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Article in *Science Bulletin* · March 2020

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Perspective

Mechanoluminescence materials for advanced artificial skin

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Mechanoluminescence (ML) materials that convert the external mechanical energy into light emission without the assistance of electron or photon excitation have been emerging because of their promising application in infrastructure health monitoring, information safety, novel light sources and displays, energy harvesting, aerospace engineering, soft electronics, smart robotics, the Internet of Things, and biomedicine [1]. The documented record of ML can be retrospect to 1605, Francis Bacon described mechanically-induced light emission during the scraping of the hard sugar with a knife “sugar shineth only while in scraping” in his celebrated work on “Of the proficience and advancement of learning, divine and human” [2], while the ML observed from the striking stone or quartz by the primitive man may have been a million years. To date, a myriad of ML materials covering conductor, semiconductor and insulator have been discovered or synthesized, especially after the development of photomultiplier tube in the mid-20th century, with a conservative estimation of half of inorganic crystals and third of organic compounds harboring ML [3]. ML can be categorized into deformation luminescence and triboluminescence according to the physical process involved in inducing luminescence. The former is ascribed to the deformation of the ML materials themselves, whereas, the latter is assigned to the triboelectricity, tribochemical reactions, and tribothermalization generated by the contact and separation of two dissimilar materials. Deformation luminescence can be further classified into elastico-mechanoluminescence (EML), plastico-mechanoluminescence, and fracto-mechanoluminescence depending on the deformation threshold involved in materials for the light emission. EML materials perform the reproducible emission within the elastic deformation, avoiding the respective plastic deformation and destructive fracture of the plastico-mechanoluminescence and fracto-mechanoluminescence materials, as well as the limitation of the tribological conditions, environment and materials during the triboluminescence, are particularly preferred for the diverse applications.

EML is typically observed in the irradiated compounds such as χ - or γ -irradiated alkali halides and the ions-doped inorganics such as aluminates, silicates, gallates, and titanates, among which

strontium aluminate (SrAl_2O_4) doped with luminescent lanthanide ions ($\text{Eu}^{2+}/\text{Dy}^{3+}$, $\text{Er}^{3+}/\text{Eu}^{2+}$, Nd^{3+} , etc.) and zinc sulfate based semiconductors including $\text{ZnS:Mn}^{2+}/\text{Cu}^{+2+}/\text{Mn}^{2+}$, Cu^{+2+} and $\text{CaZnOS:Mn}^{2+}/\text{Ln}^{3+}$ ($\text{Ln}^{3+} = \text{Tb}^{3+}$, Eu^{3+} , Pr^{3+} , Sm^{3+} , Er^{3+} , Dy^{3+} , Ho^{3+} , Nd^{3+} , Tm^{3+} , and Yb^{3+}) represent the perspective candidates for the real-world applications due to their relatively durable and high brightness of few hundreds of candelas per square meter over many thousands of cycles [4–6]. The lanthanides doped SrAl_2O_4 has an appreciable initial brightness, while the ML intensity attenuates gradually during cycles of deformation, whereby the recovery of ML performance needs exposure of the materials to an ultraviolet radiation at the end of each deformation cycle. Whereas, ZnS performs a self-recovery ML manner without any additional stimuli, possibly enabled by the drifting current within the ZnS semiconductor due to its higher conductivity compared to the SrAl_2O_4 dielectric [2]. Despite much attraction, efficient ML emission of ZnS materials is generally restricted to Mn and Cu activators. The CaZnOS ML materials can achieve multiple colors ranging from ultraviolet, visible, to infrared because of the diversity of the available dopants enabled by the lithium-assisted annealing process [4]. In this respect of novel EML materials, the recent advances of artificial intelligence with the integration of high-throughput virtual screening, automated synthesis planning, automated laboratories and machine learning algorithms alleviate the clash that often happens between theory and experiment, and thus accelerate the discovery and development of new class of EML materials [7].

The approach employed currently for the preparation of ML materials is dominated by the high-temperature solid-state reaction, in which the component oxides or salts are calcined at a temperature of over 1000 °C under high vacuum or certain atmosphere. The resultant materials are usually bulk and adamant, and therefore a grinding process is necessary for the final ML powders. Unfortunately, the ML powders obtained by the grinding process have a wide size distribution ranging from sub-micrometer to tens of micrometer and irregular morphology, impeding their practical applications, for example, in high-resolution displays or bioimaging. Solvothermal synthesis is expected to provide a solution to this problem due to its dexterity in control of the size, morphology, component, dopant, and structure of the products. The ZnS:Ag^+ , Co^{2+} @ZnS core-shell ML nanoparticles with uniform size and morphology synthesized via the solvothermal method are

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demonstrated recently, in which the undoped ZnS shell enables a 9.2-fold increase of ML compared to the original ZnS:Ag⁺, Co²⁺ by inhibiting the luminescence quenching effect caused by the solvent or ligand molecules, endowing the minimally invasive optogenetic activation when triggered by the focused ultrasound (Fig. 1a) [8]. This work also encourages the attempts to ML materials with customized luminescence properties such as color, intensity, and multistimuli-response by adjusting the component, thickness, number, and permutation of the shell layer. Most importantly, the solvothermal synthesis promise the versatile morphology of ML materials such as 0D quantum dot, 1D nanowire/nanobelt/nanorod/nanotube, 2D nanoplate/nanofilm, and 3D complexes such as helix and tetra-needle whisker. Very recently, a series of metal sulfide nanorods with multicomponent heterostructures are demonstrated by conjunction of solvothermal approach and cation-exchange reaction (Fig. 1b) [9], inspiring the preparation of 1D ML heterojunction nanomaterials, as far as we know, that have been not reported before. The 1D morphology is expected to boost the ML intensity because of the preferential piezoelectric orientation and contribute to the understanding of ML mechanism by inspecting the ML anisotropy and dynamic ML of 1D ML nanomaterials. Moreover, the heterojunction within ML materials is expected to promote the carrier transfer and recombination and thus the enhanced ML intensity.

In the majority of use cases, ML materials are blended to polymer matrix (PDMS, Ecoflex, resin, etc.) and then coated on the target structures, undermining their potential to high-end applications where the complicated and fine characteristic feature is required. Recent advances in the implementation of multimaterial multinozzle 3D printing offer the potential to construct the complex ML architectures with high precision (250 μm for the single filament), in which the composition, function and structure of the printed objects are spatially programmed at the voxel scale (Fig. 1c) [10]. However, the polymer matrix with the suitable

transparency, viscoelasticity, printability window and compatibility to ML materials needs to be designed for the well-applied printing technique.

The straightforward application of EML materials is as the optical tactile sensors for the advanced artificial skin because of the linear dependence of ML intensity on the amplitude of the applied stress within the range of elastic deformation. Compared to tactile sensors enabled by the electrical principles, such as piezoelectric, piezoresistive, capacitive, and triboelectric [11], the optical tactile sensors based on EML materials are self-powered and immune to electromagnetic interference, stray capacitances, thermal noise, and wire-bonding complexity associated with the electrical devices, and endow the real-time, long-distance, and visual sensing of pressure distribution [12]. A representative example is the photonic skin composed of ZnS:Mn²⁺/Cu²⁺@Al₂O₃ ML microparticles, PDMS matrix, and SiO₂ nanoparticles (Fig. 2), in which the SiO₂ nanoparticles are adopted to adjust the elasticity modulus of the PDMS and thus the concentration of stress to ZnS:Mn²⁺/Cu²⁺@Al₂O₃ microparticles, enabling the intense ML under weak stimuli of the moving skin [13]. In spite of these advances, the EML sensors suffer from low sensitivity with a sensing limitation of kPa magnitude and limited spatial resolution due to the poor response to tiny stress and the big size of the EML particles, respectively, which are expected to be solved by the integration of EML materials with the switch devices such as field effect transistor [14], or by the synthesis of the high-performance EML nanowire array with determined spatial resolution. On the other hand, the output signal of the EML sensors is the dynamic light, and therefore a physical presentation is required during the pressure event. This issue can be addressed by the synthesis of novel ML materials with persistent luminescence or memory capability [15] achieved by the designed trap depth and distribution. Finally, the biocompatibility of ML materials afforded by the utilization of biocompatible dopants and host materials or the suitable surface modification is of paramount

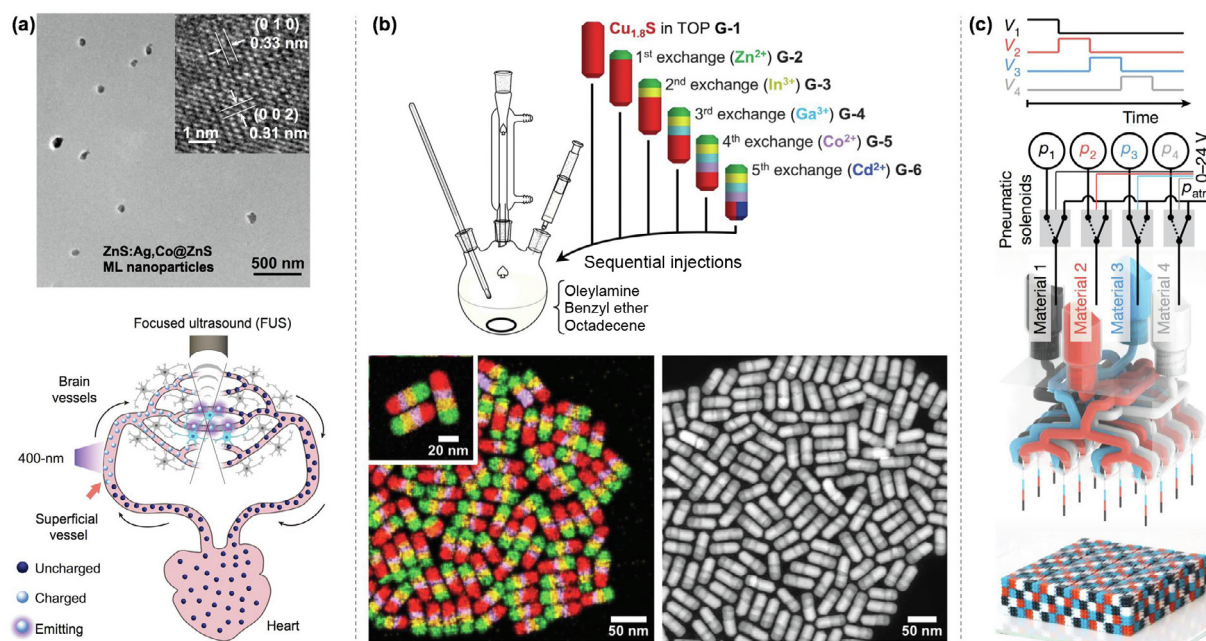


Fig. 1. (Color online) The novel approach for the synthesis and architecture assembly of ML materials. (a) ZnS:Ag, Co@ZnS core-shell mechanoluminescence nanoparticles synthesized via the solvothermal method for the minimally invasive optogenetic activation when triggered by the focused ultrasound. Reprinted with permission from Ref. [8], Copyright © 2019 National Academy of Sciences. (b) The metal sulfide nanorods with multicomponent heterostructures prepared by conjunction of solvothermal approach and cation-exchange reaction, promising the preparation of 1D mechanoluminescence heterojunction nanomaterials. Reprinted with permission from Ref. [9], Copyright © 2020 AAAS. (c) Recent advances in the implementation of multimaterial multinozzle 3D printing offers the potential to construct the complex mechanoluminescence architectures with high precision, in which the composition, function and structure of the printed objects can be spatially programmed at the voxel scale. Reprinted with permission from Ref. [10], Copyright © 2019 Springer Nature.

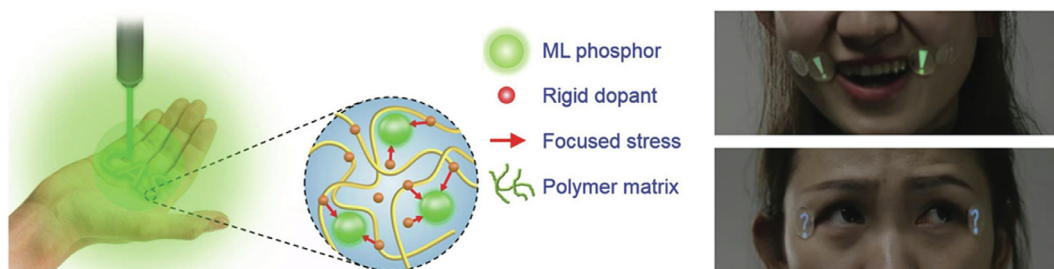


Fig. 2. Mechanoluminescence materials for the artificial skin. The ML device composed of $\text{ZnS:Mn}^{2+}/\text{Cu}^{2+}@ \text{Al}_2\text{O}_3$ ML microparticles, PDMS matrix, and SiO_2 nanoparticles for the photonic skin, in which the SiO_2 nanoparticles are adopted to adjust the elasticity modulus of the PDMS and thus the concentration of stress to $\text{ZnS:Mn}^{2+}/\text{Cu}^{2+}@ \text{Al}_2\text{O}_3$ microparticles, enabling the intense ML under weak stimuli of the moving skin. Reprinted with permission from Ref. [13], Copyright © 2018 Wiley-VCH.

importance for the practical application of the constructed artificial skin.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2016YFA0202703), the National Natural Science Foundation of China (61675027, 51622205, 51432005, 61505010, and 61875136), Beijing City Committee of Science and Technology (Z171100002017019, Z181100004418004), Beijing Natural Science Foundation (4181004, 4182080, 4184110, 2184131, and Z180011), and Shenzhen Fundamental Research Project (JCYJ20190808170601664), and Guangdong Natural Science Foundation (2020A1515011315).

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