Photo-Electrochemical Device Enabling Luminescence Switching of LaPO$_4$:Ce,Tb Nanoparticle Layers

Jonas Klein, Seyyed Mohsen Beladi-Mousavi, Marco Schleutker, Dereje Hailu Taffa, Markus Haase,* and Lorenz Walder* 

The luminescence properties of LaPO$_4$:Ce,Tb nanoparticles are known to depend on the oxidation state of the cerium ions. However, their assembly into thin films exhibiting reasonable fast Ce$^{3+/4+}$ electrochemistry is not trivial. Herein, the electrochemical luminescence switching of LaPO$_4$:Ce,Tb nanoparticles, assembled as nonconductive thin films, using two electrocatalytic processes, is demonstrated. Due to the insulating nature of these nanoporous films, redox shuttles are used to access the redox active Ce$^{3+/4+}$ species for electrochemical reactions. A series of redox shuttles with various redox potentials are employed to investigate their capability to electrochemically oxidize Ce$^{3+}$ within the nanoparticles. Thereby the formal redox potential of the Ce$^{3+/4+}$ couple in LaPO$_4$:Ce,Tb nanoparticles is determined to lie within 0.89 and 1.15 V versus Ag/AgCl. In situ observation of repetitive luminescence switching is realized by assembling a device that allows UV light to enter the nanoparticle layer. With two redox shuttles present in the electrolyte, one for the oxidation of Ce$^{3+}$ and the other for reduction of Ce$^{4+}$, quenching and restoration of the luminescence is monitored. The resulting device represents the first down-sizeable logical AND gate with UV light and voltage inputs and a visible light output based on a solid state LaPO$_4$:Ce,Tb layer.

Microcrystalline LaPO$_4$:Ce,Tb powder has been widely used as green emitting phosphor in fluorescent lamps due to its high luminescence quantum yield and chemical stability.[1–5] The luminescence is based on the UV excitation of Ce$^{3+}$ followed by Ce$^{3+}$ to Tb$^{3+}$ energy transfer and finally Tb$^{3+}$ emission.[6] Further, generation of Ce$^{4+}$ within these particles is known to efficiently quench the luminescence due to fast energy transfer via adjacent Ce$^{3+}$ ions, followed by quenching at the Ce$^{4+}$ ions.[7] Thus, the luminescence can be switched on and off by partially changing the oxidation state of cerium species at the particle surface making them an attractive material for sensing applications.[8–11] In the chemical version, potassium permanganate is commonly used to oxidize Ce$^{3+}$ and quench its luminescence while ascorbic acid is used to restore the luminescence of Ce$^{3+}$ by reducing the Ce$^{4+}$.[12–16] In the current publication an electrochemical approach towards repetitive luminescence on/off switching of thin LaPO$_4$:Ce,Tb films is investigated. Microcrystalline LaPO$_4$:Ce,Tb powder is a well-known lamp phosphor with a luminescence quantum yield in the visible range of 86%. The quantum yield of the LaPO$_4$:Ce,Tb nanoparticles used here is 43%.[3] Adding an undoped LaPO$_4$ shell to the LaPO$_4$:Ce,Tb nanoparticles would increase the luminescence quantum yield to 70% but would inhibit switching of their luminescence. Since the nanoparticles are electronically insulating a conductive additive such as carbon black would be needed, but such strongly absorbing species would negatively affect the luminescence of the electrode. To avoid this problem, small organic molecules are utilized as redox shuttles to mediate electron transfer between the LaPO$_4$:Ce,Tb nanoparticles and the current collector. Redox shuttles are commonly used as enhancing additives in fields such as biotechnology,[17,18] photocatalysis,[19–21] or batteries.[22–25] The redox shuttles are added to the electrolyte and diffuse throughout the nanoporous nanoparticle film enabling repetitive luminescence on/off switching based on the applied potential.

For this purpose, an electrochemical device was constructed, consisting of an electrode layer of LaPO$_4$:Ce,Tb nanocrystals, an electrolyte and a counter electrode. The LaPO$_4$:Ce,Tb layer was prepared from a colloidal solution of La$_{0.4}$PO$_4$:Ce$_{0.45}$,Tb$_{0.15}$ nanoparticles with an average size of 4 nm and spherical shape. The nanoparticles, which were synthesized via a already published procedure,[3] crystallized in the monoclinic structure as confirmed by powder X-ray diffraction (XRD, Figure S1, Supporting Information). The nanoparticle thin films were prepared from a mixture of this colloidal solution and a small amount of Pluronic F127 polymer, which was drop casted onto indium tin oxide (ITO) coated glass, followed by heating the electrodes to 200 °C. Addition of the polymer improved film homogeneity and prevented cracking of the layer. While heat treatment

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ensures adhesion of the film during electrochemical measurements, the temperature of 200 °C is not enough to remove the polymer from the film as shown by thermogravimetric analysis (TGA) of the composite (Figure S2, Supporting Information). Due to the nonconducting properties of the nanoparticle films, electrochemical oxidation of Ce³⁺ species through polarization of the electrodes at up to 2 V versus Ag/AgCl in 0.1 m LiClO₄ in acetonitrile could not be achieved. To enable redox reactions of the cerium atoms, redox shuttles were added to the electrolyte to transfer electrons between the current collector and the nanoparticles. As shown in Scheme 1a the films are nanoporous in the sense that the redox shuttles are able to percolate the film composed of the nanoparticles embedded in a polymer matrix. For the electrochemical oxidation of Ce³⁺ species, redox shuttles are oxidized at the current collector followed by migration into the nanoparticle film. If the redox potential of the redox shuttle (Eₛ⁰) is more positive than the redox potential of the Ce³⁺/⁴⁺ couple (Eₚ₀), electrons are transferred from Ce³⁺ ions of the LaPO₄:Ce,Tb nanoparticles to the oxidized redox shuttles. Thus, Ce⁴⁺ species are generated while the previously oxidized redox shuttles are reduced to their initial state and therefore can again undergo oxidation at the current collector, yielding a so-called catalytic current. This mechanism is schematically shown in Scheme 1b. In cyclic voltammetry (CV) measurements (three electrode setup), this electron transfer mechanism results in an increased oxidation current in the first cycle as shown in Figure 1a. Accordingly, the luminescence of the nanoparticle film is fully quenched. The electrochemical reduction of Ce⁴⁺ species follows the same principle when an electrochemically reducible redox shuttle is used (Scheme 1c). Here Eₛ⁰ has to be more negative than Eₚ⁰. In this case, an increased reduction current is observed in the first cycle of CV measurements (Figure 1b), leading to complete restoration of the luminescence. Further CVs where such kind of catalytic currents were observed are shown in Figures S3–S10, Supporting Information. The excess charge between the first and second cycle along with the amount of nanoparticles present in the film allows calculation of the quantity of oxidizable/reducible Ce³⁺/⁴⁺ to ≈2.2%. Another important quantity is the formal redox potential of cerium species at the surface of LaPO₄:Ce,Tb nanoparticles, especially since the redox potential of cerium is known to be strongly influenced by its chemical environment. Therefore, the capability to electrochemically oxidize Ce³⁺ was investigated for redox shuttles with different Eₛ⁰ (molecular structures are shown in Figure S11, Supporting Information). This variation of Eₛ⁰ shows that Eₛ⁰ has a value between 0.89 V and 1.15 V versus Ag/AgCl (Figure 1c and Table S1, Supporting Information). Prior to these measurements, the redox potentials Eₛ⁰ of the redox shuttles were determined from CV measurements using a blank ITO working electrode. Repetitive electrochemical oxidation and reduction can now be achieved with two redox shuttles present in the electrolyte, one that oxidizes Ce³⁺ and one that reduces Ce⁴⁺. In the experiments mentioned so far, the nanoparticle films had to be removed from the electrochemical cell after the measurements to check the luminescence under...
the UV light. To realize an in situ observation of the repetitive luminescence switching of the nanoparticles, we built a full thin-film electrochemical device consisting of the nanoparticle/polymer composite layer on ITO coated glass, a separator, the counter electrode and a quartz glass window (Figure 2a). For UV excitation of the composite layer, a UV transmitting electrolyte/redox shuttle combination had to be used. A 0.15 M solution of LiClO$_4$ in acetonitrile containing 1,4-di-t-butyl-2,5-dimethoxybenzene (2 mM) as oxidizing redox shuttle and 7,8-dihydro-6$H$-dipyrido[1,2-a:2',1'-c]-1,4)diazepinium (0.25 mM) as reducing redox shuttle fulfills this requirement, at least for short path ways. Potentials of 2 V for oxidation and −1 V for reduction were repeatedly applied in intervals of 1 s while UV light was cast through the quartz glass onto the nanoparticle film. Images of the device in the on/off state are displayed in Figure 2b,c. A movie showing the switching was recorded (available as Supporting Information) from which the intensity change of the nanoparticle film was monitored as a function of time using ImageJ software. Repetitive quenching and restoration of the luminescence was achieved for multiple switching cycles (Figure 2e). From the time resolved intensity change over one switching cycle, displayed in Figure 2d, the switching times to achieve a 90% change in intensity can be estimated as ≈550 ms for quenching and ≈650 ms for restoration of the luminescence. The fast switching times and the complete quenching of the luminescence indicate that the mediators are able to rapidly access most LaPO$_4$:Ce,Tb nanocrystals of the layer. In fact, switching remains possible even when the layer of LaPO$_4$:Ce,Tb particles is diluted with an inert solid nanomaterial. Here, we used LaPO$_4$:Eu nanocrystals, since this material cannot be oxidized or reduced within our potential range. In our diluted device, the nanoparticle layer consisted of a 1:19 mixture of LaPO$_4$:Ce,Tb and LaPO$_4$:Eu particles of which the latter alone shows a red color under UV excitation. The device therefore displays a yellow color in the reduced state (−1 V) and red color when cerium species are oxidized (+2 V) and shows that not only on/off-switching but also switching between two different emission colors is possible (see Figure 3).
Furthermore, this indicates that even in this diluted system, with respect to LaPO₄:Ce;Tb, the redox shuttles reach all nanoparticles within the layer and electrons are not transferred via adjacent LaPO₄:Ce;Tb particles. With the applied voltage and UV light as inputs and visible light as output the device based on LaPO₄:Ce;Tb represents a logical AND gate (Figure S12, Supporting Information). Our results also show that neither high temperature sintering processes nor the addition of solid conductive additives are required to utilize the redox-dependent optical properties of nonconductive nanoparticles in an electrochemical device. The redox shuttle-based working principle of our device may therefore enable the use of a large variety of different functional materials in opto-electrochemical devices.

In summary, the electrochemical luminescence switching of LaPO₄:Ce;Tb nanoparticle thin films is demonstrated by a mediated electron transfer mechanism via small organic molecules (redox shuttles) present in the electrolyte. The formal redox potential of the Ce⁴⁺/³⁺ species within the nanoparticles was determined within a narrow range by using redox shuttles with different redox potentials. Construction of a device containing an oxidizing and a reducing redox shuttle allowed in situ observation of repetitive luminescence on/off switching.

**Experimental Section**

*Nanoparticle Synthesis:* For the synthesis of La₀.₄PO₄:Ce₀.₄₅,Tb₀.₁₅ nanoparticles, LaCl₃·7H₂O (1.49 g, 4 mmol), CeCl₃·7H₂O (1.68 g, 4.5 mmol), and TbCl₃·6H₂O (0.56 g, 1.5 mmol) were dissolved in 10 mL methanol. To the clear solution, diethylphosphonate (3.35 mL, 33 mmol) and diphenylether (30 mL) were added before the methanol was removed on a rotary evaporator. After heating the solution to 105 °C under vacuum, tributylamine (9.54 mL, 40 mmol) and a solution of phosphoric acid in dihexylether (2 mL, 6.4 mL) were added at room temperature under nitrogen and then the mixture was heated to 200 °C for 16 h under nitrogen. The precipitate was centrifuged, washed with chloroform and dispersed in 300 mL methanol. Upon purification by dialfiltration (5 kD membrane, 3 × 300 mL methanol), the nanoparticles were obtained as colloid in ~30 mL methanol. The nanoparticles were characterized by powder XRD on a Panalytical Empyrean diffractometer using Bragg-Brentano geometry, Cu Kα radiation and a step size of 0.039° 2θ. LaPO₄:Eu nanoparticles were similarly synthesized starting with LaCl₃·7H₂O (3.342 g, 9 mmol) and EuCl₃·6H₂O (0.366 g, 1 mmol).

*Film Preparation:* Nanoparticle films were prepared on ITO coated glass, which was cleaned by subsequent ultrasonication in muscovol, water and acetone. Pluronic F127 (12 600 g mol⁻¹, molar nanoparticle/polymer ratio 1/0.005) was added to 1 mL of the methanolic nanoparticle solution (0.16 M). 15 µL of this mixture was drop casted onto the ITO substrate (1 cm² coated area) followed by heating the electrodes to 200 °C for 30 min. TGA of the composite and its individual components were performed on a NETZSCH STA 449 system with helium atmosphere.

*Electrochemistry:* Electrochemical measurements were performed in a three electrode system with an Ag/AgCl reference electrode and a platinum wire counter electrode. A 0.1 M solution of LiClO₄ in acetonitrile served as electrolyte. Redox shuttles (structures shown in Figure S1, Supporting Information) were added to the electrolyte to a concentration of 1 mM (separate solutions). To perform electrochemical reduction of Ce⁴⁺ species, the nanoparticle films were chemically oxidized by immersion of the electrodes into an aqueous solution of KMnO₄ (1 mM) prior to electrochemical measurements. Cyclic voltammograms of the nanoparticle films in the electrolytes containing different redox shuttles were recorded with an Autolab PGSTAT 20 potentiostat. After the measurements, the electrodes were removed from the electrochemical cell and the success of the electrochemical luminescence switching was qualitatively checked under a UV light (254 nm).

*Device Fabrication:* On a 2.5 × 3 cm ITO glass, a nanoparticle film (1 × 1 cm) was prepared based on the above described method with a fourfold diluted solution. A 2.5 × 3 cm carbon plate with a 0.5 × 0.5 cm cavity (overlapping with the nanoparticle film) was used as counter electrode and separated from the ITO glass by a 50 µm gasket. A 2.5 × 2.5 cm quartz glass was placed on top of the carbon plate to close the device and allow entrance of UV light into the cell. Via vacuum backfilling, the device was filled with a 0.15 m solution of LiClO₄ in acetonitrile containing the redox shuttles 1,4-di-t-butyl-2,5-dimethoxybenzene (2 mM) and 7,8-dihydro-6H-dipyrido[1,2-a:2′,1′-c][1,4] diazepinium (0.25 mM). The device was switched between 2 V and −1 V in 1 s intervals. A second device was built identically but the nanoparticle layer was prepared from a combined solution consisting of 95% of a methanolic solution (0.16 M) of 4 nm LaPO₄:Eu particles and 5% of a methanolic solution (0.16 M) of 4 nm LaPO₄:Ce,Tb particles. Pluronic F127 was added as described above. 30 µL of this undiluted mixture were drop casted onto the ITO (1 cm² coated area). Here too, potentials of −1 V and +2 V were applied but not in 1 s intervals.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

electrochemistry, lanthanides, logic gates, luminescence switching, redox mediators

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[1] N. Hashimoto, Y. Takada, K. Sato, S. Ibuki, J. Lumin. 1991, 49, 893.
[2] K. Riwozki, H. Meyssamy, H. Schnablegger, A. Kornowski, M. Haase, Angew. Chem., Int. Ed. 2001, 40, 573.
[3] K. Köpme, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Möller, M. Haase, Angew. Chem., Int. Ed. 2003, 42, 5513.
[4] K. Köpme, O. Lehmann, M. Haase, Chem. Mater. 2006, 18, 4442.
[5] A. Oertel, C. Lengler, T. Walther, M. Haase, Chem. Mater. 2009, 21, 3883.
[6] V. Pankratov, A. I. Popov, S. A. Chernov, A. Zharkowskaya, C. Feldmann, Phys. Status Solidi B 2010, 247, 2252.
[7] M. Kitsuda, S. Fujihara, J. Phys. Chem. C 2011, 115, 8808.
[8] C. Li, W. Di, Z. Liu, K. Zheng, W. Qin, Analyst 2014, 139, 4547.
[9] G. Vinothkumar, A. I. Lalitha, K. S. Babu, Inorg. Chem. 2019, 58, 349.
[10] G. Yan, Y. Zhang, W. Di, W. Qin, Dyes Pigm. 2018, 159, 28.
[11] W. Di, N. Shirahata, H. Zeng, Y. Sakka, Nanotechnology 2010, 21, 365501.
[12] Q. Li, V. W.-W. Yam, Angew. Chem., Int. Ed. 2007, 46, 3486.
[13] Y. Takano, S. Fujihara, ECS J. Solid State Sci. Technol. 2012, 1, R169.
[14] G. Phaomei, R. S. Ningthoujam, W. R. Singh, R. S. Loitongbam, N. S. Singh, A. Rath, R. R. Juluri, R. K. Vatsa, Dalton Trans. 2011, 40, 11571.
[15] G. Chen, H. Zhao, F. Rosei, D. Ma, J. Phys. Chem. C 2013, 117, 10031.
[16] S. Fujihara, Y. Takano, M. Kitsuda, Int. J. Appl. Ceram. Technol. 2015, 12, 411.
[17] F. P. V. der Zee, F. J. Cervantes, Biotechnol. Adv. 2009, 27, 256.
[18] K. Watanabe, M. Manefield, M. Lee, A. Kouzuma, Curr. Opin. Biotechnol. 2009, 20, 633.
[19] R. Abe, T. Takata, H. Sugihara, K. Domen, Chem. Commun. 2005, 3829.
[20] Y.-N. Liu, C.-C. Shen, N. Jiang, Z.-W. Zhao, X. Zhou, S.-J. Zhao, A.-W. Xu, ACS Catal. 2017, 7, 8228.
[21] M. L. K. Sanchez, C.-H. Wu, M. W. W. Adams, R. B. Dyer, Chem. Commun. 2019, 55, 5579.
[22] Z. Chen, Y. Qin, K. Amine, Electrochim. Acta 2009, 54, 5605.
[23] J. Chen, C. Buhrmester, J. R. Dahn, Electrochem. Solid-State Lett. 2005, 8, A59.
[24] M. N. Golovin, D. P. Wilkinson, J. T. Dudley, D. Holonko, S. Woo, J. Electrochem. Soc. 1992, 139, 5.
[25] J. R. Dahn, J. Jiang, L. M. Moshurchak, M. D. Fleischauer, C. Buhrmester, L. J. Krause, J. Electrochem. Soc. 2005, 152, A1283.