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Luminescence amplification at $BiVO_4$ photoanodes by photoinduced electrochemiluminescence

Jing Yu,[a] Hiba Saada,[b] Rawa Abdallah,[c] Gabriel Loget,*[b] and Neso Sojic*[a]

[a] J. Yu, Prof. N. Sojic
University of Bordeaux, Bordeaux INP, ISM, UMR CNRS 5255, 33607 Pessac, France
E-mail: neso.sojic@enscbp.fr

[b] H. Saada, Dr. G. Loget
Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR6226 - ScanMAT-UMS2001, F-35000 Rennes, France
E-mail: gabriel.loget@univ-rennes1.fr

[c] Dr. Rawa Abdallah
Lebanese University, EDST, AZM Center for Research in Biotechnology and Its Applications, Laboratory of Applied Biotechnology, LBA3B, El Mitein Street, Tripoli, Lebanon

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Abstract: Photoinduced electrochemiluminescence (PECL) combines semiconductor (SC) photoelectrochemistry with electrochemiluminescence (ECL). In PECL, the incident light is converted to a different wavelength by an electrochemical reaction at a SC photoelectrode and allows to trigger ECL at unprecedented low potentials. This concept has been employed so far to design up-conversion systems using Si or III-V SCs. Nevertheless, PECL strongly suffers from the photoelectrochemical instability of these low bandgap SCs. Here, we report for the first time an original light conversion strategy based on PECL of a luminol derivative (L-012) at $BiVO_4$ photoanodes in water. An incident light photo-excites simultaneously the L-012 fluorescence and the photoanode. However, the resulting fluorescence signal is surpassed by the PECL emission. In addition, we show that, with this system, PECL can be induced at a potential as low as -0.4 V for several hours and that it can be employed to finely tune L-012 luminescence. This remarkable light enhancement and the record low applied potential are promising for the design of new analytical strategies and light-addressable systems.

Depleted semiconductors (SCs) in contact with an electrolyte phase and illuminated by a sub-bandgap wavelength can afford redox reactions through the transfer of minority carriers at the solid/liquid interface.[1,2] In the case of *n*-type SCs (*n*-SCs), photogenerated holes (h^+) can trigger oxidation reactions at a potential considerably reduced than that commonly required at conducting electrodes. These materials can thus be employed as photoanodes, a concept that has attracted a tremendous amount of research for the design of solar-to-fuel photoelectrochemical conversion devices.[3] Among *n*-SCs, $BiVO_4$ has been extensively studied and has emerged among one of the most promising photoanode[4,5] because of its electronic and optical properties (bandgap of ~2.4-2.5 eV), its stability, its non-toxicity and the impressive recent progress made on this material.[6–8] An antagonist concept to SC photoelectrochemistry is electrochemiluminescence (ECL) in which the excited state of molecules is triggered by an initial electrochemical reaction, leading *in fine* to light emission at the solid/liquid interface.[9] ECL involves highly exergonic redox reactions and is a manifestation of the inverted Marcus region. Therefore, it implies usually electrochemical reactions occurring at very negative or positive potentials. ECL provides an outstanding sensitivity and is widely used as a sensing,[10] imaging[11] and diagnosis techniques.[12,13] Merging these two phenomena (i.e. SC photoelectrochemistry and ECL) opens up new possibilities, among which, a considerable decrease in the potential required for light emission and original light conversion schemes. This unique concept, referred to as "photoinduced electrochemiluminescence" (PECL), has been only demonstrated in a few studies.[14–16] In PECL, ECL is induced at the surface of an illuminated SC photoelectrode and the incident wavelength that is used to excite the SC (λ_{exc}) is converted by the ECL reaction to the emission wavelength (λ_{em}). A major challenge of PECL is to overcome the competing photocorrosion mechanisms, particularly pronounced in aqueous electrolytes, which degrade SC electrodes and prevent ECL emission.[17] PECL has been so far reported for designing electrochemically-assisted up-conversion systems ($\lambda_{exc} > \lambda_{em}$) at Si and III-V SC photoelectrodes using organic luminophores dissolved in dried organic electrolytes,[14,15] or, more recently, in water with the co-reactant system $Ru(bpy)_3^{2+}$/tri-n-propylamine. The later example allowed to induce light at a potential of +0.5 V vs Ag/AgCl[16] (all the potentials of this study are reported *vs* this reference electrode) which is much lower than the typical potentials > 1 V typically required with conventional electrodes.[18] In a recent work, Su et al. reported the illumination of the glassy carbon electrodes with a wavelength > 500 nm and the ECL increase of luminol.[19] In the present study, we report the PECL of a luminol analog (L-012: 8-amino-5-chloro-2,3-dihydro-7-phenyl-pyrido[3,4-d]pyri-dazine-1,4-dione)[20,21] at $BiVO_4$ photoanodes in a configuration favorable to L-012 fluorescence (FL). L-012 was selected because it produces brighter ECL emission than luminol. This is the first example of PECL at an oxide photoelectrode, moreover, the system fundamentally differs from previous studies where FL was avoided by using an incident wavelength λ_{exc} higher than the absorption band ($\lambda_{exc} > \lambda_{abs}$) of the ECL emitter.[14-16] Here, we show that anodic PECL of this system can be induced at a potential as low as -0.4 V to amplify the overall luminescence (i.e. FL+PECL) in a precise manner. In the present configuration, FL is generated and PECL enhances the luminescence signal.

The concept presented here is based on the use of a λ_{exc} wavelength, which can photo-excite both the SC and the luminophore. As shown in Figure 1a, when no electrochemical

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potential is applied to the surface (i.e. in open circuit condition), only FL is emitted at the liquid/solid interface, provided that the incident light is transmitted through the $BiVO_4$ surface. However, as depicted in Figure 1b, when a potential (E) is applied, PECL can also be generated on the photoanode, which amplifies the intensity of the light emission. Figure 1c presents the optical features of the key elements of our experiments. The luminophore, L-012, absorbs below 465 nm (purple spectrum) and fluoresces with a maximum intensity at λ_{em} = 503 nm (blue spectrum). We chose a 375 nm light-emitting diode (LED, red spectrum) as an excitation source because it is located below the $BiVO_4$ bandgap (green dashed line of Figure 1c (515 nm), Figure S1) and can induce L-012 FL.

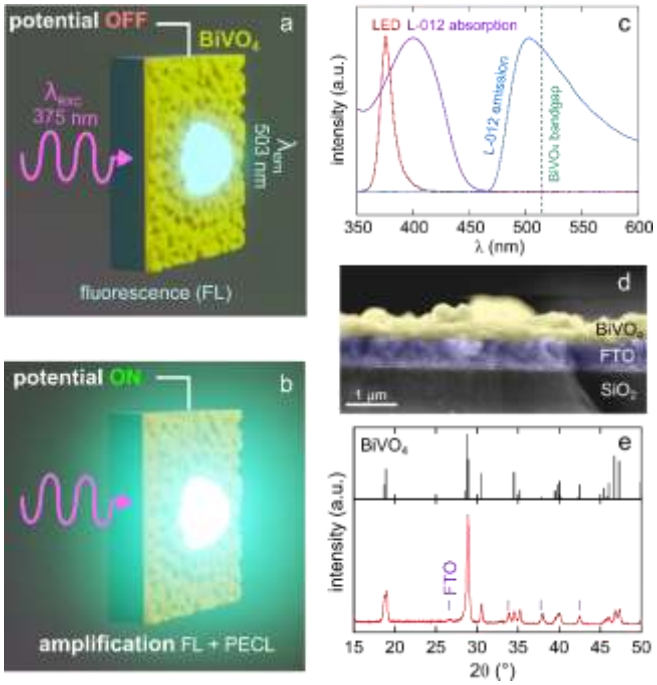


Figure 1. a,b) Schemes illustrating the luminescence amplification principle. In a), FL is generated at a $BiVO_4$/liquid interface when a backside 375 nm illumination is applied. In b), the luminescence is amplified by imposing a potential to the surface which triggers PECL. c) Normalized spectra showing the emission of the LED used in this work (red), L-012 absorption (purple) and the emission of L-012 (blue), the two last spectra were recorded in 0.1 M NaOH with a L-012 concentration of 10 mM. The experimentally-determined bandgap of $BiVO_4$ is represented by the green dotted line. d) Colored SEM cross-section showing the FTO/$BiVO_4$ surface used as a photoanode in this work (scale bar: 1 µm). e) XRD pattern of an FTO/$BiVO_4$ surface (red curve), the top black lines indicate the predicted peak position for $BiVO_4$ (ICSD #100604), the peaks corresponding to FTO (ICSD #39178) are indicated by purple lines.

The $BiVO_4$ layers were deposited on fluoride-doped SnO_2 (FTO) substrates by a previously-reported procedure,[22] which consists in electroplating Bi^0 onto FTO and converting it to $BiVO_4$ by an annealing procedure (see SI for details). Scanning electron microscopy (SEM), presented in Figures 1d and S2 showed that the $BiVO_4$ layer thickness was ~0.6 µm. The crystallinity of the layer was investigated by X-ray diffraction (XRD) measurements, which unveiled the pattern expected for monoclinic $BiVO_4$ (red and black curves of Figure 1e, respectively). Furthermore, photocurrent spectroscopy revealed that our $BiVO_4$ layer had an indirect bandgap[23] of 2.4 eV (Figure S1), in good agreement with the expected theoretical value.[5] UV-vis measurements showed the partial transparency of the SiO_2/FTO/$BiVO_4$ surface in the 350-400 nm range (Figure S3), as required to transmit λ_{exc} to the solution phase (red spectrum in Figure 1c). These surfaces were then employed as anodes in the photoelectrochemical cell depicted in Figure S4 which contained an electrolyte composed of 10 mM L-012 in 1 M NaOH. This cell comprised a LED (λ_{exc} = 375 nm), placed below the FTO side of the photoanode to illuminate it. An optical fiber was positioned above $BiVO_4$ in the electrolyte solution and coupled to a spectrometer. This photoelectrochemical setup allowed to record emission spectra as a function of the incident illumination intensity (P_{LED}) and E.

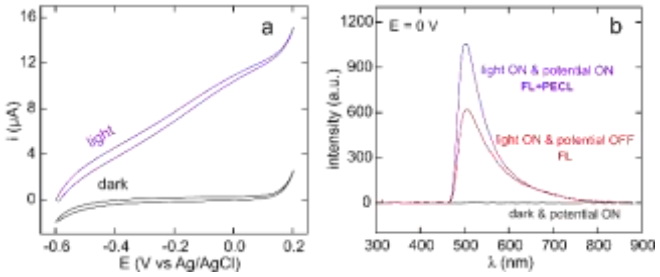


Figure 2. a) CVs recorded at $BiVO_4$ at 20 mV s^{-1} in the dark (black) and under illumination (purple). b) Luminescence spectra recorded at 0 V in the dark (black curve), at open circuit under LED illumination (red curve, FL) and at 0 V under LED illumination (purple curve, FL+PECL). The measurements were recorded with P_{LED} = 15.3 mW (λ_{exc} = 375 nm) in 0.1 M NaOH with an L-012 concentration of 10 mM.

Figure 2a shows cyclic voltammograms (CVs) recorded in the dark and under illumination (dark and purple curves, respectively). While negligible currents were measured in the dark, an anodic photocurrent appeared under LED illumination, suggesting the consumption of the photogenerated holes in an oxidation process. This CV is very similar to those previously reported for $BiVO_4$ photoanodes[5] and demonstrates the photoactivity of our surface under these conditions. The influence of the applied potential on luminescence is clearly shown in Figure 2b. Without LED illumination, no emission was measured regardless of whether a potential was applied (black curve) or not (Figure S5). Conversely, under illumination, intense peaks appeared. The emission at open circuit (red curve) is caused by the L-012 FL and exhibits a maximum at λ_{em} = 503 nm. Remarkably, applying a potential E = 0 V to the $BiVO_4$ surface considerably amplifies the luminescence, resulting in an increase of the luminescence intensity (i.e. λ_{em}) by more than 70% (purple spectrum).

In order to precisely focus on PECL, in the following, the FL spectrum (recorded before each measurement) was subtracted from the overall luminescence (FL+PECL). Figure 3a shows the effect of E on PECL intensity in the -0.4 to 0.1 V range and reveals that PECL increases with potential. Precisely, its intensity raised by 5.5 times in this potential range. It is also striking to observe that PECL could be measured at a potential as low as -0.4 V (Figure 3a, purple spectrum), which is, to the best of our knowledge, the lowest potential ever reported for ECL generation of a luminol derivative. The effect of P_{LED} is also remarkable because it allows controlling the h^+ density and, thus, the photocurrent (Figure S6). In Figure 3b, P_{LED} is varied from 1.3 to 15.3 mW and the potential is kept constant (E = 0 V). This graph shows clearly that P_{LED} has a strong influence on PECL and

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allowed to increase its intensity by more than 13 times. This is, on the first basis, not obvious because FL also increases with P_{LED} (Figure S7). But, as already mentioned, since the FL signal was subtracted from the luminescence spectra (FL+PECL) on Figure 3, these plots illustrate the effects of the imposed potentials (Figure 3a) or of the illumination powers (Figure 3b) on the PECL signal. These results show that FL and PECL phenomena do not scale in the same way and that the latter results in stronger light emission. A series of results, obtained by varying E and P_{LED}, are gathered in Figure 3c, which plots the PECL maximum intensity as a function of these parameters, and clearly illustrate how they influence PECL. While PECL is not generated at low P_{LED}, it becomes very high for high E and P_{LED} values. Quantitatively, the highest amplification was obtained for +0.1 V and 15.3 mW.

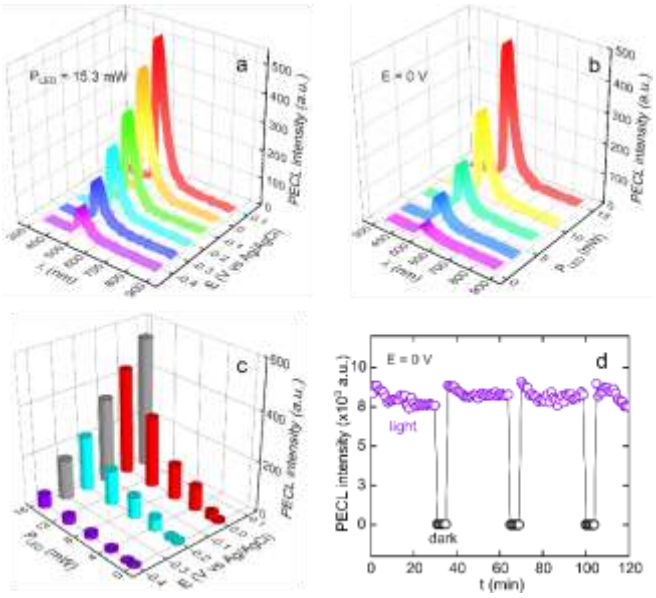


Figure 3. a) PECL spectra recorded with a constant LED illumination at different potentials E. b) PECL spectra recorded at a constant potential (0 V) at different LED illumination power (P_{LED}). c) Graph showing the intensity of the PECL peak as a function of the applied potential and the illumination power. d) Graph showing the PECL intensity as a function of the time at 0 V under intermittent light illumination. PECL spectra were obtained by subtracting the FL spectra recorded under open-circuit potentials from the luminescence spectra (FL+PECL). The measurements presented in panels a) and d) were recorded with P_{LED} = 15.3 mW. All measurements were performed at λ_{exc} = 375 nm in 0.1 M NaOH with an L-012 concentration of 10 mM.

Our electrochemical and spectroscopic data allows to clearly relate the luminescence amplification to the photoanodic activity of $BiVO_4$. At this stage, we rationally assume that PECL is triggered by the direct oxidation of the luminophores and the hydroxyl anions by photogenerated h^+.[4,5,19] Nevertheless, it is also plausible that concomitant photoelectrochemical processes such as a local pH decrease caused by OH^- consumption[24] or H_2O_2 generation,[25] could also play a role in the PECL and we are currently investigating these hypotheses. We finally tested the stability of our system by measuring the PECL intensity as a function of time under intermittent illumination. As reported in Figure 3d, PECL responds instantaneously to illumination and is rather stable at 0 V over 2 h.

In conclusion, we have studied L-012 luminescence at $BiVO_4$ photoanodes using a light source suitable for exciting the luminophore fluorescence as well as the SC photoelectrode. When an appropriate potential is applied to the photoanode, bright emission is obtained with a significant PECL contribution, which increases with the potential, to the overall light intensity. We have shown that, due to the low oxidation potential of L-012, the high photovoltage and the chemical stability of $BiVO_4$, PECL can be induced on the $BiVO_4$ surface at a potential as low as of -0.4 V for several hours. This concept can be employed to precisely tailor L-012 emission and this report constitutes the first example of PECL where $\lambda_{exc} < \lambda_{em}$. We think that this promising concept could find potential applications in biosensing and light-addressable devices.

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Keywords: photoelectrochemistry • bismuth vanadate • electrochemiluminescence • luminol • amplification

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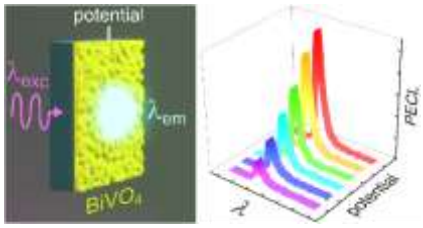
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Photoinduced electrochemiluminescence (PECL) can be induced at $BiVO_4$ photoanodes in an aqueous electrolyte containing a luminol derivative (L-012), at a record potential of -0.4 V. Here, the incident light simultaneously triggers L-012 fluorescence and PECL. We show that the latter process considerably amplifies the luminescence and that the potential control allows to finely tune the overall luminescence.

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