

Piezo-photonics: from fundamentals, materials to applications

Jianhua Hao

Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, P. R.
China

jh.hao@polyu.edu.hk

Chao-Nan Xu

National Institute of Advanced Industrial Science and Technology (AIST), Saga 841-0052, Japan

Department of Molecular and Material Science, Kyushu University, Fukuoka 816-8580, Japan

cn-xu@aist.go.jp

Abstract

The piezo-photonic effect is the coupling between piezoelectric properties and photoexcitation, where the strain-induced piezopotential modulates/controls the relevant optical process. Specifically, metal ions as activators are capable of responding to the photoexcitation properties and subsequently emitting light as also called mechanoluminescence in general and piezoluminescence especially for piezoelectrics. Such phenomena are very helpful for our understanding the fundamentals of materials and conceiving widespread device applications. In this article, we will briefly introduce physical mechanisms of piezo-photonics including piezoluminescence. Some host materials and metal-ion activators will be described for demonstrating piezo-photonic effect. We will provide a unified profile and recent prototypical demonstrations of light-emission triggered by various mechanical stimuli. The devices based on these materials offer the advantages of remote detection, nondestructive analysis and repeatability, hence they are promising candidates for applications in stress sensing, structural health diagnosis, 3D handwriting, magnetic-optical sensor, energy harvester, biomedicine, novel light source and display.

Keywords: piezoresponse; luminescence; optical properties

Introduction

Many emerging applications require advanced photonics and optoelectronics to be directly triggered and/or tuned by mechanical inputs from their environment. Some inorganic or organic materials exhibit light emission when an external mechanical stimulus is applied, termed as mechanoluminescence (ML). Xu firstly reported intense and reproducible luminescence during exposure of certain material to mechanical stimuli including ZnS:Mn^{2+} and $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, and introduced the principles and applications of hybrid inorganic/organic composites and related sensors or sensitive artificial skin^{1,2}. Wang introduced the field of piezo-photonics in semiconductors, which regarded as a two-way coupling of piezoelectric-photoexcitation.^{3,4} Therefore, metal ions as activators in ML may serve for demonstrating piezo-photonic effect since they are capable of responding to photoexcitation properties and subsequently emitting light.

It is known that luminescence is a phenomenon in which the excitation energy of a substance excited by external energy is given off as photon, resulting in the form of light emission. One may classify luminescence according to the excitation sources. Typically, photoluminescence (PL) is stimulated by photon energy while electroluminescence (EL) is by triggered by electric field, and so on. The PL and EL based materials are extensively applied to display system, light-emitting diode (LED), solid-state lighting and biomedicine.^{5,6} The most useful form of ML is elasticoluminescence (ESL) developed by Xu's group, also called piezoluminescence for piezoelectric material has attracted considerable attention because it can be repeatedly used for mechano-optical conversion. ESL materials and devices offer the advantages of wireless detection and nondestructive analysis, making it a promising candidate for various applications, such as stress sensing and damage diagnosis.⁷⁻¹² Here, we will first introduce the physical mechanisms of piezo-photonics, followed by the relevant materials considerations and processing. We will review the development of recent prototypical demonstrations and applications. Finally, a brief summary and perspective on the piezo-photonics will be outlined.

Fundamental principle and materials considerations

Piezo-photonic effect is a two-way coupling between piezoelectricity and photoexcitation properties as shown in **Figure 1a**.¹³ The piezo-photonic effect is to use the piezopotential to tune the energy band, carrier detrapp and recombination, and hence induce photon process, such as light

emission. Apart from the two-way coupling effect, the coupling between other external stimuli and piezophotonic effect may lead to more physical effects. As an example, magnetic-induced luminescence (MIL) as shown in Figure 1a can be observed via strain-mediated coupling, which will be described in subsequent section. Figure 1b shows commonly used luminescent ions in a periodic table.⁵ In order to realize piezo-photonic effect, two classes of metal ions are mainly used as activators for piezophotonics, namely, lanthanide (Ln) ions and transition metal (TM) ions. The luminescence of Ln and TM ions doped phosphors can cover a broad optical spectral range, including UV, visible, and infrared regions.⁵ Ln ions, including Pr^{3+} , Sm^{3+} , co-doped Ce^{3+} and Ho^{3+} , and Eu^{2+} have been used in ESL phosphors.^{8,10, 14-16} Because of the larger spatial extension of the spectroscopically active *d* electrons, the energy level structures of TM ions are sensitive to their coordination environment associated with external perturbations, such as mechanical strain. Up to now, TM ions such as Mn^{2+} , Cu, and co-doped Mn^{2+} and Cu have been used by different groups.^{11,13,17-20} As a typical example of ZnS:Mn , the fundamental principle of the light emission under mechanical stress is shown in Figure 1c. The imposed stress gives rise to piezopotential in wurtzite-structured ZnS, which tilts the bands of ZnS. Then, the detrapped electrons at the defect states can escape to the conduction band, followed with the recombination of electrons and holes nonradiatively. The released energy excites the Mn^{2+} dopant ions, and photon emission occurs when the excited Mn^{2+} ions return to the ground state.^{20,21} Currently, luminescent metal ion-doped hosts have been fabricated in different forms, including crystal, powders, nanowires, nanoparticles and thin films. Figure 1d displays the ultrasonic-, impact-, tribo- and compress-luminescence of CaZnOS:Mn^{2+} polymer films under different kinds of stress excitation.¹¹ Hao's group developed a method of controllable piezoelectric-induced strain from $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}\text{O}_3$ (PMN-PT), which has firstly been used for piezo-photonics research field. With the novel technique, dual-mode emissions can be generated and modulated precisely (Figure 1e).¹⁷

Recent prototypical demonstrations and applications

Recently, there is a great trend to apply piezo-photonic materials to demonstrate interesting multifunctional applications. This section will briefly describe some latest research examples in this field. Generally, it is still difficult to predict and quantify the risk level for microstrains below 100 μst using conventional ESL materials. Therefore, it is important to develop novel materials

with thresholdless high sensitivity and quantify emission intensity for microstrains. Recently, Xu's group found the high-performance piezo multifunctional material that exhibits both piezoelectricity and efficient luminescence.¹⁰ The study was performed by doping lanthanide Pr^{3+} ions into the LiNbO_3 host. By precisely tuning the Li/Nb ratio in nonstoichiometric $\text{LiNbO}_3\text{:Pr}^{3+}$, a material that exhibits a high luminescence intensity. **Figure 2a** shows the light emission of the $\text{Li}_{1.00}\text{NbO}_3\text{:Pr}^{3+}$ sheet during tensile strain tests. Particularly, $\text{LiNbO}_3\text{:Pr}^{3+}$ shows excellent strain sensitivity at the lowest strain level, with no threshold for stress sensing. These multipiezo properties are very useful for multifunctional device applications. As aforementioned, it is interesting that piezoelectric PMN-PT actuator is utilized to produce piezopotential occurred in the materials and then demonstrate piezo-photonic effect. Further to the earlier study on proving piezo-photonic effect by this strategy,¹⁷ Hao's group further developed composite based hybrid devices and they are capable of sensing different types of external stimuli, including electric field, uniaxial strains of stretch and mechanical writing, and piezoelectric biaxial strain (Figure 2b).²² Furthermore, Zhang et al. recently presented addressable and color-tunable piezo-photonic light-emitting stripes by replacing PMN-PT crystal with piezoelectric films. Each actuator can be manipulated independently, offering an opportunity to control of the light emission in single pixel.²³ Interestingly, Pan's group demonstrated the pressure sensor matrix composed of the ZnS:Mn based polymer layers.^{20,24} Figure 2c shows the schematic of the pressure mapping process by piezo-photonic effect.²⁴ The dynamic pressure mapping device promises prospective applications in real-time pressure sensing and 3D handwriting.

Apart from the above stress-optical sensing, the relevant materials have been explored to apply in other emerging applications.²⁵ As shown in **Figure 3a**, Xu's group first attempted to use ML light source for a fluorescent probe molecule in bioimaging and phototherapy, even in the dark biotissues.²⁶ The light source induced by ultrasonic wave is also demonstrated for a photo-activation of TiO_2 photo catalyst.²⁷ Jeong et al report a wind-driven device which is capable of emitting warm/neutral/cool white light from Cu doped ZnS based composites.¹⁹ Such novel displays/lighting systems could pave the way to new environmentally friendly lights, which reduce energy waste and promote sustainability (Figure 3b). Compared to PL and EL, the realization of light-emission stimulated by magnetic field faces a great challenge and hence the phenomenon of intrinsic MIL is extremely rare. Hao's group firstly proposed a strategy to observe MIL by coupling magnetic effect to piezophotonic effect,^{13,28} as shown in Figure 1a. Most recently, remote and

temporal tuning of luminescence are also demonstrated, achieving proof-of-concept devices including tunable white-light and red-green-blue full-color displays, as shown in Figure 3c.²⁹

Conclusion

Piezo-photonics has attracted much attention because it may find broad applications in mechano-optical conversion, structural health diagnosis, nondestructive analysis, novel light sources and displays. By manipulating the strain and piezopotential of the composite phosphors, many devices could be conceived and made based on the principle of piezo-photonics. Despite encouraged progress, there are still many issues to be addressed. It is vital to investigate the effects of piezopotential on optical processes deeply. Although the coupling between piezoelectricity and photonexcitation in the existing materials promises device characteristics, it is essential to understand generalized energy conversion mechanism and then enhance energy gain in diverse systems.^{1,7,30} Considering their superior flexibility and mechanical strength, optical properties in new 2D piezo-optical materials are expected to become increasingly important in developing ultrathin and flexible devices.³¹⁻³⁵ Lastly, the experimental methods and protocols should be developed to suit for characterizing piezo-photon effect and quantifying the properties of relevant materials and device systems.

Acknowledgments

This work was supported by the grants to J.H. Hao from the Research Grants Council of Hong Kong (GRF No. PolyU 153281/16P) and NSFC (Grant No. 11474241), grants to C. N. Xu by JSPS (KAKENHI No. 25249100, JP16F16076 and JP17H06375).

References

1. C. N. Xu, T. Watanabe, M. Akiyama, X. G. Zheng, *Appl. Phys. Lett.*, **74**, 1236(1999), *ibid.*, **74**, 2414 (1999).
2. C. N. Xu, Coatings, in *Encyclopedia of Smart Materials*, edited by Schwartz M (Wiley, New York, USA, 2002), pp. 190-201.
3. Z. L. Wang, *Nano Today*, **5**, 540 (2010).
4. Z. L. Wang, *Piezotronics and Piezo-Phototronics* (Springer, 2013).
5. G. Bai, M.-K. Tsang, J. Hao, *Adv. Funct. Mater.* **26**, 6330 (2016).
6. G. Bai, M.-K. Tsang, J. Hao, *Adv. Opt. Mater.* **3**, 431 (2015).

7. H. Matsui, C. N. Xu, Y. Liu, H. Tateyama, *Phys. Rev. B*, **69**, 235109 (2004).
8. J. Botterman, K. V. Eeckhout, I. D. Baere, D. Poelman, P. F. Smet, *Acta Mater.* **60**, 5494 (2012).
9. Y. Sagara, T. Kato, *Nat. Chem.* **1**, 605 (2009).
10. D. Tu, C.-N. Xu, A. Yoshida, M. Fujihala, J. Hirotsu, X.-G. Zheng, *Adv. Mater.*, **29**, 1606914 (2017).
11. J. C. Zhang, C. N. Xu, S. Kamimura, Y. Terasawa, H. Yamada, X. Wang, *Opt. Express*, **21**, 12976 (2013).
12. J. Li, C.-N. Xu, D. Tu, X. Chai, X. Wang, L. Liu, E. Kawasaki, *Acta Mater.* **145**, 462 (2018).
13. M.-C. Wong, L. Chen, M.-K. Tsang, Y. Zhang, J. Hao, *Adv. Mater.* **27**, 4488 (2015).
14. S. Kamimura, H. Yamada, C.-N. Xu, *Appl. Phys. Lett.* **101**, 091113 (2012).
15. H. Zhang, H. Yamada, N. Terasaki, C.-N. Xu, *Appl. Phys. Lett.* **91**, 0819051 (2007).
16. Y. Liu, and C. N. Xu, *Appl. Phys. Lett.*, **84**, 5016 (2004).
17. Y. Zhang, G. Gao, H. L. W. Chan, J. Dai, Y. Wang, J. Hao, *Adv. Mater.* **24**, 1729 (2012).
18. D. Tu, C.N. Xu, Y. Fujio, A. Yoshida, *Light-Sci. & Applications*, **4**, e356 (2015).
19. S. M. Jeong, S. Song, K.-I. Joo, J. Kim, S.-H. Hwang, J. Jeong, H. Kim, *Energy Environ. Sci.*, **7**, 3338 (2014).
20. X. Wang, H. Zhang, R. Yu, L. Dong, D. Peng, A. Zhang, Y. Zhang, H. Liu, C. Pan, Z. L. Wang, *Adv. Mater.*, **27**, 2324 (2015).
21. Y. Zhang, W. Jie, P. Chen, W. Liu, J. Hao, *Adv. Mater.*, DOI: 10.1002/adma.201707007 (2018).
22. L. Chen, M.-C. Wong, G. Bai, W. Jie, J. Hao, *Nano Energy* **14**, 372 (2015).
23. Y. Chen, Y. Zhang, D. Karnaushenko, L. Chen, J. Hao, F. Ding, O. G. Schmidt, *Adv. Mater.* **29**, 1605165 (2017).
24. X. Wang, R. Ling, Y. Zhang, M. Que, Y. Peng, C. Pan, *Nano Research*, **11**, 1967 (2018).
25. D. Peng, B. Chen, F. Wang, *ChemPlusChem*, **80**, 1209 (2015).
26. N. Terasaki, H. W. Zhang, H. Yamada, C.N. Xu, *Chem. Commun.*, **47**, 8034 (2011).
27. N. Terasaki, H. Yamada, C.N. Xu, *Catal. Today*, **201**, 203 (2013).
28. O. Graydon, *Nat. Photonics*, **9**, 558 (2015).
29. M.-C. Wong, L. Chen, G. Bai, L.-B. Huang, J. Hao, *Adv. Mater.* **29**, 1701945 (2017).
30. B. Huang, M. Sun, D. Peng, *Nano Energy* **47**, 150 (2018).
31. G. Bai, S. Yuan, Y. Zhao, Z. Yang, S. Y. Choi, Y. Chai, S. F. Yu, S. P. Lau, J. Hao, *Adv. Mater.*, **28**, 7472 (2016).
32. Z. Yang, W. Jie, C.-H. Mak, S. Lin, H. Lin, X. Yang, F. Yan, S. P. Lau, J. Hao, *ACS Nano* **11**, 4225 (2017).
33. W. Jie, Z. Yang, G. Bai, J. Hao, *Adv. Opt. Mater.* **6**, 1701296 (2018).
34. W. Wu, L. Wang, R. Yu, Y. Liu, S. Wei, J. Hone, Z. L. Wang, *Adv. Mater.* **28**, 8463 (2016).
35. W. Wu, Z. L. Wang, *Nat. Rev. Mater.* **1**, 16031 (2016).

Figure Captions

Figure 1 (a) Schematic showing the coupling on the basis of piezo-photonics and magnetic-induced luminescence.¹³ (b) Metal-ions in piezo-photonics materials.⁵ (c) Energy diagram showing piezo-photonic effect initiated luminescence.²⁰ (d) Ultrasonic-, impact-, tribo- and compress-luminescence of CaZnOS:Mn²⁺ polymer films.¹¹ (e) PMN-PT used for piezophotonics to generate dual-mode emissions.¹⁷

Figure 2 (a) ML response of the LiNbO₃:Pr³⁺ sheet. The inset shows the ML response of the sheet in the strain range from 0 to 300 μst .⁹ (b) Composite phosphors and devices sensing different types of external stimuli.²² (c) Schematic of the pressure mapping process by piezo-photonic effect.²⁴

Figure 3 (a) ML light source for a fluorescent probe molecule in potential biological application.²⁶ (b) Wind-driven displays/lighting from ZnS:Cu based composites.¹⁹ (c) Full-color display by temporal and remote tuning of piezo-photonic-effect-induced color gamut from piezophosphor (ZnS: Al, Cu) coupled with other phosphors (YAG: Ce and (Ca_x,Sr_{1-x})S:Eu).²⁹

Author biographies

Jianhua Hao

Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, P. R. China. Email: jh.hao@polyu.edu.hk. Phone: (852) 27664098. Fax: (852)23337629



Prof. Hao obtained his B.Sc., M.Sc., and Ph.D. degrees at Huazhong University of Science and Technology. After working at Penn State, University of Guelph, and University of Hong Kong, he joined the faculty in the Hong Kong Polytechnic University (PolyU). He is currently a Professor and Associate Head of the Department of Applied Physics in PolyU. He has published more than 240 SCI papers. His research interests include metal-ion-doped luminescent materials, functional thin films and heterostructures, piezo-photonics and nano energy.

Chao-Nan Xu

National Institute of Advanced Industrial Science and Technology (AIST), Saga 841-0052, Japan. Email: cn-xu@aist.go.jp. Phone: (81) 942813660. Fax: (81) 942813696



Prof. Xu, received PhD 1991 from Kyushu University, now is Principle Research Manager, the leader of research team since 2001, adjunct Professor at Kyushu University since 2005, founding Chair of Mechanoluminescence Technology Consortium. She has innovated over 150 patents and published over 200 original papers. She pioneered the new field of mechanoluminescence and novel applications, has received numerous honors, including CerSJ Fellow Awards, Academic Prize on Ceramics, Distinguish Researcher of MEXT Minister Prize, Distinguished Innovation, Japan.

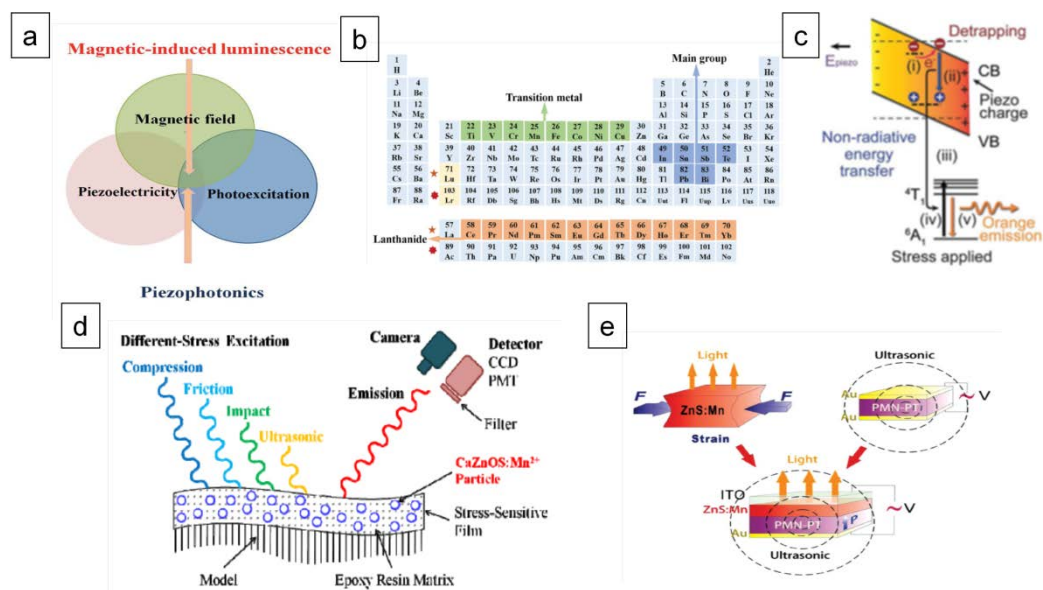


Fig.1

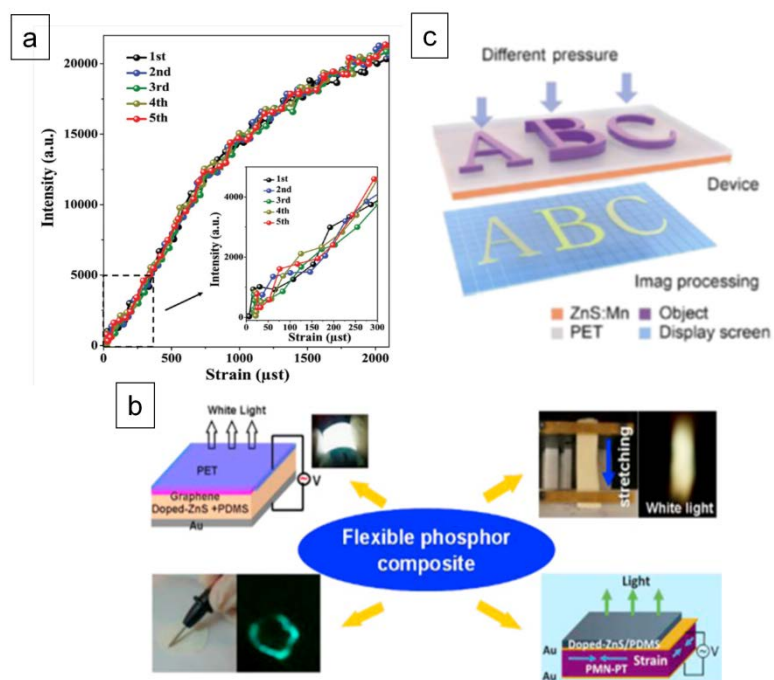


Fig.2

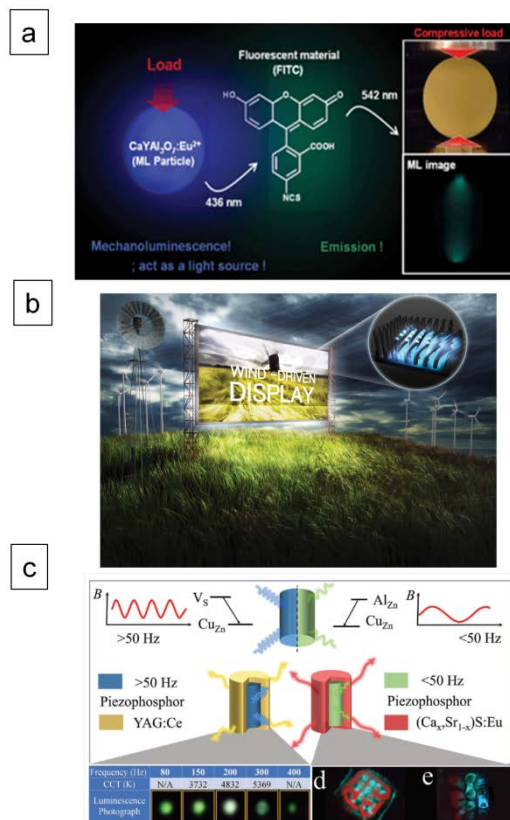


Fig.3