

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- **Title:** Round-the-clock Photocatalytic Hydrogen Production with High Efficiency by a Long Afterglow Material
- Authors: Guanwei Cui, Xiuli Yang, Yujia Zhang, Yaqi Fan, Ping Chen, Hongyu Cui, Yan Liu, Xifeng Shi, Qiaoyan Shang, and Bo Tang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201810544 Angew. Chem. 10.1002/ange.201810544

Link to VoR: http://dx.doi.org/10.1002/anie.201810544 http://dx.doi.org/10.1002/ange.201810544

WILEY-VCH

Round-the-clock Photocatalytic Hydrogen Production with High Efficiency by a Long Afterglow Material

Guanwei Cui, Xiuli Yang, Yujia Zhang, Yaqi Fan, Ping Chen, Hongyu Cui, Yan Liu, Xifeng Shi, Qiaoyan Shang and Bo Tang*

Abstract: Long afterglow materials can store and release light energy after illumination. Here, a brick-like, micron-sized $Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$ long afterglow material is used for hydrogen production via the photocatalytic reforming of methanol under roundthe-clock conditions for the first time, achieving a solar-to-hydrogen (STH) conversion efficiency of 5.18%. This material is one of the most efficient photocatalysts and provides the possibility of practical use on a large scale. Its remarkable photocatalytic activity is attributed to its unique carrier migration path and large number of lattice defects. Our findings expand the application scope of long afterglow materials and provide a new strategy to design efficient photocatalysts by constructing trap levels that can prolong carriers' lifetimes.

Hydrogen is the cleanest energy with a high energy density and is widely used as a raw material for chemical production,^[1] Especially in applications related to traffic and transportation, hydrogen can be utilized as fuel for hydrogen fuel cells to power locomotives and provide clean kinetic energy.^[2] However, hydrogen is flammable and explosive. Moreover, hydrogen molecules can seep into metallic crystal lattices, causing "hydrogen embrittlement".^[3] Therefore, the safe storage and transportation of hydrogen is difficult. On-site hydrogen production is an effective way to solve this problem. However, hydrogen is mainly produced at a large scale by the thermal cracking of hydrocarbons or water-gas shift (WGS) reactions under high temperatures. Recently, Lin et al. realized hydrogen production at a low temperature of 150°C by reforming methanol and water using Pt/MoC catalysts,^[4] but this process requires a considerable amount of external thermal energy. On-site hydrogen production still remains difficult. Solar energy is clean energy with almost unlimited reserves and has attracted considerable attention in recent decades.^[5] Photocatalytic hydrogen production can solve not only the on-site hydrogen production problem but also the issues related to the energy economy. However, to date, the highest solar-to-hydrogen (STH) conversion efficiency is no more than 5% for a particulate photocatalyst system, which is still far below the estimated

 Title(s), Initial(s), Surname(s) of Author(s) including Corresponding Author(s)
College of Chemistry, Chemical Engineering and Materials Science Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong Key Laboratory of Molecular and Nano Probes, Ministry of Education Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan, 250014 (P. R. China)

E-mail: tangb@sdnu.edu.cn

Supporting information for this article is given via a link at the end of the document. industrial requirement of 10%.^[6] In addition to a low solar energy conversion efficiency, another limitation of the practical use of photocatalytic technology is that optoelectronic devices and materials cannot maintain operation in the dark without energy storage. To overcome these restrictions, new kinds of materials or methods are needed.

Long afterglow materials, also named long lasting phosphors, persistent luminescence materials or energy storage materials, can maintain an afterglow for minutes to hours after excitation.^[7] Under light irradiation, the excited electrons are trapped and stored; when subjected to peripheral thermal perturbations, the stored electrons are released and combine with the holes, accompanied by light emission. Considering the whole photoluminescence process, the carriers can be regarded as having an extremely long lifetime, which is beneficial to photocatalysis. We proposed that if long-lived carriers could be applied in photocatalysis, they would significantly improve the photocatalytic efficiency and could realize a continuous photocatalytic reaction in the dark. This type of material could solve the abovementioned issues. To the best of our knowledge, although long afterglow materials have been used in many fields, such as safety displays, biological imaging and light sources, [8-13] there are no reports on such materials being directly applied in photocatalytic hydrogen production.

Long afterglow materials mainly include rare earth-doped aluminate, silicate, stannite, phosphate, gallate and germanate.^[14] Among them, silicate long afterglow materials have the advantages of a high luminescence intensity, long afterglow time, excellent chemical stability and low cost, making photocatalysts.[15,16] them suitable for use as $Sr_2MgSi_2O_7{:}Eu^{2+}{,}Dy^{3+}$ is a commonly used silicate long afterglow material with excellent luminescence performance. Due to the similar radii of Eu²⁺ (198 pm), Dy³⁺ (192 pm) and Sr²⁺ (195 pm), the former two ions can perfectly replace Sr2+ while maintaining its unit cell size during synthesis.^[17] Meanwhile, oxygen vacancies, which can store electrons, will be formed around the doped rare earth ions.^[18] Therefore, Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ is expected to undergo round-the-clock photocatalytic hydrogen evolution.

Based on the above considerations, we synthesized a brick-like, micron-sized, long afterglow material, Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺, by the sol-gel method.^[19] This material showed good photoluminescence and photoelectrical response characteristics. Photogenerated carriers with long lifetime were successfully applied in the photocatalytic reforming reaction of methanol and water to produce hydrogen under light and dark conditions, with an STH conversion efficiency of 5.18%, which is one of the highest efficiencies reported.^[6]

WILEY-VCH



 $\begin{array}{l} \label{eq:Figure 1.} \mbox{ Horphology and Structure characterizations of $$r_2MgSi_2O_7:Eu^{2+},Dy^{3+}$. $$c$, $$XRD of $$r_2MgSi_2O_7:Eu^{2+},Dy^{3+}$. $$c$, $$XRD of $$r_2MgSi_2O_7$ and $$r_2MgSi_2O_7:Eu^{2+},Dy^{3+}$. $$d$, $$ES-mapping of $$r_2MgSi_2O_7:Eu^{2+},Dy^{3+}$. $$c$, $$XRD of $$x_2MgSi_2O_7:Eu^{2+},Dy^{3+}$. $$es the second sec$

The morphology and structure of the as-prepared Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ were determined by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM). The material has an irregular morphology with large particles composed of regular brick-like polyhedral particles with sizes of 1-2 microns (Figure 1, a, b). The XRD peaks of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ (Figure 1, c) approximately agree with the those of the Sr₂MgSi₂O₇ host material, which has a tetragonal phase structure (PDF No. 75-1736).^[17,19,20] This agreement indicates that the crystal structure of the host material is not fundamentally changed by the doped Eu²⁺ and Dy³⁺. However, the intensity of the diffraction peak centred at 20=32.02° and 32.78°, corresponding to the (220) and (130) crystal plane of Sr₂MgSi₂O₇, decreased significantly after doping with Eu²⁺ and Dy³⁺, indicating that the doped Eu²⁺ and Dy³⁺ were indeed incorporated into the Sr₂MgSi₂O₇ material and occupied the Sr²⁺ sites.^[17] No crystal phase peaks ascribed to rare earth oxides were observed in the XRD peaks of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺, showing that the doped Eu²⁺ and Dy³⁺ were evenly distributed in the long afterglow materials, which was further confirmed by the EDS-mapping images (Figure 1, d-i). The contents of doped Eu²⁺ and Dy³⁺ were 0.48% and 1.04%, respectively. The chemical states of Sr, Mg, Si, O, Eu and Dy in Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ were determined from the XPS spectra (Figure S1). Four peaks centred at 1164.66 eV, 1154.19 eV, 1135.06 eV, and 1124.94 eV in the Eu 3d binding energy region were ascribed to Eu³⁺ 3d3/2, Eu²⁺ 3d3/2, Eu³⁺ 3d5/2, and Eu²⁺ 3d5/2 (Figure 4, b); two peaks centred at 1297.43 eV and 152.88 eV were assigned to Dy³⁺ 3d and Dy³⁺ 4d (Figure 4, c),

respectively.^[13, 21, 22] In addition, the doping of rare earth ions can cause lattice distortion of the Sr₂MgSi₂O₇ matrix and create surface defects which can be observed in the HRTEM images (Figure S2). It is ascribed to the presence of large number of oxygen vacancies,^[23-25] which is further confirmed by EPR spectra. As shown in figure S3, the low-field signal with g-factor=1.97, close to the free-electron value (g=2.0023) is generally attributed to an unpaired electron trapped on an oxygen vacancy site.^[26] It is generally believed that the existence of a large number of lattice defects is beneficial to the enhancement of photocatalytic activity.^[27]



Figure 2. Optical properties and photoelectricity response characterization of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺. a, Ultraviolet–visible absorbance spectrum of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ and Sr₂MgSi₂O₇. b, Excitation and emission spectra of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺. c, Luminescence and Decay curves of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ in the dark. d, Photocurrent density of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ irradiated by 300 W Xe lamp.

The colour changes of a material directly correspond to the changes in its light absorbance properties. As shown in Figure 2a, after doping with Eu²⁺ and Dy³⁺, the colour of the Sr₂MgSi₂O₇ host material changed from white to yellow. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) showed that the maximum absorption wavelength significantly expanded from 425 nm to 480 nm after doping with rare earth ions. As estimated from the absorption tail,^[28] the absorption energy gap of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ was approximately 2.34 eV, which is significantly lower than the forbidden band width of 7.9 eV of Sr₂MgSi₂O₇ reported previously.^[29] This lower gap is attributed to the appearance of a doped energy band in the forbidden band of Sr₂MgSi₂O₇ afforded by Eu²⁺ and Dy³⁺.^[18,29] As shown in Figure 4a, according to the ultraviolet photoelectron spectroscopy (UPS, Figure S4) and valence bond X-ray photoelectron spectroscopy (VBXPS, Figure S5) data and the previously reported results,^[30,31] the Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ valence band top and conduction band bottom are located at -1.44 eV, and the intermediate state level formed by rare-earth Eu²⁺, which acts as the valence band, is located at 1.58 eV (the intrinsic valence band of the Sr₂MgSi₂O₇ host material is located at 6.46 eV). Therefore, the energy band of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ meets the

requirements for a hydrogen evolution redox potential. The asprepared long afterglow material showed long afterglow emission with a maximum emission peak at 465 nm under ultraviolet excitation and the emission persisted for more than 20 hours (Figure 2, b-c; Figure S6). To determine whether the photoexcited carriers can be transferred to the interface of the as-prepared long afterglow material, photocurrent measurements were performed. As shown in Figure 2d, the long afterglow material showed good photoelectric response characteristics. Interestingly, the photoelectric response curve exhibits a unique hill peak shape, which may be due to the cumulative storage and slow release characteristics of the photogenerated carriers. This is consistent with the characteristics of the long afterglow. The abovementioned results indicate that this material has the capacity for continuous round-the-clock photocatalytic hydrogen evolution.



Figure 3. Photocatalytic performance of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺, a, H₂ evolution in different pH reactive mediums. b, Time course of H₂ evolution under dark for Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ and Sr₂MgSi₂O₇ after irradiation by 500 W high-pressure Hg lamp for 15 min. c, Stability test of H₂ evolution (evacuation every 5 h) for Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ under UV light irradiation. d, H₂ evolution under different temperature in the dark for Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ after irradiation by UV light.

The photocatalytic properties of the as-prepared materials were investigated for photocatalytic hydrogen evolution from the reforming reaction of methanol and water under ultraviolet light, visible light and dark conditions. Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ showed high reactivity over a wide pH range of 5-10, even in the pure water reaction medium without any buffer (Figure 3a). Under the optimal photocatalytic reaction conditions, the maximum H₂ production rate achieved was 14 mmol/g•h under irradiation by a 500 W high-pressure mercury lamp with a maximum absorption wavelength of 365 nm. Correspondingly, under the assumption that all incident light was absorbed by the photocatalyst, the STH conversion efficiency was 5.18% per gram of $Sr_2MgSi_2O_7$: Eu²⁺, Dy³⁺, which is one of the highest conversion efficiencies of light energy reported in the field of photocatalytic H₂ evolution. Moreover, under visible light irradiation, H₂ evolved at a rate of 60 µmol/g•h with an STH conversion efficiency of 0.18%. Most notably, the as-prepared long afterglow material achieved good hydrogen evolution performance in the dark after illumination. As shown in Figure 3b, after being irradiated by UV light for 15 min, H₂ production gradually increased over time in the dark, and the amount of hydrogen reached 264 µmol/g after 8 hours with an STH conversion efficiency of 0.39%. Due to its chemical stability, Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ exhibited a long lifetime, maintaining the same photoactivity after 6 cycles (Figure 3c). In contrast, the host material Sr₂MgSi₂O₇ exhibits photocatalytic hydrogen production under only UV light conditions, not under visible light and dark conditions (Figure S7). This indicates that the presence of Eu²⁺ and Dy³⁺ is necessary for hydrogen production under visible light and dark conditions.



Figure 4. Proposed mechanism involved in the photocatalytic process. a, Energy-level and photogenerated electrons transfer process diagrams. b, XPS spectra of Eu3d before and after photocatalytic reaction. c, XPS spectra of Dy3d and Dy4d before photocatalytic reaction. d, XPS spectra of Dy3d and Dy4d after photocatalytic reaction.

The excellent photocatalytic hydrogen evolution performance of Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ was suggested to be due to the unique carrier migration pathway that causes its long afterglow. According to the previous reported results, [29,32] although the mechanism of persistent luminescence is still open to question, herein, the emission mechanism of the long afterglow material is proposed as follows (Figure 4a): When the electrons in the ground-state 4f of Eu²⁺ are excited to the energy level of 5d, they are further excited to the conduction band of the Sr₂MgSi₂O₇ host material by thermal energy, and Eu²⁺ becomes Eu³⁺. The excited electrons in the conduction band will be trapped by Dy³⁺, with the formation of Dy^{2+} (Path I denoted by the red arrows). Then, when the trapped electrons in the ground state of Dy²⁺ are released to the conduction band, they will recombine with Eu³⁺ to reform Eu²⁺ with the emission of a long afterglow (Path II denoted by the blue arrows). During the photocatalytic reaction under light irradiation, most of the excited electrons in the conduction band originating from Eu²⁺ can directly interact with the reaction substrates, while the electrons that are not consumed can continue to be transferred; these electrons are trapped by Dy³⁺ ions and are therefore stored temporarily. As a

WILEY-VCH

result, the carrier lifetime is improved, and thus, the catalytic efficiency is ultimately improved in light conditions. Under dark conditions after irradiation, the excited electrons in the conduction band released from Dy²⁺ by the thermal disturbance can continue to interact with the substrates to result in continuous hydrogen production. The catalytic reaction in this dark environment will break the electron transport pathway and quench the long afterglow. This quenching phenomenon was observed during the catalytic reaction. Under dark conditions, the intensity of the long afterglow luminescence obviously decreased with the addition of methanol (Figure S8). This decrease preliminarily demonstrates that the active electrons for the photocatalytic reaction originate from the photogenerated carriers to produce the long afterglow. In addition, as shown in Figure 3d, the H₂ production rates were related to the reaction temperature in the dark environment, showing the maximum hydrogen production rate at 77 °C. This is consistent with the thermoluminescence phenomenon of Sr₂MgSi₂O₇:Eu²⁺,Dv^{3+,[33]} further indicating that the carriers utilized during hydrogen production by the material are derived from active electrons trapped during the long afterglow luminescence processes. The XPS results show that after the photocatalytic reaction, the content ratio between ${\rm Eu}^{2+}$ and ${\rm Eu}^{3+}$ increased from 0.52:1 to 0.84:1(Figure 4 b); for Dy³⁺, although no reduced chemical state Dy^{2+} was detected, a slight bonding energy shift of 0.17 and 0.66 eV for the Dy 3d and Dy 4d electrons, respectively, was observed before and after the photocatalytic reaction (Figure 4 c, d). It is preliminary suggested that the Eu²⁺ and Dy³⁺ doped in Sr₂MgSi₂O₇ may be the key active sites of the photocatalytic reaction. Detailed photocatalytic reaction mechanisms will be studied in our future work.

In summary, a long afterglow material, Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺, was applied to hydrogen production by the photocatalytic reforming of methanol and water under round-the-clock conditions for the first time. An STH conversion efficiency of 5.18% was obtained, which is one of the highest efficiencies obtained to date. This exceptional photocatalytic activity is attributed to the unique carrier transport path and large number of lattice defects. Compared with thermodynamic hydrogen production, the photocatalytic process has the advantages of being clean, safe and economical. We believe that through energy level renovation or assembly with other materials, it is possible to effectively expand the spectral utilization range of such long afterglow materials and further improve their light energy conversion efficiency. Our findings widen the application scope of long afterglow materials and provide a strategy to design efficient photocatalysts by constructing trap levels that can prolong carriers' lifetimes.

Experimental Section

Experimental Details see the supporting information.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21535004, 91753111, 21575082, 21507074, 21390411) and the Key Research and Development Program of Shandong Province (2018YFJH0502), Development plan of science and technology for Shandong Province of China (2013GGX10706), Shandong Province Natural Science Foundation (ZR2015BM023), and A Project of Shandong Province Higher Educational Science and Technology Program (J13LD06).

Keywords: round-the-clock .Long afterglow . photocatalytic hydrogen evolution• methanol • water

- [1] a) A. Midilli, M. Ay, I. Dincer, & M. A. Rosen, Renew. Sust. Energ. Rev. 2005, 9, 255-271; b) X. Chen, S. Shen, L. Guo, & S. S. Mao, Chem. Rev. 2010, 110, 6503-6570; c) S. Y. Tee, K. Y. Win, W. S. Teo, L.-D. Koh, S. Liu, C. P. Teng and M.-Y. Han, Adv. Sci. 2017, 4, 1600337.
- [2] M. Z. Jacobson, W.G. Colella, D.M. Golden, Science 2005, 308, 1901.
- S. Dutta, J. Ind. Eng. Chem. 2014, 20, 1148-1156. [3]
- L. Lin, W. Zhou, R. Gao, S. Yao, X. Zhang, W. Xu, S. Zheng, Z. Jiang, [4] Q. Yu, Y.-W. Li, C. Shi, X.-D. Wen, D. Ma, Nature 2017, 544, 80.
- a) P. Zhang, T. Wang, X. Chang, J. Gong, Accounts Chem. Res. 2016, [5] 49, 911-921; b) N. S. Lewis, D. G. Nocera, PNAS 2006, 103, 15729; c) K. C. Christoforidis, P. Fornasiero, Chemcatchem 2017, 9, 1523-1544; d) G. Cui, W. Wang, M. Ma, J. Xie, X. Shi, N. Deng, J. Xin and B. Tang, Nano Lett. 2015, 15, 7199-7203.
- a) J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. [6] Lee, J. Zhong, Z. Kang, Science 2015, 347, 970; b) Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. D. Sharp, A. Kudo, T. Yamada, K. Domen, Nat. Mater. 2016, 15, 611;c) R. G. Li, Chinese J. Catal. 2017, 38, 5-12; d) L. Liao, Q. Zhang, Z. Su, Z. Zhao, Y. Wang, Y. Li, X. Lu, D. Wei, G. Feng, Q. Yu, X. Cai, J. Zhao, Z. Ren, H. Fang, F. Robles-Hernandez, S. Baldelli, J. Bao, Nat. Nanotechnol. 2014, 9, 69-73. [7]
 - Y. Li, M. Gecevicius, J. Qiu, Chem. Soc. Rev. 2016, 45, 2090-2136.
- [8] T. Maldiney, A. Bessiere, J. Seguin, E. Teston, S. K. Sharma, B. Viana, A. J. Bos, P. Dorenbos, M. Bessodes, D. Gourier, D. Scherman, C. Richard, Nat. Mater. 2014, 13, 418-426.
- Z. J. Li, H. W. Zhang, M. Sun, J.S. Shen, H. X. Fu, J. Mater. Chem. [9] 2012, 22, 24713.
- Q. Zhou, F. Peng, Y. Ni, J. Kou, C. Lu, Z. Xu, J. Photoch. Photobio. A [10] 2016, 328, 182-188.
- H. C. Sun, L. K. Pan, X. Q. Piao, Z. Sun, J. Mater. Chem. A 2013, 1, [11] 6388-6392.
- [12] F. Locardi, E. Sanguineti, M. Fasoli, M. Martini, G. A. Costa, M. Ferretti, V. Caratto, Catal. Commun. 2016, 74, 24-27.
- [13] X. Zhang, Z. Zhou, F. Ye, X. Liu, Q. Li, Mat. Sci. Semicon. Proc. 2015, 40. 130-135.
- [14] H. Terraschke, C. Wickleder, Chem. Rev. 2015, 115, 11352-11378.
- L. He, B. Jia, L. Che, W. Li, W. Sun, J. Lumin. 2016, 172, 317-322. [15]
- X. Liu, X. Zhang, Z. Zhou, Mater. Res. Bull. 2016, 79, 84-89. [16]
- [17] H. Wu, Y. Hu, L. Chen, X. Wang, Mater. Lett. 2011, 65, 2676-2679.
- [18] H. Duan, Y. Z. Dong, Y. Huang, Y. H. Hu, X. S. Chen, Phys. Lett. A 2016. 380. 1056-1062.
- [19] H. Ji, G. Xie, Y. Lv, H. Lu, J. Sol-Gel Sci. Techn. 2007, 44, 133-137.
- [20] F. Ye, S. Dong, Z. Tian, S. Yao, Z. Zhou, S. Wang, Opt. Mater. 2013, 36. 463-466.
- [21] Y. Uwamino, T. Ishizuka, H. Yamatera, J. Electron. Spectrosc. 1984, 34, 67-78.
- M. N. K. Bhuiyan, M. Menghini, C. Dieker, J. W. Seo, J.-P. Locquet, R. [22] Vitchev, C. Marchiori, MRS Proceedings 2011, 1252, 1252.

WILEY-VCH

- [23] Y. Zhu, Q. Ling, Y. Liu, H. Wang, Y. Zhu, Appl. Catal. B- Environ. 2016, 187, 204-211.
- [24] H. Furusho, J. Hölsä, T. Laamanen, M. Lastusaari, J. Niittykoski, Y. O kajima, A. Yamamoto, *J. Lumin.* 2008, *128*, 881-884.
- [25] J. Holsa, T. Laamanen, M. Lastusaari, P. Novak, J. Rare. Earth. 2011, 29, 1130-1136.
- [26] a) L. Zhang, C. Li, S. Wang, Q. Su, J. Luminescence, 2007, 126, 551– 555; b) H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, W. Cai, Adv. Funct. Mater. 2010, 20, 561 - 572; c) F. Lei, Y. Sun, K. Liu, S. Gao, L. Liang, B. Pan, .Y. Xie, J. Am. Chem. Soc. 2014, 136, 6826–6829.
- [27] D. Chen, Z. Wang, T. Ren, H. Ding, W. Yao, R. Zong, Y. Zhu, *The J. Phys. Chem. C* 2014, *118*, 15300-15307.
- [28] M. Hojamberdiev, M. F. Bekheet, J. N. Hart, J. J. M. Vequizo, A.Yamakata, K. Yubuta, A. Gurlo, M. Hasegawa, K. Domen, K. Teshima, *Phys. Chem. Chem. Phys.* **2017**, *19*, 22210-22220.
- [29] P. Dorenbos, Phys. status. solidi. B 2005, 242, R7-R9.
- [30] D. P. Xu, L. J. Yu, X. D. Chen, L. Chen, Q. Q. Sun, H. Zhu, H. L. Lu, P. Zhou, S. J. Ding, D. W. Zhang, *Nanoscale. Res. Lett.* **2017**, *12*, 311.
- [31] X. Chen, L. Liu, P. Y. Yu, S. S. Mao, Science 2011, 331, 746.
- [32] Y. Li, M. Gecevicius, J. Qiu, Chem. Soc. Rev. 2016, 45, 2090-2136.
- [33] I. P. Sahu, D. P. Bisen, N. Brahme, M. Ganjir, *luminescence* 2015, 30, 1318-1325.

WILEY-VCH

10.1002/anie.201810544

Entry for the Table of Contents

Layout 1:

COMMUNICATION

A brick-like, micron-sized Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ long afterglow material is used for hydrogen production via the photocatalytic reforming of methanol under round-the-clock conditions for the first time, achieving a solar-to-hydrogen (STH) conversion efficiency of 5.18%. This material is one of the most efficient photocatalysts and provides the possibility of practical use on a large scale.



Guanwei Cui, Xiuli Yang, Yujia Zhang, Yaqi Fan, Ping Chen, Hongyu Cui, Yan Liu, Xifeng Shi, Qiaoyan Shang and Bo Tang*

Page No. – Page No.

Round-the-clock Photocatalytic Hydrogen Production with High Efficiency by a Long Afterglow Material