

**Enhancement of Photovoltaic Performance of TiO₂-Based Dye-sensitized Solar
Cells by doping Ca₃La_{3(1-x)}Eu_{3x}(BO₃)₅**

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Preparation of TiO₂ nanoparticle:

TiO₂ colloid was prepared by means of the modified hydrothermal method combined with both the hydrothermal and sol-gel treatments, in which tetraisopropyl titanate was used as a precursor, acetic anhydride as a hydrolysis inhibitor, and the concentrated nitric acid as a peptizing agent. In a typical procedure, a mixture of 7.2 ml tetraisopropyl titanate and 1.6 ml acetic anhydride was added dropwise into 36.0 ml deionized water in a four-neck flask. After stirring for about 1 h, 0.5 ml of the concentrated nitric acid (16 mol/L) was added in drops to the mixture solution, the solution was peptized for 75 min in a water bath with temperature is kept at 80 °C under the conditions of ultrasonic vibration and magnetic stirring. To accomplish a complete hydrolysis reaction, the stirring for 90 min was required. After cooling down, the mixture was diluted with deionized water to final 46.5 ml. The resulting gelatin like was loaded into titanium autoclave and heated at 230 °C for 24 h. Subsequently, the obtained suspension-containing precipitate was diluted with absolute ethanol to 100 ml and thoroughly dispersed under ultrasonic vibration at atmospheric conditions until a homogeneously dispersed and stable colloid appeared. Finally, it was concentrated by a rotary evaporator and was centrifuged to produce a colloidal solution containing 40 wt.% TiO₂ in ethanol.

Table S1 Instrumental parameters of the D₈ Bruker diffractometer used for Rietveld refinements of Ca₃La₃(BO₃)₅ and its derivations phosphors

Primary and second radius	217.5 mm
Receiving slit length	16 mm
Glancing angle	13.65 °
Source and sample length	12 mm
Primary soller slit aperture	2.5 °
Reception slit divergence angle	0.2 °
Receiving slit width	0.1 mm
Peak-shape function	Lorentzian

Table S2 Selected bond distances and bond angles for CLBO HL

Distance(Å)	Angle(deg)		
Ca-O polyhedral coordination (8-CN) ¹			
Ca(1)-O (1)×4	2.45(2) ²	O(4) ⁱ -Ca(1)-O(4) ⁱⁱ	93.63(2)
Ca(1)-O (3)×2	2.39(1)	O(4) ⁱ -Ca(1)-O(1) ^{iv}	80.00(2)
Ca(1)-O (4)×2	2.37(3)	O(3)-Ca(1)-O(3) ^v	144.76(3)
		O(1) ⁱⁱⁱ -Ca(1)-O(1) ^{iv}	92.69(2)
		O(1) ⁱⁱⁱ -Ca(1)-O(3)	77.81(3)
La-O polyhedral coordination (10-CN)			
La(1)-O(1)×4	2.65(2)	O(4) ^x -La(1)-O(3) ^{xiv}	64.58(2)
La(1)-O(2)×3	2.60(3)	O(3) ^{xiv} -La(1)-O(3) ^{xv}	50.71(3)
La(1)-O(3)×2	2.74(3)	O(3)-La(1)-O(1) ⁱⁱ	73.76(2)
La(1)-O(4)	2.56(2)	O(2) ^x -La(1)-O(2) ^{xi}	82.13(2)
		O(1) ^{viii} -La(1)-O(2) ^{xii}	71.37(3)
B-O tetrahedron coordination (3-CN)			
B(1)-O(4)×2	1.36(2)	O(4) ⁱ -B(1)-O(1) ^{iv}	119.76(2)
B(1)-O(1)	1.39(3)	O(1) ⁱⁱⁱ -B(1)-O(1) ^{iv}	120.58(3)
B(2)-O(2)×3	1.39(3)	O(2) ^x -B(2)-O(2) ^{xi}	120.00(2)
B(3)-O(3)×3	1.38(2)	O(3) ^{xiv} -B(3)-O(3) ^v	119.89(2)

¹ Symmetry codes: i) -y+1, x-y+1,z; ii) -x+y, -x+1, z; iii) x-y+1, x, z+0.5; iv) -x+1,-x+y, z+0.5; v)-x+1, -y+1, z+0.5; viii) y-1, x, z-0.5; x) x, y, z-1; xi) x-y+1, x+1, z-0.5; xii) y-1, -x+y, z-0.5; xiv) x-y, x, z-0.5; xv) y, -x+y+1, z-0.5; ² average value.

Figure S1:

Photovoltaic properties of DSSC for the 15 μm thick Eu^{3+} -doped TiO_2 electrodes were measured under a simulated solar light irradiation of $100 \text{ mW}/\text{cm}^2$ as shown in Fig. S1. Obviously, with the increase of CLBO: 0.06Eu^{3+} amount in the DSSC (Fig.S1(a)), the photovoltaic performance has the same tendency with the 3 μm thick Eu^{3+} -doped TiO_2 electrodes as shown in Fig.4(d). However, the doping concentration quenching is different (7% vs. 6%). Meanwhile, the photovoltaic performance is slightly improved as shown in Fig.S1(b) when doped the same amount of CLBO: 0.06Eu^{3+} in the 3 μm thick (red line) and 15 μm thick Eu^{3+} -doped TiO_2 photoelectrode (green line). These phenomena maybe due to the better dispersion or (and) less phase and domain interfaces for the CLBO: 0.06Eu^{3+} in the 15 μm thick Eu^{3+} -doped TiO_2 electrode when compared with 3 μm thick Eu^{3+} -doped TiO_2 electrode (the interfaces can capture photo-generated electrons and holes, hinder the charge carrier transportation, leading to a decrease in photocurrent).

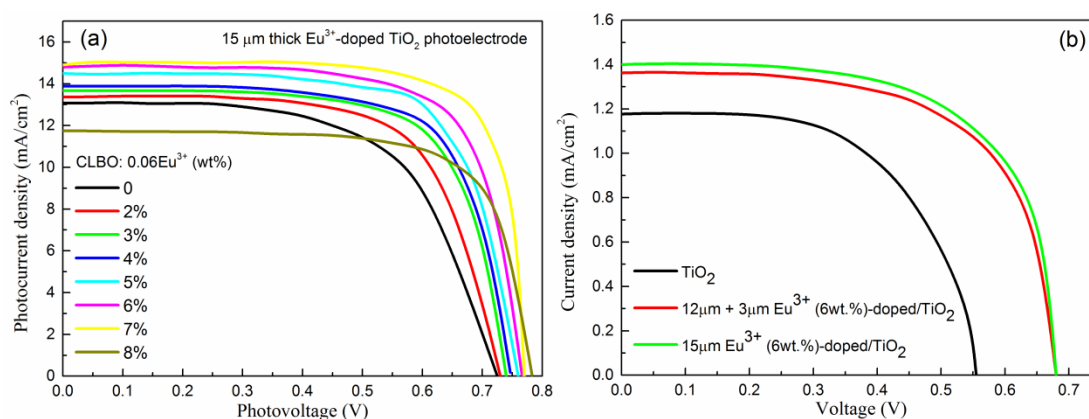


Fig.S1 a) I - V curves of the DSSC contains different amount of CLBO: 0.06Eu^{3+} doping under a simulated solar light irradiation for the 15 μm thick co-sensitized TiO_2 photoelectrodes, b) comparison of the I - V curves of DSSCs without and with CLBO: 0.06Eu^{3+} doping in the forms of 3 μm thick and 15 μm thick Eu^{3+} -doped TiO_2 photoelectrode, respectively.

Figure S2:

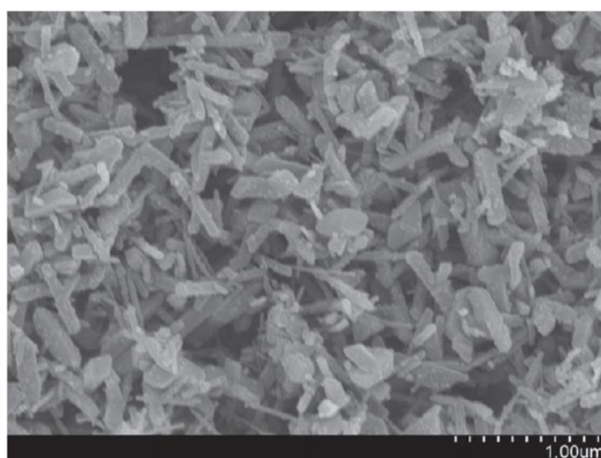


Fig.S2. SEM image of CLBO: 6% Eu^{3+} (2wt.%) doped in TiO_2 film

Figure S3:

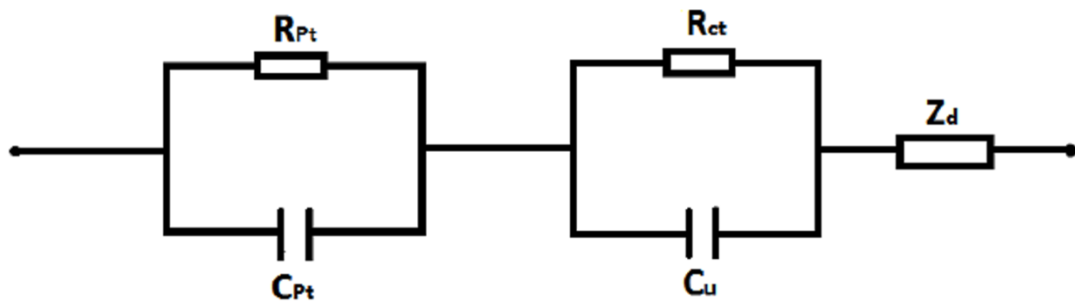


Fig.S3. Simulation circuit to model the DSSC. R_{ct} and C_u stand for the resistance and capacitance on the interface of TiO_2 electrode and electrode, R_{Pt} and C_{Pt} represent the resistance and capacitance on the interface of electrolyte and Pt doped counter electrode, respectively. Z_d is the impedance of I/I_3^- diffusing in electrolyte.