethanol (20 g) was prepared. The precursor was added dropwise to the solution and kept for constant stirring at room temperature for 24 h. The white gel-type material was formed, which was recovered by centrifugation followed by washing with ethanol and distilled water and finally dried at 313 K.

Synthesis of a Clay-Cluster Hybrid (Will be Denoted as CCH Subsequently) and Its Casting in Different Forms. About 20 mL of aqueous solution of aminoclay (250 mg/mL) was prepared by sonication. This was mixed with 20 mL of Au_{30} @BSA solution (10:1 weight % of clay/cluster) under constant stirring. The reaction was continued for 12 h. Then, the resultant solution (I) was air-dried at room temperature. Finally, a luminescent solid clay-cluster hybrid (CCH) was formed.

PVA (6 weight %) was added to I to prepare precursor solutions for making various shapes. The solution was dried in a Petridish to form the film samples. Using plaster of paris, the dog bone-shaped die was made. Here, die is the molding device, which was used for shaping the CCH. The dog bone-shaped luminescent PVA-added CCH was made using this die.

Formation of Luminescent Mats by Electrospinning. Claycluster luminescent nanofibers were made using the ESPIN-NANO electrospinning machine. The same mixture, which was used to make the dog bone-shaped sample, was loaded into a 2 mL syringe for electrospinning. The luminescent spun mat was collected on top of the Al sheet. The parameters used for spinning were: flow rate, 0.15 mL/h; voltage, 18 kV, and working distance, 12 cm.

Stress–Strain Experiments. Tensile strength measurements of cluster-sandwiched aminoclay materials were conducted by Nano Plug and Play servo-hydraulic testing machine of 5 kN capacity, which comes with an application software capable of doing tension, compression, three-point bend, fatigue tests, and so forth. Materials were stretched in different percentages of elongation, for example, 80, 140, 250, and 300%. Experiments were carried out with both dog bone-shaped and rectangular film samples. In both cases, the trend of the luminescence with % of elongation was the same. Five positions were marked for each sample, shown in Figure 5A. Luminescence was measured before and immediately after the tensile strength experiments. The gauge length of the sample was 17 mm, the rate of elongation of the specimen was calculated by [(final gauge length – initial gauge length)/initial gauge length \times 100].

Writing Experiments. The luminescent membrane was placed inside a ziplock cover, and a pattern was drawn on it with the tip of a cotton swab. After this, we saw it under UV light. To show the uniform pressure sensitivity across the membrane, the grid pattern was drawn. In a similar way, the alphabet *a* was written on another membrane.

Characterization. UV–vis spectra were recorded using a PerkinElmer Lambda 25 UV–vis spectrometer. Photoluminescence measurement for Au_{30} @BSA was carried out in a HORIBA, Jobin Yvon NanoLog instrument. Solid-state luminescence of CCH was measured in a Witec GmbH, Alpha-SNOM alpha300 S confocal Raman instrument. For excitation, a 532 nm laser source was used, and the emission spectrum was recorded. Particle size and zeta potential measurements in solution were conducted using a Malvern Zetasizer Nano ZSP instrument. FESEM measurements were carried



Figure 1. (A) Schematic representation of the formation of the organo-inorganic CCH material. The inset shows the TEM image (i) and photograph (ii) of the intense red luminescent aggregates formed during the reaction of the clay and cluster. The schematic of the aminoclay sheet is presented for representation purpose only. (B) TEM image of the aminoclay sheet. (C) MALDI MS of the Au_{30} @BSA. (D) Optical (left) and fluorescence (right) images of CCH. (E) Luminescence spectrum of CCH showed a maximum at 650 nm for 365 nm excitation.



Figure 2. Electron microscopic characterization of the composite. (A) FESEM images of a cross-sectional view of CCH. The inset shows the TEM image of the cluster-attached clay sheets. (B) Layers of clay sheets are seen clearly in a zoomed-in image.

out using a Thermo Scientific Verios G4 UC instrument. Highresolution TEM (HRTEM) was carried out with a JEOL 3010 (JEOL Ltd.), a 300 kV instrument equipped with an ultrahigh-resolution pole piece. Dark field imaging was performed using an Olympus BX-51 microscope having a 100 W quartz halogen light source mounted on a CytoViva microscope setup. Matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) measurements of proteins and clusters were conducted using an Applied Biosystems Voyager-DE PRO MALDI TOF spectrometer. A pulsed nitrogen laser of 337 nm was used for ionizing the proteins and the clusters, using the sinapic acid matrix. pXRD data were collected with a Bruker AXS, D8 Discover diffractometer using Cu K α (λ = 1.54 v) radiation.

RESULTS AND DISCUSSION

Preparation of the Luminescent Organo-Inorganic Hybrid Material. Aminoclay, a synthetic clay, is aminopropylfunctionalized 2D magnesium phyllosilicate. Dispersing the assynthesized aminoclay in water results in the protonation of amine groups and leads to its exfoliation into individual 2D clay sheets. The parent cluster Au₃₀@BSA was characterized by (A) UV-vis and (B) luminescence spectra, shown in Figure S1. The cluster showed an emission at 650 nm. The light brown color of the cluster solution in visible light and its bright red color under UV light are shown in the inset of Figure S1B. The hydrodynamic diameter of the cluster solution was 6 nm, as shown in Figure S2. Mixing a clear solution of the exfoliated clay with an aqueous solution of Au₃₀@BSA NCs (10:1 weight %) resulted in the immediate formation of a slight turbid solution, indicating a reaction between the two. The turbidity of the reaction mixture increased with time and was left under stirring for 12 h at room temperature for completion of the reaction. Finally, the turbid solution was air-dried at room temperature to obtain a brown translucent film. Here, the oppositely charged clusters and clay sheets attach together through Coulombic interaction to create a hybrid material in the course of the reaction. The formation of the CCH is represented schematically in Figure 1A.

Randomly oriented clay sheets were observed in the course of the reaction (shown in inset a), which shows red luminescence under UV light due to the presence of the clusters (shown in inset b). The TEM image of the parent aminoclay is shown in Figure 1B. MALDI MS of pure BSA (green trace) and the Au₃₀@BSA cluster (purple trace) is shown in Figure 1C. BSA showed its molecular ion peak at m/z 66.42 kDa, and the cluster showed the peak at m/z 72.28 kDa. The difference in the m/z value in MALDI MS spectra of the cluster than the parent protein confirmed the atomicity of the Au₃₀ core within BSA.⁴⁰ Bright red luminescence of CCH was seen by fluorescence microscopy, shown in Figure 1D (right side). The luminescence spectrum of CCH showed a maximum at 650 nm (Figure 1E), similar to the cluster, which confirmed that the cluster is intact in the hybrid. The oxidation state of Au remains unchanged after the formation of CCH. The lifetime of the hybrid material is similar to that of the cluster, 0.13 ns (62%), 1.23 ns (25%), and 33.0 ns (13%). The QYs of Au₃₀@BSA and the CCH are 29 and 40%, respectively. This hybrid material is very stable up to 200 °C and in the pH range of 1-14. The sample was characterized in detail to reveal the structure of the composite material.

Formation of the Nacre-like Layered Structure. Selfordering of the hybrid material into multilayered structures is shown in Figure 2. Removal of water from the composite material led to self-ordering and stacking of layers, which is confirmed from the FESEM image, presented in Figure 2A. FESEM images were measured from using dried samples. Due to opposite electrostatic charges present on the cluster and the clay sheets, they attract each other, forming a single layer of CCH. These layers stack together to form a hierarchical layered structure, which can be seen from Figure 2B, although the clusters, due to their very small core size (~1 nm), cannot be seen in the FESEM images. However, the red luminescence of CCH confirms their presence. The TEM image of CCH (shown in inset of Figure 2A) shows the clear presence of clusters attached to aminoclay sheets. The wavy nature of the surface showed the nanoscale roughness of CCH, which is clear from Figure S3.

Intercalation of Au₃₀ Clusters into Layered Galleries. From the data presented, the layered structure of the biomimetic material, CCH, and the attachment of the NCs with aminoclay were confirmed. However, the position of the clusters in the composite was not clear from microscopic studies. To prove our hypothesis that clusters intercalate between the layers of aminoclay sheets in CCH, pXRD was performed. The parent aminoclay shows several peaks in its pXRD pattern corresponding to different crystallographic planes of the clay (Figure S4). The peak at $2\theta = 6.1^{\circ}$ (shown in Figure 3A) corresponds to an interlayer spacing of 1.45 nm between the aminoclay sheets [(001) plane]. The peak shifts to $2\theta = 1.5^{\circ}$ in CCH, corresponding to an interlayer spacing of 6.00 nm. The increase in interlayer spacing from the aminoclay to CCH points to intercalation of the Au₃₀@BSA cluster between the aminoclay sheets. Complete disappearance of the aminoclay peak in CCH suggests that CCH is a pure phase and excess aminoclay does not exist. Although the clusters intercalated between the clay sheets could not be clearly resolved in FESEM, a distance of 6 nm between the layers was confirmed (Figure 3B). A long-range ordered structure of CCH is shown in Figure 3C.

Probable Mechanism for the Interaction of Au₃₀ Clusters and Aminoclay. The mechanism of formation of



Figure 3. (A) Powder XRD data of the cluster, aminoclay, and CCH. Intercalation of the cluster is evident. (B) FESEM image showing a cross-sectional view of CCH. This shows the 6.00 nm spacing between the layers. (C) FESEM image showing the long-range ordered structure of CCH.

the intercalated hybrid structure was investigated by zeta potential measurements and DLS. Host-guest interaction of biomolecules and organoclay was studied earlier. Successful intercalation depends on two factors, electrostatic interaction between the host and the guest and the size of the guest molecules. In our case, Coulombic interactions between the positively charged aminoclay sheets and negatively charged NCs helped to form the coassembly of the clusters in between the delaminated sheets. The zeta potential value for aminoclay was +25.6 mV, and for NCs, it was -22.0 mV. The zeta potential value of the solution after the formation of CCH was +8.5 mV (shown in Figure 4B). Considerable reduction of the



Figure 4. (A) Time-dependent DLS data show the conversion of a nanometer-scale material into micron-scale particles. (B) Zeta potential values are shown in a tabular form.

positive charge of aminoclay in presence of NCs confirmed that CCH was formed through electrostatic interactions between the positively charged aminopropyl moieties of the clay and the negatively charged carboxylate groups on the protein surface. The reduced zeta potential value of CCH also contributed to their aggregation, and the solution thus becomes turbid. Finally, a uniformly stacked hybrid organoinorganic structure was formed from solution during drying.

Regular stacking of the hybrid material also depends on the size of the guest molecule. An earlier report³⁴ showed the formation of regular stacking between myoglobin (Mb) and aminoclay, while disordered stacking was observed for hemoglobin (Hb) (with aminoclay). The surface charge of



Figure 5. (A) Schematic representation of the tensile strength experiment. This experiment was carried out using dog bone-shaped luminescent PVA-added CCH samples. Samples were stretched up to 80, 140, and 250% of their original size. Each point, where the luminescence spectrum was collected, is marked by an asterisk (*) and labeled 1, 2, 3, 4, and 5 (corresponding to the different positions of the sample). (B) Stress–strain curve of the experiment. These three measurements correspond to three separate samples. (C) Corresponding changes in the luminescence profile. The spectra were collected from points (*) illustrated in (A).

both Hb and Mb is the same; however, the size of Hb is larger than that of Mb. Although this interaction is initiated through opposite charges, Hb failed to produce the regularly stacked structure due to larger size. In our case, the hydrodynamic size of Au_{30} @BSA is only 6 nm (shown in Figure S2). This size is small enough to be accommodated between the clay sheets, and thus, a regular hierarchical structure could be formed in this case.

The attachment of the clusters to aminoclay sheets and subsequent formation of larger ordered aggregates was probed by time-dependent DLS measurements. A systematic increase in the hydrodynamic diameter of the aggregates in the reaction mixture with time is shown in Figure 4A. This points to the fact that the cluster-attached aminoclay sheets stacked together to form larger structures in solution as the reaction progressed. These subsequently act as the nucleation sites for the new cluster-attached aminoclay sheets for deposition and micrometer-sized aggregates started to form (shown in the inset of Figure 4A), making the solution turbid. These ultimately come together during drying to form highly ordered hierarchical structures.

Stress–Strain Behavior of CCH. Cluster-sandwiched clay materials were cast in different shapes, such as film, dog bone, and so forth, to study their mechanical properties. During casting of the sample, PVA was added to the mixture. Since the clusters are already intercalated with CCH, the addition of PVA is not expected to alter the interlayer spacing. The layered structure of CCH was retained, as shown in Figure S5. Although the polymer and clay interaction is not new in the

literature,^{41,42} this composition is completely new, where PVA acts as a binder for our hybrid material. To study the stress–strain behavior, we have performed tensile strength measurements. This material showed highly ductile behavior after mixing with PVA (6 weight %). It could stretch up to 300% without failure (Figure S6).

For a systematic understanding of the mechanical property of the material, tensile strength experiments were conducted under the displacement control mode. This was performed in such a way that the final elongation of the sample was 80, 140, and 250% of the original sample length. A schematic representation of the experiment is shown in Figure 5A. The corresponding stress-strain curves are shown in Figure 5B, respectively. Interestingly, the change in the luminescence of the material was observed upon elongation, and a new luminescence peak at 575 nm emerged along with the peak of cluster luminescence at 650 nm. Here, the luminescence spectra were measured immediately after the tensile strength experiments, using 365 nm excitation. The intensity of the 575 nm peak (with respect to the 650 nm peak) was dependent on the degree of elongation of the sample. The luminescence spectra collected from different locations (1, 2, 3, 4, and 5) of the dog bone-shaped material after 80, 140, and 250% elongation are shown in Figure 5C. Intensity of the 575 nm peak increases with the degree of elongation of the sample. The change in the luminescence spectrum was not uniform throughout the length of the sample. The intensity of the 575 nm peak was maximum at the center, that is, at position 1, and minimum at the edges, that is, at positions 4 and 5. Positions 3

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Figure 6. Characterization and application of nanofibers made from CCH. (A,B) FESEM image of an electrospun cluster-based clay material, in different magnifications. (C) TEM image of the fiber. (D) Dark field image of a single fiber showing the red luminescence (i). Inset shows bright field image of a single fiber (ii), and same image is shown in the gray scale (iii). (E) Writing experiment on the electrospun mat (see the inset) shows white light emission from the luminescent mat under UV light. Mechanochromic luminescence is shown by drawing the grid pattern on the luminescent mat with the tip of the cotton swab. The same effect is shown on another mat by writing "a" in a similar fashion (see the inset). White light emission was seen from the red luminescent mat under UV light in both cases. The UV light source of 365 nm excitation was used to visualize the luminescent pattern.

and 4 showed intermediate intensity. With regard to the intensity of the 575 nm peak for different degrees of elongation, only a small hump was observed for 80% elongation. The same peak became more prominent for the sample stretched to 140% and at 250%, the intensity surpassed that at 650 nm. It is important to mention that the spectra collected from different points across the length of the sample prior to elongation showed only the 650 nm peak at comparable intensity (Figure S7). Upon elongation at 250%, the peak at 650 nm got split and at 600 nm, a shoulder peak was observed. The spectra did not show significant change with time, in the course of 1 week, suggesting that irreversible changes have happened to the composite.

Luminescence in noble metal NCs is perceived to originate due to ligand to metal charge transfer (LMCT). In Au₃₀@BSA, the Au core is protected by cysteine residues of the protein through the formation of Au-S bonds. The presence of these Au-S bonds was confirmed by the extended X-ray absorption fine structure experiment in an earlier report.⁴³ In CCH, the cluster layer is sandwiched between two aminoclay layers. Stretching of the sample is likely to perturb the structure of the confined proteins. These, in turn, would affect the Au-S bonds. Thus, small changes in the bond length of Au-S bonds or their relative orientations around the Au core can happen, which would perturb the electronic states of the cluster. This can bring about changes in the luminescence of the cluster. This is proposed as one of the possible reasons for the emergence of the peak at 575 nm. Under high pressures, red shifts of the absorption and the emission onset of the $Au_{21}(SR)_{12}(dppm)_2$ (SR = cyclohexanethiolate; dppm = bisdiphenylphosphinemethane) and Au₂₈(S-TBBT)₂₀ (S-TBBT = tert-butyl-benzenethiolate) NCs were shown in a recent report.⁴⁴ This red shift is due to the narrowing of the energy levels of NCs because of the delocalization of the core electrons to the ligands under compression. These highpressure experiments were carried out in a diamond anvil cell, and the effects of compression on clusters were monitored in

situ using the changes in the optical properties. In our studies, a blue-shifted peak was observed under elongation. This new report supports our observation that the change in luminescence of CCH upon stretching originates from the alteration of the cluster structure, which cannot go back to a relaxed state due to its confinement within the aminoclay sheets. The change in the peak width in the newly originated peak was also observed. This may be due to the reason that all the clusters have not undergone the same amount of the structural change at the same percentage of strain.

Application of Mechanochromic Luminescence. The change in the luminescence spectrum of the confined sandwiched cluster upon application of mechanical forces is the first of this kind in the literature of such clusters. Some gold complexes are known to show mechanoresponses.^{45,46} Disruption of an ordered structure could lead to changes in photoluminescence. Organoboron materials showed solid-state mechanochromic luminescence.^{47,48}

These clusters have long been utilized as chemical sensors to sense analytes such as toxic metal ions (such as Hg^{2+} and Pb^{2+}), explosives (such as 2,4,6-trinitrotoluene and 1,3,5-trinitroperhydro-1,3,5-triazine), and small molecules (such as dopamine, halocarbons, etc.).^{49,50} In these cases, analytes interact with the cluster chemically and thus quench the luminescence. In order to utilize the newly found mechanochromic luminescence of the clusters in CCH, we proceeded to make large-area electrospun mats incorporating the composites. The reason for choosing the nanofiber mat was to have 1D geometry, which is known to have enhanced the performance due to their large surface-to-volume ratio.⁵¹ Electrospun mats of luminescence cluster-coated polymers have been shown to enhance sensitivity toward analytes.^{50,52}

Electrospun mats were created using the same composite material used for mechanical studies. This mat exhibited bright red luminescence, indicating intactness of the confined clusters (shown in Figure S8). After the electrospining process, the morphology of the fibers in the electrospun mat was studied in detail through microscopy. Uniform fibers were clearly seen in FESEM images (Figure 6A,B) at different magnifications, constituting the mat. Similar observations regarding the dimension of the fibers were also obtained from the TEM images (Figure 6C). The luminescence property of a single fiber was measured through fluorescence microscopy. The image showing a red luminescent fiber is shown in Figure 6D. The corresponding optical image is shown in the inset of Figure 6D. Pressure-sensitive nature of the incorporated fiber mat was examined by a writing experiment using a cotton swab. The areas where pressure was exerted during this writing experiment appeared white when exposed to UV light, while rest of the mat retained red luminescence (Figure 6E). Such a change in the luminescence in response to mechanical forces can be used as a security feature for devices.

SUMMARY AND CONCLUSIONS

In conclusion, protein-protected noble metal clusters were intercalated between the layers of aminoclay sheets to create a luminescent hierarchical organo-inorganic hybrid material. Coulombic interactions between these two species helped them to assemble and to create a higher order, insoluble structural material. FESEM studies proved the layered structure of CCH, and intercalation of the luminescent clusters between these clay layers was proven by pXRD measurements. DLS and zeta potential measurements shed light on the mechanistic pathway of the formation of CCH. High ductility of the material was shown by tensile strength measurements. Structural distortion in the cluster-sandwiched material led to the emergence of a new emission peak. This new property could be utilized to create a cluster-based pressure sensor. The mechanochromic luminescence response of the composite could also be utilized for monitoring physical damage in structures.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c19239.

UV–vis spectrum, emission spectrum, DLS data of Au_{30} @BSA, pXRD data of aminoclay, stress–strain behavior of the dog bone sample, and luminescence spectra collected before the tensile strength experiment (PDF)

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Author Contributions

D.G. synthesized the cluster and CCH and designed and conducted all laboratory experiments. D.G. conducted spectroscopic and mass spectrometric experiments and wrote the draft of the manuscript. M.A.G. synthesized the aminoclay. N.M. performed the tensile strength experiments. P.G. supervised the tensile strength experiments. P.S. helped with the electrospinning experiments for making nanofibers. Microscopic measurements were conducted by A.S., P.S., S.B., A.C., and B.M. The whole project was supervised by T.P. The manuscript was written with contributions of all authors. **Notes**

The authors declare no competing financial interest.

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REFERENCES

(1) Chakraborty, I.; Pradeep, T. Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles. *Chem. Rev.* **2017**, *117*, 8208–8271.

(2) Xie, J.; Zheng, Y.; Ying, J. Y. Protein-Directed Synthesis of Highly Fluorescent Gold Nanoclusters. J. Am. Chem. Soc. 2009, 131, 888–889.

(3) Xavier, P. L.; Chaudhari, K.; Baksi, A.; Pradeep, T. Protein-Protected Luminescent Noble Metal Quantum Clusters: An Emerging Trend in Atomic Cluster Nanoscience. *Nano Rev.* **2012**, *3*, 14767– 14782.

(4) Ghosh, D.; Baksi, A.; Mudedla, S. K.; Nag, A.; Ganayee, M. A.; Subramanian, V.; Pradeep, T. Gold-Induced Unfolding of Lysozyme: Toward the Formation of Luminescent Clusters. *J. Phys. Chem. C* **2017**, *121*, 13335–13344. (5) Kang, X.; Zhu, M. Tailoring the Photoluminescence of Atomically Precise Nanoclusters. *Chem. Soc. Rev.* **2019**, *48*, 2422–2457.

(6) Goswami, N.; Zheng, K.; Xie, J. Bio-NCs - The Marriage of Ultrasmall Metal Nanoclusters with Biomolecules. *Nanoscale* **2014**, *6*, 13328–13347.

(7) Weiss, A. Secret of Chinese Porcelains. *Angew. Chem.* **1963**, *75*, 755–762.

(8) Sposito, G.; Skipper, N. T.; Sutton, R.; Park, S.-H.; Soper, A. K.; Greathouse, J. A. Surface Geochemistry of the Clay Minerals. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 3358–3364.

(9) Sanchez, C.; Belleville, P.; Popall, M.; Nicole, L. Applications of Advanced Hybrid Organic-Inorganic Nanomaterials: From Laboratory to Market. *Chem. Soc. Rev.* **2011**, *40*, 696–753.

(10) Scheuermann, G. M.; Thomann, R.; Mülhaupt, R. Catalysts Based Upon Organoclay with Tunable Polarity and Dispersion Behavior: New Catalysts for Hydrogenation, C-C Coupling Reactions and Fluorous Biphase Catalysis. *Catal. Lett.* **2009**, *132*, 355–362.

(11) Balazs, A. C.; Emrick, T.; Russell, T. P. Nanoparticle Polymer Composites: Where Two Small Worlds Meet. *Science* **2006**, *314*, 1107–1110.

(12) Bonderer, L. J.; Studart, A. R.; Gauckler, L. J. Bioinspired Design and Assembly of Platelet Reinforced Polymer Films. *Science* **2008**, *319*, 1069–1073.

(13) Hsu, R.-S.; Chang, W.-H.; Lin, J.-J. Nanohybrids of Magnetic Iron-Oxide Particles in Hydrophobic Organoclays for Oil Recovery. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1349–1354.

(14) Viseras, C.; Cerezo, P.; Sanchez, R.; Salcedo, I.; Aguzzi, C. Current Challenges in Clay Minerals for Drug Delivery. *Appl. Clay Sci.* **2010**, *48*, 291–295.

(15) Tzitzios, V.; Basina, G.; Bakandritsos, A.; Hadjipanayis, C. G.; Mao, H.; Niarchos, D.; Hadjipanayis, G. C.; Tucek, J.; Zboril, R. Immobilization of Magnetic Iron Oxide Nanoparticles on Laponite Discs -An Easy Way to Biocompatible Ferrofluids and Ferrogels. *J. Mater. Chem.* **2010**, *20*, 5418–5428.

(16) Whilton, N. T.; Burkett, S. L.; Mann, S. Hybrid Lamellar Nanocomposites Based on Organically Functionalized Magnesium Phyllosilicate Clays with Interlayer Reactivity. *J. Mater. Chem.* **1998**, *8*, 1927–1932.

(17) Mann, S.; Burkett, S. L.; Davis, S. A.; Fowler, C. E.; Mendelson, N. H.; Sims, S. D.; Walsh, D.; Whilton, N. T. Sol-Gel Synthesis of Organized Matter. *Chem. Mater.* **1997**, *9*, 2300–2310.

(18) Burkett, S. L.; Press, A.; Mann, S. Synthesis, Characterization, and Reactivity of Layered Inorganic-Organic Nanocomposites Based on 2:1 Trioctahedral Phyllosilicates. *Chem. Mater.* **1997**, *9*, 1071–1073.

(19) Bromley, K. M.; Patil, A. J.; Seddon, A. M.; Booth, P.; Mann, S. Bio-Functional Mesolamellar Nanocomposites Based on Inorganic/ Polymer Intercalation in Purple Membrane (Bacteriorhodopsin) Films. *Adv. Mater.* **2007**, *19*, 2433–2438.

(20) Datta, K. K. R.; Achari, A.; Eswaramoorthy, M. Aminoclay: A Functional Layered Material with Multifaceted Applications. *J. Mater. Chem. A* **2013**, *1*, 6707–6718.

(21) Patil, A. J.; Li, M.; Dujardin, E.; Mann, S. Novel Bioinorganic Nanostructures Based on Mesolamellar Intercalation or Single-Molecule Wrapping of DNA Using Organoclay Building Blocks. *Nano Lett.* **2007**, *7*, 2660–2665.

(22) Mann, S. Self-assembly and Transformation of Hybrid Nano-Objects and Nanostructures under Equilibrium and Non-equilibrium Conditions. *Nat. Mater.* **2009**, *8*, 781–792.

(23) Wegst, U. G. K.; Bai, H.; Saiz, E.; Tomsia, A. P.; Ritchie, R. O. Bioinspired Structural Materials. *Nat. Mater.* **2015**, *14*, 23–36.

(24) Sellinger, A.; Weiss, P. M.; Nguyen, A.; Lu, Y.; Assink, R. A.; Gong, W.; Brinker, C. J. Continuous Self-Assembly of Organic-Inorganic Nanocomposite Coatings that Mimic Nacre. *Nature* **1998**, *394*, 256–260.

(25) Mayer, G. Rigid Biological Systems as Models for Synthetic Composites. *Science* **2005**, *310*, 1144–1147.

(26) Munch, E.; Launey, M. E.; Alsem, D. H.; Saiz, E.; Tomsia, A. P.; Ritchie, R. O. Tough, Bio-Inspired Hybrid Materials. *Science* **2008**, 322, 1516–1520.

(27) Das, P.; Malho, J.-M.; Rahimi, K.; Schacher, F. H.; Wang, B.; Demco, D. E.; Walther, A. Nacre-Mimetics with Synthetic Nanoclays

up to Ultrahigh Aspect Ratios. *Nat. Commun.* **2015**, *6*, 5967–5980. (28) Luz, G. M.; Mano, J. F. Biomimetic Design of Materials and Biomaterials Inspired by the Structure of Nacre. *Philos. Trans. R. Soc., A* **2009**, 367, 1587–1605.

(29) Liu, Y.; Yu, S.-H.; Bergström, L. Transparent and Flexible Nacre-Like Hybrid Films of Aminoclays and Carboxylated Cellulose Nanofibrils. *Adv. Funct. Mater.* **2018**, *28*, 1703277–1703285.

(30) Kakisawa, H.; Sumitomo, T. The Toughening Mechanism of Nacre and Structural Materials Inspired by Nacre. *Sci. Technol. Adv. Mater.* **2011**, *12*, 064710–064714.

(31) Gerhard, E. M.; Wang, W.; Li, C.; Guo, J.; Ozbolat, I. T.; Rahn, K. M.; Armstrong, A. D.; Xia, J.; Qian, G.; Yang, J. Design Strategies and Applications of Nacre-Based Biomaterials. *Acta Biomater.* **2017**, *54*, 21–34.

(32) Deville, S.; Saiz, E.; Nalla, R. K.; Tomsia, A. P. Freezing as a Path to Build Complex Composites. *Science* **2006**, *311*, 515–518.

(33) Mao, L.-B.; Gao, H.-L.; Yao, H.-B.; Liu, L.; Colfen, H.; Liu, G.; Chen, S.-M.; Li, S.-K.; Yan, Y.-X.; Liu, Y.-Y.; Yu, S.-H. Synthetic Nacre by Predesigned Matrix-Directed Mineralization. *Science* **2016**, *354*, 107–110.

(34) Patil, A. J.; Mann, S. Self-Assembly of Bio-Inorganic Nanohybrids using Organoclay Building Blocks. J. Mater. Chem. 2008, 18, 4605–4615.

(35) Martin, J. E.; Patil, A. J.; Butler, M. F.; Mann, S. Guest-Molecule-Directed Assembly of Mesostructured Nanocomposite Polymer/Organoclay Hydrogels. *Adv. Funct. Mater.* **2011**, *21*, 674–681.

(36) Patil, A. J.; Muthusamy, E.; Seddon, A. M.; Mann, S. Higher-Order Synthesis of Organoclay Pipes using Self-Assembled Lipid Templates. *Adv. Mater.* **2003**, *15*, 1816–1819.

(37) Lin, L.; Liu, M.; Chen, L.; Chen, P.; Ma, J.; Han, D.; Jiang, L. Bio-Inspired Hierarchical Macromolecule-Nanoclay Hydrogels for Robust Underwater Superoleophobicity. *Adv. Mater.* **2010**, *22*, 4826–4830.

(38) Patil, A. J.; Li, M.; Mann, S. Integrative Self-Assembly of Functional Hybrid Nanoconstructs by Inorganic Wrapping of Single Biomolecules, Biomolecule Arrays and Organic Supramolecular Assemblies. *Nanoscale* **2013**, *5*, 7161–7174.

(39) Patil, A. J.; Muthusamy, E.; Mann, S. Fabrication of Functional Protein-Organoclay Lamellar Nanocomposites by Biomolecule-Induced Assembly of Exfoliated Aminopropyl-Functionalized Magnesium Phyllosilicates. J. Mater. Chem. **2005**, *15*, 3838–3843.

(40) Ghosh, D.; Bodiuzzaman, M.; Som, A.; Raja, S.; Baksi, A.; Ghosh, A.; Ghosh, J.; Ganesh, A.; Samji, P.; Mahalingam, S.; Karunagaran, D.; Pradeep, T. Internalization of a Preformed Atomically Precise Silver Cluster in Proteins by Multistep Events and Emergence of Luminescent Counterparts Retaining Bioactivity. *J. Phys. Chem. C* **2019**, *123*, 29408–29417.

(41) Johnsy, G.; Datta, K. K. R.; Sajeevkumar, V. A.; Sabapathy, S. N.; Bawa, A. S.; Eswaramoorthy, M. Aminoclay: A Designer Filler for the Synthesis of Highly Ductile Polymer-Nanocomposite Film. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2796–2803.

(42) Verho, T.; Karppinen, P.; Gröschel, A. H.; Ikkala, O. Imaging Inelastic Fracture Processes in Biomimetic Nanocomposites and Nacre by Laser Speckle for Better Toughness. *Adv. Sci.* 2018, *5*, 1700635.

(43) Chevrier, D. M.; Thanthirige, V. D.; Luo, Z.; Driscoll, S.; Cho, P.; MacDonald, M. A.; Yao, Q.; Guda, R.; Xie, J.; Johnson, E. R.; Chatt, A.; Zheng, N.; Zhang, P. Structure and Formation of Highly Luminescent Protein-Stabilized Gold Clusters. *Chem. Sci.* **2018**, *9*, 2782–2790.

(44) Li, Q.; Mosquera, M. A.; Jones, L. O.; Parakh, A.; Chai, J.; Jin, R.; Schatz, G. C.; Gu, X. W. Pressure-Induced Optical Transitions in Metal Nanoclusters. *ACS Nano* **2020**, *14*, 11888–11896.

(45) Lee, Y.-A.; Eisenberg, R. Luminescence Tribochromism and Bright Emission in Gold(I) Thiouracilate Complexes. J. Am. Chem. Soc. 2003, 125, 7778–7779.

(46) Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A. A.; Patterson, H. H.; Staples, R. J.; Fackler, J. P., Jr. Syntheses, Structure, and Photoluminescence Properties of the 1-Dimensional Chain Compounds [(TPA)2Au][Au(CN)2] and (TPA)AuCl (TPA = 1,3,5-Triaza-7-phosphaadamantane). *Inorg. Chem.* **2002**, *41*, 6274–6280.

(47) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. Polymorphism and Reversible Mechanochromic Luminescence for Solid-State Difluoroboron Avobenzone. J. Am. Chem. Soc. **2010**, 132, 2160–2162.

(48) Sun, X.; Zhang, X.; Li, X.; Liu, S.; Zhang, G. A Mechanistic Investigation of Mechanochromic Luminescent Organoboron Materials. *J. Mater. Chem.* **2012**, *22*, 17332–17339.

(49) Mathew, A.; Sajanlal, P. R.; Pradeep, T. Selective Visual Detection of TNT at the Sub-Zeptomole Level. *Angew. Chem., Int. Ed.* **2012**, *51*, 9596–9600.

(50) Ghosh, A.; Jeseentharani, V.; Ganayee, M. A.; Hemalatha, R. G.; Chaudhari, K.; Vijayan, C.; Pradeep, T. Approaching Sensitivity of Tens of Ions Using Atomically Precise Cluster-Nanofiber Composites. *Anal. Chem.* **2014**, *86*, 10996–11001.

(51) Ling, S.; Qin, Z.; Huang, W.; Cao, S.; Kaplan, D. L.; Buehler, M. J. Design and Function of Biomimetic Multilayer Water Purification Membranes. *Sci. Adv.* **201**7, *3*, No. e1601939.

(52) Subramanian, V.; Jena, S.; Ghosh, D.; Jash, M.; Baksi, A.; Ray, D.; Pradeep, T. Dual Probe Sensors Using Atomically Precise Noble Metal Clusters. *ACS Omega* **2017**, *2*, 7576–7583.