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Increased efficiency and stability of Dye-Sensitized Solar Cells (DSSC) photoanode by intercalation of Eosin Y into Zn/Al layered double hydroxide

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33 **Increased efficiency and stability of Dye-Sensitized Solar Cells (DSSC)** 34 **photoanode by intercalation of Eosin Y into Zn/Al layered double hydroxide**

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42 **Abstract**

43 Layered Double Hydroxides (LDH) are versatile materials that can be applied to different fields.
44 Recently their employment in Dye-Sensitized Solar Cells (DSSCs) technology has been reported.
45 The heart of this technology is the photoanode, a semiconductor layer sensitized with dye molecules
46 able to absorb the sunlight. However, the traditional dye molecules are quite expensive and sensitive
47 to thermal degradation and the sensitization process requires time and costs. The possibility to directly
48 intercalate the dye in the LDH interlayer makes these materials very promising as innovative
49 photoanodes. This aspect in fact would help to reduce both the time and the costs, overcome charge-
50 transfer and recombination phenomena issues and finally increase the Photo-Conversion Efficiency
51 (PCE) and stability. In this work, an Eosin Y-intercalated ZnAl LDH was prepared by coprecipitation
52 and applied as photoanode material. For this purpose, a screen-printing ink was formulated and then
53 applied onto a conductive transparent substrate. Then, complete DSSC prototypes were assembled
54 and tested. A comparison with an analogous LDH intercalated with terephthalate and sensitized with
55 Eosin Y showed a beneficial effect due to the presence of the dye intercalated in the structure rather
56 than adsorbed on the surface, increasing the stability (tested for 1500 hours) and efficiency of the
57 related DSSCs. A 0.11 mA cm⁻² of J_{sc}, 568 mV of V_{oc} and a PCE of 0.019% were obtained for the
58 Eosin Y intercalated LDH based photoanode. Moreover, the interaction between the intercalated dye
59 and the LDH sheets allowed to reduce charge recombination phenomena and thus to increase V_{oc}
60 and PCE values.

61 **Keywords:** Zn/Al Layered Double Hydroxides, Coprecipitation method, Dye-Sensitized Solar
62 Cells (DSSC), dye intercalation, photoanode, light absorption, charge recombination.

63 **Introduction**

Layered double hydroxides (LDH) are anionic clays, with the general formula $M(II)_1-xM(III)_x(OH)_2]^{x+}(A^{n-}_{x/n}).mH_2O$, largely employed in different fields (Cavani et al., 1991a; Xu et al., 2011; Z. Yang et al., 2016; Mishra et al., 2018), from sensors (Baig and Sajid, 2017; Asif et al., 2018; Tang et al., 2020), polymer additives (Jin et al., 2020), drug delivery (Barkhordari and Yadollahi, 2016; Shahabadi and Razlansari, 2018), cosmetics (Li et al., 2017) and absorbers (F. Yang et al., 2016; Abdellaoui et al., 2017; Zubair et al., 2017; Daud et al., 2019) to catalysts and catalyst precursors (Cavani et al., 1991a; Basile et al., 2002, 2004; F Basile et al., 2010; F. Basile et al., 2010; Xu et al., 2011; Monti et al., 2013; Fasolini et al., 2019; Gjyli et al., 2019; Tabanelli et al., 2019), electrocatalysis (Wang et al., 2018), photocatalysis (Mohapatra and Parida, 2016; J. Wu et al., 2018; Rasouli, 2018; Darie et al., 2019; Zhang et al., 2020) and photo-electrochemistry (Arif et al., 2020; Luo et al., 2020; Zhang et al., 2021). An interesting application in which LDH could play an important role and which has not been widely explored yet is as photoanode material for Dye-Sensitized Solar Cells (DSSCs). These solar cells are usually composed of a semiconductor sensitized with a dye molecule, a counter electrode and a liquid electrolyte to close the circuit (Benesperi et al., 2018). Up to now, LDH have been used in DSSCs mainly as gelling agents for liquid electrolytes to increase the device stability (Bastianini et al., 2014; Du et al., 2015). Traditionally, DSSCs photoanode is composed by TiO_2 , sensitized with organic or metallorganic dyes (Bendonì et al., 2016), or, by perovskites (Park, 2015). Recently, due to the high surface area and easily synthetic procedure, different LDH based on NiAl (Foruzin et al., 2019), ZnTi (Liu et al., 2019), ZnAl (Tadanaga et al., 2016; Zhu et al., 2017) and composites with ZnO (Salih et al., 2019) and TiO_2 (Foruzin et al., 2019) were prepared, sensitized with commercial or organic dyes (L. Pinto et al., 2019) and finally tested as DSSC photoanode. Nevertheless, the layered and versatile LDH structure could be used to directly incorporate the dye molecules. This approach helps to overcome the traditional issues related to charge-transfer and recombination phenomena that typically occur at the interfaces TiO_2 /dye/electrolyte that reduce the final Photo-Conversion Efficiency (PCE). Moreover, the long-term stability of the related DSSCs should be improved by incorporating the dye directly in the crystal structure of the photoanode material, thus avoiding the corrosive action of the electrolyte. Finally, the production process of traditional DSSCs would be reduced in terms of time and costs by removing the sensitization step. Literature reports just one work that proposes the intercalation of the active dye inside the interlayers of a ZnAl LDH through a hot water sol-gel process for the application in DSSCs. However, no value of DSSCs efficiency or detailed characterizations were discussed (Tadanaga et al., 2016). Thus, this study aims to provide a deeper understanding of the performances of dye intercalated LDH applied as DSSC photoanodes. Usually, LDH are synthesized using carbonate anions due to the ease of synthesis and the possibility of facile carbonate decomposition by calcination

98 to directly obtain mixed oxides (Cavani et al., 1991b). Nevertheless, any anion can be theoretically
99 intercalated into LDH and a variety of them has been reported (Rives and Angeles Ulibarri, 1999;
100 Costantino et al., 2008; Conterosito et al., 2018), from the more classical NO_3^- and halogens (Meng
101 et al., 2004), or silicates (Albertazzi et al., 2007; Basile et al., 2009) to organic molecules such as
102 terephthalate (Vucelic et al., 1995), dyes (Zaghouane-Boudiaf et al., 2012; Gao et al., 2017; Gao and
103 Yan, 2017a; Gao et al., 2018; Daud et al., 2019; Prasad et al., 2019) or porphyrins (Wypych et al.,
104 2003; Káfuňková et al., 2010) until to cellulose (Kang et al., 2009; Yadollahi et al., 2014; Iftekhar et
105 al., 2017), graphene (Cao et al., 2016; Daud et al., 2016), drugs (Ladewig et al., 2009) or DNA
106 (Desigaux et al., 2006; Oh et al., 2006). Different methodologies have been investigated to produce
107 LDH with the desired anion in the interlayer (Conterosito et al., 2013, 2018). For example, acid-base
108 exchange or diffusion-controlled reactions (Iyi et al., 2011; Conterosito et al., 2013) can lead to the
109 substitution of an anion with an inorganic or organic one. Anions can also be inserted by a
110 reconstruction mechanism, in which an LDH is transformed into a mixed oxide and then immersed
111 in a solution containing the desired anion that contributes to the reformation of a differently
112 intercalated LDH (Guo et al., 2013). The intercalated anion can also be substituted by liquid-assisted
113 grinding in which an LDH is ground in the presence of a small amount of solvent where the target
114 anion is dissolved (Milanesio et al., 2010). However, these methods require a multi-step synthesis,
115 where the desired anion is inserted in a second moment. In this work, we selected the classical
116 coprecipitation of cations into an aqueous solution where the anion is dissolved, as a one-pot, facile,
117 reliable, fast and energy-efficient method to produce LDH for DSSC applications. In particular, a
118 ZnAl-based LDH was selected because this composition is the one suitable for DSSCs application
119 (Tadanaga et al., 2016; Liu et al., 2019; Zhu et al., 2017) and because zinc is one of the most used
120 metal for photoanodes productions (ZnO form). Eosin Y dye (Figure 1) was selected as intercalated
121 anion due to its high absorption coefficient, low-cost and ease of handling, and finally for its metal-
122 free structure. This method is simpler and more easily scalable than one-pot synthesis involving
123 microwave, hydrothermal or sonication, which were thus not considered. The intercalation of Eosin
124 Y in the LDH structure (**LDH-E**) allows to obtain a peculiar interaction between the dye and the
125 inorganic framework, which may favour electron transfer, if compared to the classical surface
126 adsorption of the dye. To prove this, the synthesized LDH was compared with a ZnAl LDH
127 intercalated with a non-dye anion (terephthalate; **LDH-T** Figure 1). Although classical synthesis of
128 LDH incorporates CO_3^{2-} anions in the interlayer, terephthalate anion was chosen in this work for
129 comparison with Eosin, to obtain LDH with similar interlayer height, which may affect the
130 electrostatic and H bond interaction, as well as the photoelectrochemical properties of the materials.
131 The as-obtained powders were characterized by XRD, TEM and TGA and were used to prepare the

screen-printing inks and the correspondent films. These films were used as photoanodes for DSSCs application and deeply characterized from the photovoltaic and electrochemical points of view. Finally, the long-term stability of the obtained devices was evaluated. The PCE and electrochemical properties were found to be higher than the one found in the literature (Tadanaga et al., 2016) demonstrating for the first time the beneficial effects of the direct dye intercalation inside the LDH structure. In particular, a current density of 0.11 mA cm^{-2} , open circuit potential of 568 mV and a PCE of 0.019% were achieved in this work compared with 0.060 mA cm^{-2} and 300 mV reported in the literature (Tadanaga et al., 2016).

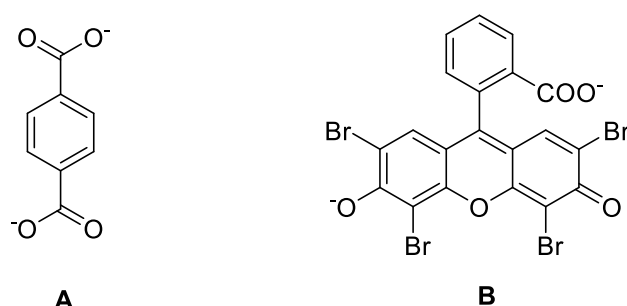


Figure 1. Chemical structure of (A) terephthalate and (B) Eosin anions.

2. Experimental

2.1 Synthetic procedure

The Eosin intercalated and the terephthalate intercalated layered double hydroxides, named **LDH-E** and **LDH-T**, respectively, were synthesized by coprecipitation at constant pH. Eosin Y (99%, Sigma Aldrich, 0.014 mol, 9.09 g,) or sodium terephthalate (99%, Sigma Aldrich, 0.014 mol, 2.97 g,) were dissolved in 140 ml of water kept at pH 9.5. The solution was heated to 60°C and kept under vigorous stirring. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Sigma Aldrich 0.014 mol, 4.17 g) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Sigma Aldrich, 0.007 mol, 2.69 g) were dissolved in 10.5 ml of distilled water and added dropwise to the solution containing Eosin Y or sodium terephthalate. The pH was kept at 9.5 by the addition of a 1.5 M NaOH aqueous solution. The resulting suspension was aged for 1 h at 60°C under stirring. The obtained solid was filtered, washed with distilled water up to neutral pH and dried at 70°C overnight. Distilled water was bubbled with nitrogen for 3 h before the synthesis to remove eventually dissolved carbonates. The solutions were kept under nitrogen atmosphere to avoid the dissolution of CO_2 from air.

2.2 Sample characterizations

159 X-ray diffraction (XRD) analyses were carried out with a Philips PW1050/81 diffractometer equipped
160 with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit (Cu K α , λ
161 =0.15418 nm). A 2 θ range from 5° to 80° was investigated at a speed of 0,05°/s. Low angle analysis,
162 between 2° and 16° (0,05°/s) with narrower slits, had to be carried out in a separate experiment, as
163 the X-ray coming from the source would hit the detector without diffracting, increasing the noise of
164 the analysis. TEM analyses were performed with a TEM/STEM FEI TECNAI F20 microscope
165 combined with Energy Dispersive X-Ray Spectrometry (EDS), at 200 keV. The powder was first
166 suspended in ethanol and treated with an ultrasonic probe for 15 min, then deposited on a “multifoil-
167 carbon film” sustained by a Cu grid. Thermogravimetric analyses (TGA) were performed on a TA
168 Instruments SDT Q600, under air atmosphere (flow rate: 100 ml/min) heating ramp of 5°C/min from
169 25 °C to 200 °C with a dwelling time of 30 minutes at this temperature and at 5°C/min up to 600°C
170 followed by 120 minutes isotherm. Reflectance UV-VIS tests were performed on the as-prepared
171 powders after drying at 70°C in a Perkin Elmer Lambda 19 in the range 180-800 nm.

172 **2.3 Inks formulation and films deposition**

173 Two different screen-printing inks were formulated containing the LDH-T or the LDH-E compound.
174 Screen-printing inks were prepared by mixing the respective powders with organic additives:
175 terpeneol (Sigma-Aldrich) as solvent, lauric acid as dispersant (Merck, Germany), ethyl cellulose as
176 binder (Sigma-Aldrich, Germany) and finally, glycerol (Merck, Germany) as plasticizer. The
177 powders were firstly dispersed in the solvent and the different organics were added to obtain a stable
178 suspension. The as-formulated inks were finally homogenized in a three-roll mill equipped with ZrO₂
179 rollers (Exakt 80E, Exakt, Nordestedt, Germany). LDH based inks were deposited onto TiO₂ blocking
180 layer coated Fluorine-doped Tin Oxide (FTO) glass substrates (sheet resistance 7 Ω /sq, Sigma-
181 Aldrich) using a semi-automatic screen-printer (AUR'EL 900, AUR'EL Automation s.p.a., Italy)
182 (Sangiorgi et al., 2014). The films were dried by an IR thermal treatment performed at 180°C for 3
183 hours to avoid the LDH and Eosin Y degradation. To confirm it, XRD was carried out on the LDH-
184 E powder after the drying at 180°C, which showed that the pattern of the LDH structure was still
185 present and was coherent with the intercalation of Eosin in the interlayer (Figure S1) and showed the
186 same interlayer distance (Figure S2). A lower crystallinity of the reflects related to the 009 Miller
187 index and partially to the 006 were observed due to a partial loss of interlayer water, after the thermal
188 treatment. The thickness of each film was set at 12 μ m as confirmed by profilometry.

189 **2.4 DSSCs assembly**

190 LDH-T and LDH-E photoanodes were kept at 100°C for 30 minutes, in order to eliminate air
191 moisture. The sensitization process on LDH-T was done immersing the photoanodes in 0.003 M

ethanol solutions of Eosin Y dye for 18 hours to assure the complete sensitizer uptake (sample named **LDH-T+Eosin**). A pre-drilled FTO glass, coated with a sputtered platinum thin layer, was used as counter-electrode. After sensitization, the electrodes were assembled into a sandwich-type cell and sealed with a hot-melt gasket made of Meltonix (thickness 25 μm , Solaronix, Switzerland). The electrolyte (Iodolyte Z100, Solaronix, Switzerland) was introduced in the cell via vacuum back-filling through the hole at the counter electrode. Finally, the hole was sealed using a Meltonix (Solaronix, Switzerland) film and a small cover glass. The active area of the solar cells was fixed at 0.25 cm^2 .

2.5 DSSCs tests

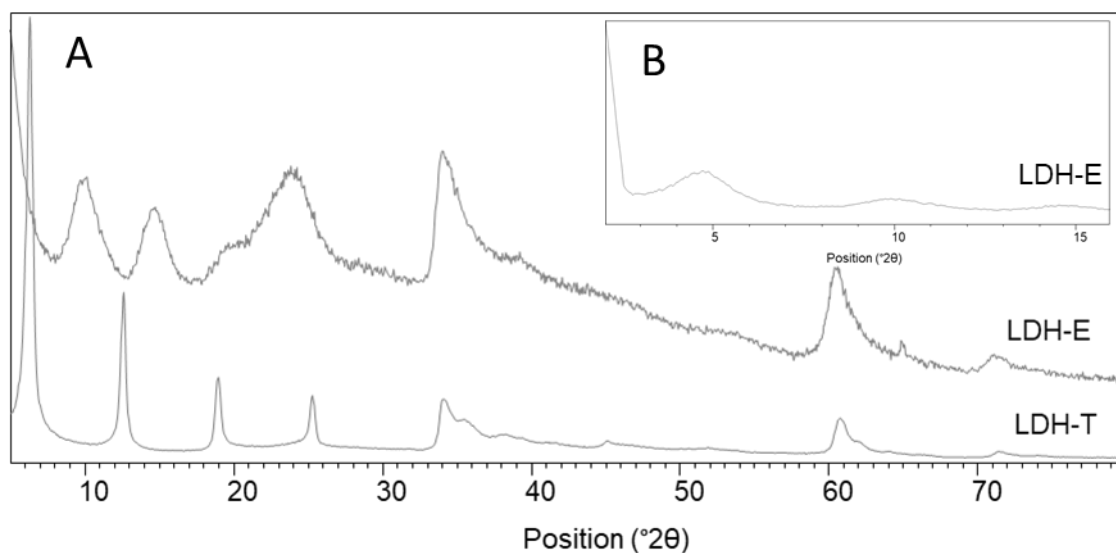
To evaluate the DSSC cells' performance, J-V curves were collected under 1000 W m^{-2} AM 1.5 G illumination (calibrated with a reference standard silicon cell) using an Abet Technologies Solar Simulator (SUN 2000, USA) and a Keithley 2400 source/meter (Keithley, USA). The Incident Photon-to-Current Conversion Efficiency (IPCE) was quantified with an IPCE PVE300 system (Bentham, United Kingdom) with a dual Xenon/Quartz halogen light source, in the wavelength range between 300 and 750 nm. EIS analyses were recorded over a frequency range of 10^5 Hz to 5×10^{-2} Hz with an amplitude of 10 mV at the V_{oc} in the dark. All the electrochemical characterizations were carried out with an AUTOLAB PGSTAT302N-FRA32M (Eco Chemie, the Netherlands) and elaborated using Nova 2.1 software. The EIS analyses were fitted by Z-View software (Scribner Associates). Finally, long-term stability tests were done on the obtained DSSCs. The devices were stored in the dark at room temperature and pressure for 1500 hours and the J-V curves were acquired during the whole period.

3. Results and discussion

3.1. Structure and morphology of the obtained samples

The coprecipitation synthesis was used to produce intercalated Eosin Y (LDH-E) and sodium terephthalate (LDH-T) as anions into the layered double hydroxide structure. Powder X-ray diffractograms of the obtained samples are shown in Figure 2A. Both samples show reflections that are commonly ascribed to the pattern of LDH (Cavani et al., 1991a). In particular, the samples show 6 main reflections centred at 4.6° (003), 10.4° (006), 14.6° (009), 24.1° (0012), 34.1° (0015) and 60.6° (110) for LDH-E and at 6.5° (003), 12.7° (006), 19.1° (009), 25.4° (0012), 34.1° (0015) and 60.6° (0015) for LDH-T. To better identify the low angle peaks of LDH-E, an analysis from 2° to 16° was carried out which is reported in Figure 2B. A good multiple relationship between d values of basal (003), second order (006) and third order (009) reflections is observed, which is characteristic of layered double hydroxide structure and indicative of the width of the interlayer containing the

224 anion (Gao and Yan, 2017b). This value is given by the lattice parameter c , which can be calculated
 225 from the d values of these reflections: $c = 1/3(d_{003} + 2d_{006} + 3d_{009})$. The obtained values are reported
 226 in Table 1. These values highlight a clear difference among the two samples, namely the d values and
 227 consequently the c parameter. In fact, the reflections are shifted toward lower angles for LDH-E. This
 228 results in a higher c parameter which entails a larger gap between the hydroxide sheets of the layered
 229 double hydroxide. As expected, Eosin Y, which is a bigger anion than terephthalate, contributes to
 230 increasing the width of the interlayer. Noteworthy, the lattice parameter c of the two samples is
 231 consistent with the dimension of the two interlayered molecules (Table 1), which further confirms
 232 the success of the synthesis. Another difference found between the diffractograms is the crystallinity
 233 degree, which is correlated to the full width at half maximum of the peaks (FWHM). Average
 234 crystallite dimension was calculated with the Scherrer equation for the reflects at low angles (4.7° ,
 235 10.4° and 14.6° for LDH-E and 6.3° 12.8° and 19.1° for LDH-T), which indicates the crystallite size
 236 in the stacking direction. It resulted to be 5.4 and 21.4 nm respectively. The low intensity of the
 237 reflection and the presence of shoulders did not allow the calculation at higher angles. LDH-T is
 238 highly crystalline while a lower crystallinity degree is displayed by LDH-E. Nevertheless, this
 239 synthetic method allowed to obtain more crystalline materials compared to the sol-gel method
 240 reported in the literature for the preparation of ZnAl-Eosin LDH systems (Tadanaga et al., 2016)



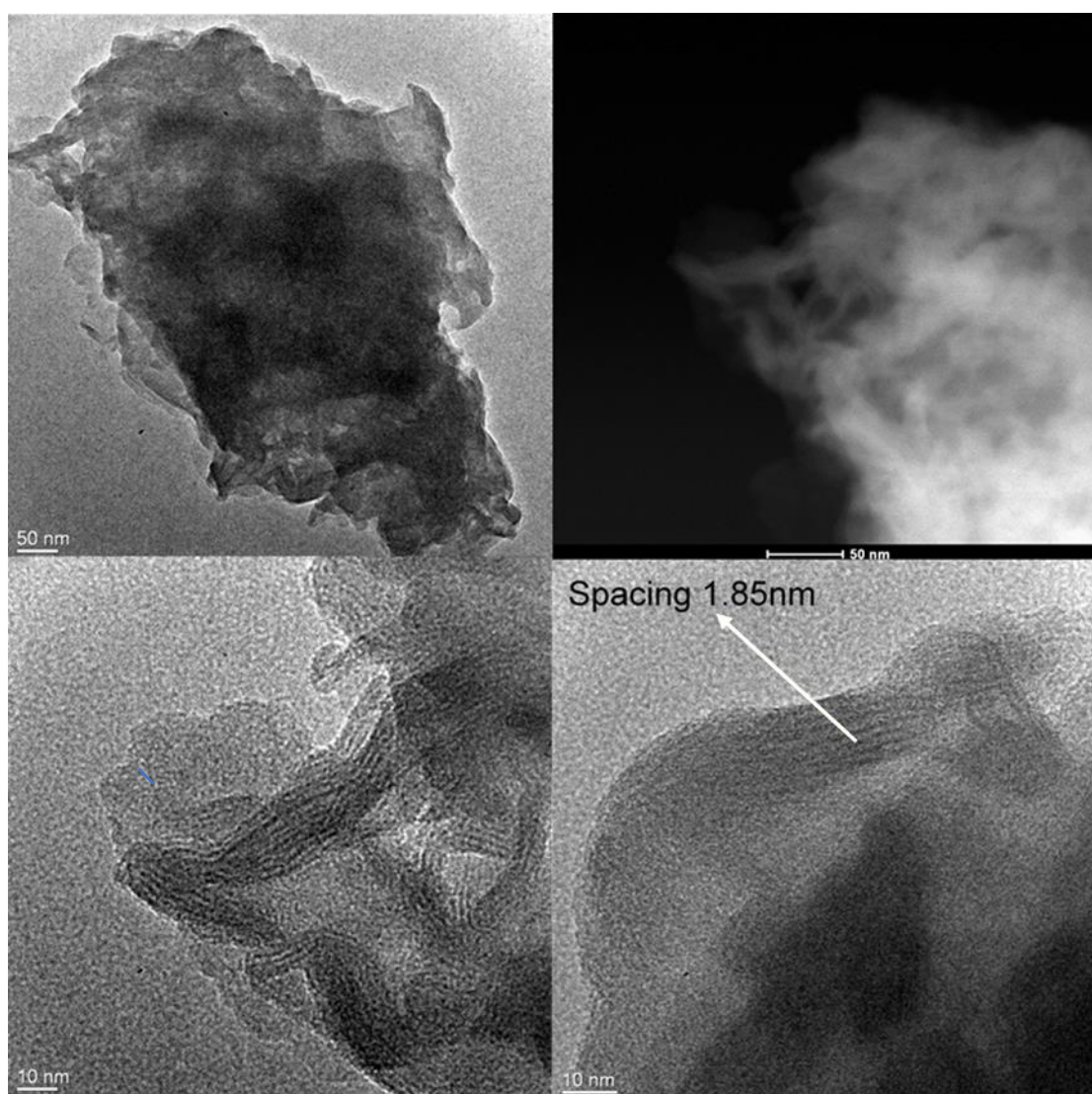
241
 242 *Figure 2. X-ray diffraction analysis of LDH-E (yellow) and LDH-T (red) obtained by*
 243 *coprecipitation: (A) XRD analysis of both samples from 5° to 80° 2θ; (B) XRD analysis of LDH-E*
 244 *from 2° to 16° 2θ.*

245
 246
 247 *Table 1. d values of basal (003) second order (006) and third order (009) reflections and lattice*
 248 *parameter c for LDH-E and LDH-T.*

Sample	d_{003} (nm)	d_{006} (nm)	d_{009} (nm)	Anion dimension (nm)	c (nm)
LDH-E	1.91	0.84	0.60	1.03	1.80
LDH-T	1.38	0.69	0.46	0.70	1.38

249

250 TEM analysis was used to probe the morphology of the LDH-E sample at low scales. This showed
 251 the presence of channels and continuous stacked layers with a wide length. Interestingly, the distance
 252 between the observed layers is 1.85 nm, which is consistent with the lattice parameter c observed
 253 with XRD analysis and the intercalation of Eosin Y molecule.



254

255

Figure 3. TEM images of LDH-E.

256 The thermal stability of LDH-E and LDH-T was evaluated by TGA/DTG (Figure 4). The analysis of
 257 the former shows four degradation steps. The first one, below 200°C, corresponds to the removal of
 258 water from the LDH interlayer (Ahmed et al., 2012). The three other peaks are related to the
 259 dehydration of the hydroxide layer and the decomposition of the Eosin Y anion and hydroxide

decomposition to mixed oxide (Cavani et al., 1991a; Ahmed et al., 2012). In general, the material is stable up to 200°C while a fast decomposition is observed at higher temperatures. LDH-T also shows a weight loss below 200°C due to water loss, together with a sharp reduction in weight around 450°C. The latter is due to the decomposition of terephthalate anion and of the LDH structure as typical for these materials.

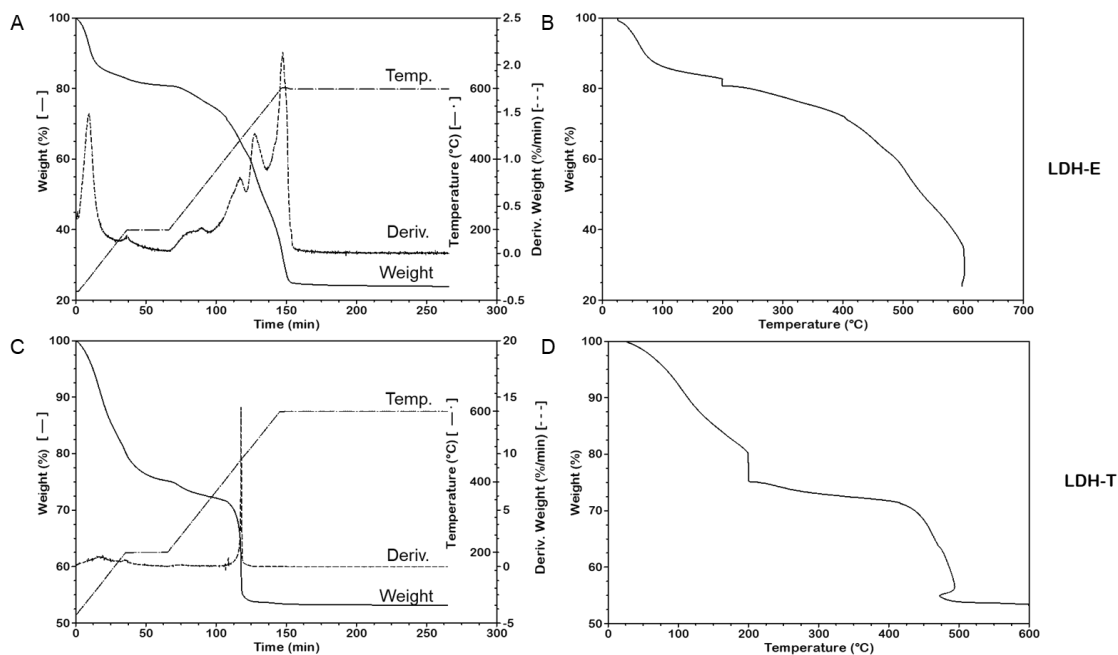
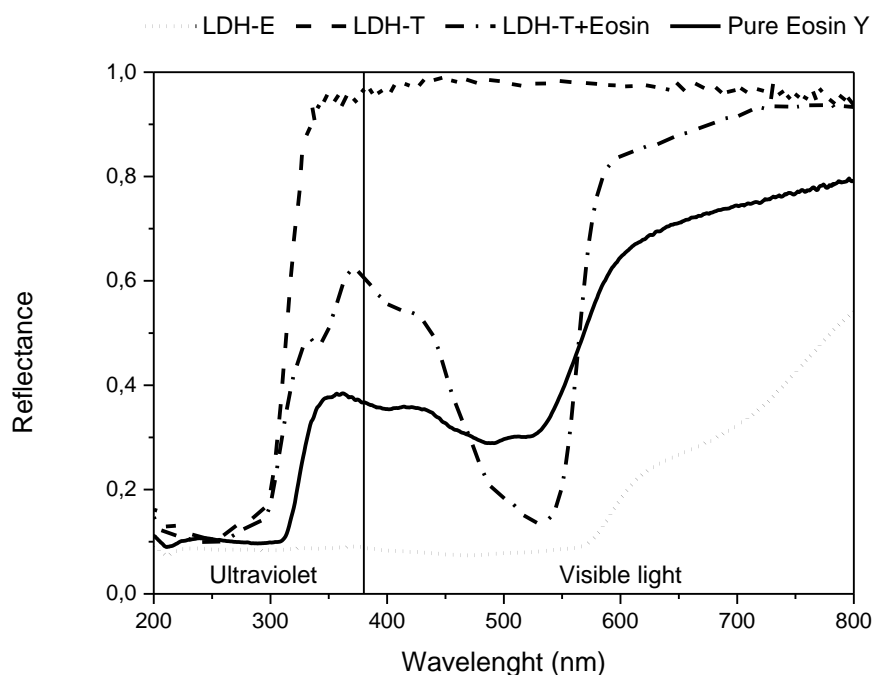


Figure 4. TGA/DTG analysis of LDH-E sample as function of time (A) and temperature (B) and LDH-T sample as function of time (C) and temperature (D).

The optical properties of the synthesized LDH, after drying at 70°C, were evaluated by reflectance spectroscopy. For comparison, pure Eosin Y was also analyzed. Terephthalate containing LDH without Eosin sensilization (LDH-T) showed no absorbance, i.e. total reflectance, in the visible range, while the presence of Eosin Y intercalated into the LDH structure (LDH-E) provided high absorption in the UV range. Pure Eosin Y powder also presented both high absorption below 300 nm and good absorption in the visible range. When sensitized with Eosin Y, LDH-T was characterized by the absorption peak of Eosin Y at around 530 nm, linked with absorption in UV range (L. Pinto et al., 2019). However, the highest absorbance was displayed by LDH-E, which showed a total absorbance in the range of 200-550 nm that slightly decreased above 550 nm. This indicates that the absorption properties of Eosin Y are maintained even when the molecule is inserted inside the LDH structure, making its application as a photoanode possible. Its higher absorbance compared to the

281 sensitized LDH is probably related to the higher amount of Eosin Y that can be loaded on the sample
 282 by exploiting the LDH interlayer.



283

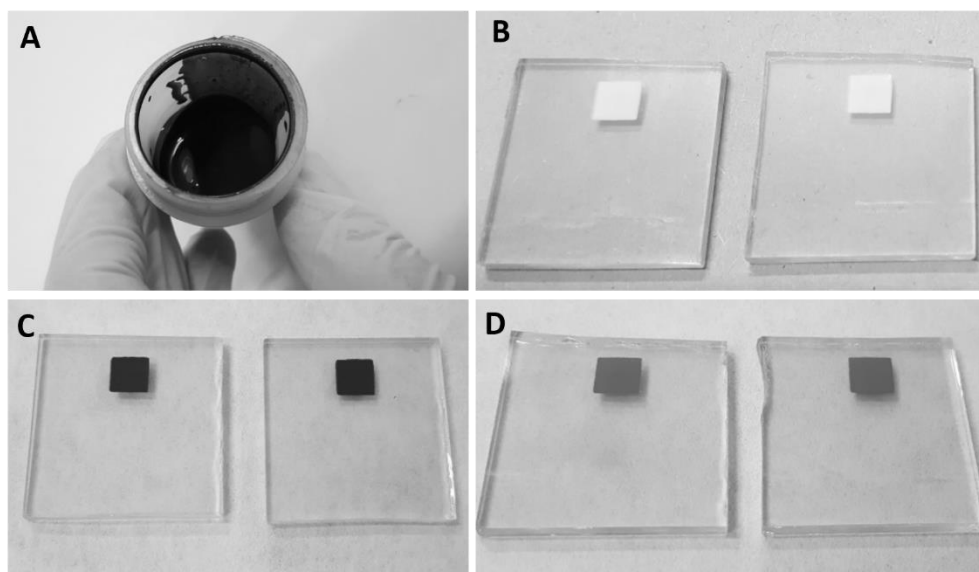
284 *Figure 5. Reflectance spectra of pure Eosin Y, LDH-E, LDH-T and LDH-T+Eosin Y.*

285

286 3.2 DSSCs tests

287 Pictures of the LDH-E based ink, the correspondent screen-printed photoanodes and the ones
 288 produced with the LDH-T sensitized with ink are reported in Figure 6.

289

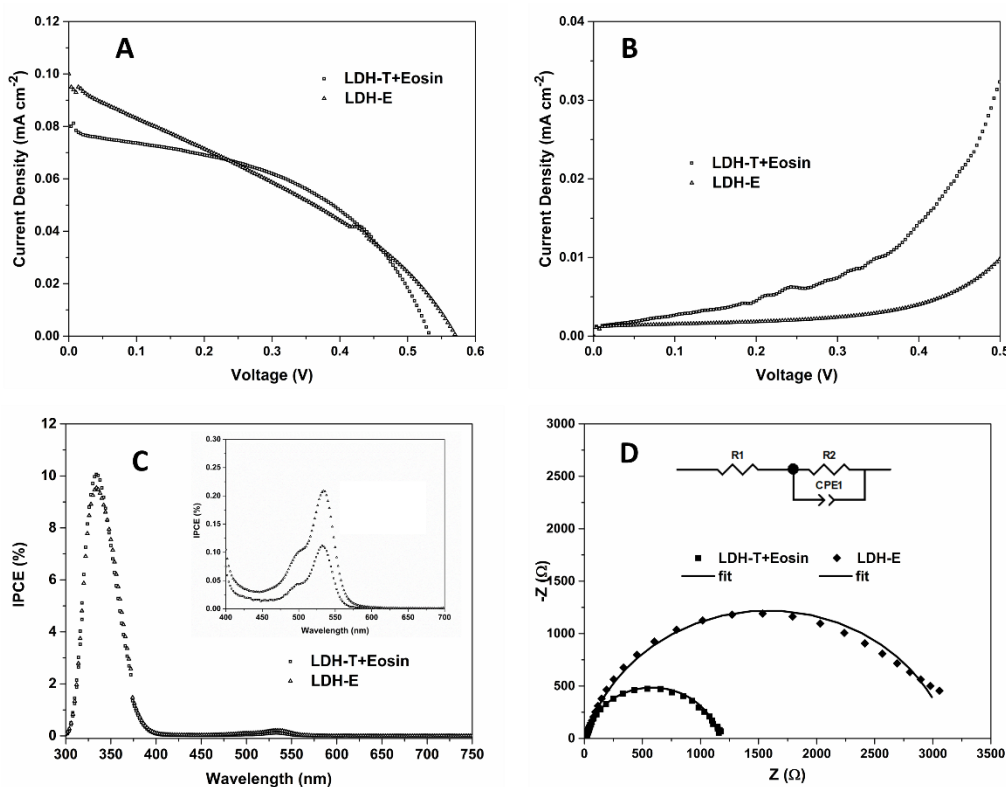


290

291 Figure 6. LDH-E screen-printing ink (A) and the related photoanodes(C), the ones based on LDH-T
 292 (B) and the LDH-T+Eosin (D).

293

294 The Current-Voltage curves in the dark and under illumination are reported in Figure 7 A and B and
 295 the extrapolated photovoltaic parameters are reported in Table 2.



296

297 Figure 7. Current-Voltage curves under illumination (A); in the dark (B); IPCE spectra with
 298 magnification in the region of Eosin Y absorption (C); Nyquist plots acquired in the dark and
 299 equivalent circuit used to fit the experimental points (D).

300

301 Table 2. Photovoltaics parameters, efficiencies (PCEs) and IPCE of the prepared DSSCs.

sample	Jsc (mA cm ⁻²)	Voc (mV)	FF (%)	PCE (%)	IPCE _a (%)
LDH-T+Eosin	0.08	532	46	0.019	0.11
LDH-E	0.11	568	30	0.019	0.21

^a calculated at 534 nm.

302

303 The results reported in Table 2 show that the highest current density value (J_{sc}) was obtained for
304 LDH-E based DSSCs probably due to high light-harvesting produced by the intercalated Eosin Y
305 inside the LDH structure. The IPCE spectra (reported in Figure 7-C and values in Table 2) confirm
306 the trend observed for J_{sc} with the highest IPCE value (0.21 %) obtained for the DSSC based on the
307 LDH-E photoanode. However, the low Fill Factor (FF) value affects negatively the final PCEs of the
308 LDH-E based devices (as highlighted in the J-V curve reported in Figure 7-A). The whole FF values
309 are limited probably due to the low film adhesion on the FTO substrate and the high internal electrical
310 resistance. In fact, the XRD analyses reported in Figure 3 and Table 1 report a low degree of
311 crystallinity for LDH-E material if compared with LDH-T. Moreover, the highest value of Open
312 Circuit Potential (V_{oc}) of 658 mV was achieved for LDH-E photoanode and this behavior is ascribed
313 to the low recombination rate between the photoanode and the electrolyte. In fact, the onset of the
314 dark current curve (Figure 7 B) occurs at lower bias for LDH-T+Eosin based DSSCs while the ones
315 based on LDH-E suppressed the dark current shifting their onset at higher potentials (Bendoni et al.,
316 2015). Moreover, at the same potential, the lowest quantity of dark current was produced by the LDH-
317 E photoanode. The dye intercalation inside the ZnAl LDH structure therefore reduces the
318 recombination phenomena increasing the V_{oc} value. To explain these results in more detail, EIS
319 analyses in the dark were done on the same devices and the Nyquist plots and equivalent circuit used
320 to fit the experimental points are reported in Figure 7-D. The Nyquist plots show for each DSSC a
321 single semicircle at high and medium frequency due to the high impedance of the devices tested. The
322 main components are related to the photoanode and the photoanode/electrolyte interfaces. In fact, in
323 the equivalent circuit reported in Figure 7-D, R1 describes the electrical resistance of substrate and
324 film while R2 and CPE1 describe the charge-transfer resistance and charge accumulation at the
325 photoanode/electrolyte interface. Considering the R2 values, 1148 Ω , and 3139 Ω were obtained for
326 LDH-T+Eosin and LDH-E respectively, suggesting for the latter a slower charge recombination
327 (Dessì et al., 2015; Mátravölgyi et al., 2017). These results confirm the ones related to the dark current
328 density and explain the highest V_{oc} value obtained for LDH-E photoanode due to the beneficial effect
329 of the Eosin Y intercalation. Finally, the stability of LDH-based DSSCs was evaluated and the results
330 about the main photovoltaics parameters are shown in Figure 8.

331

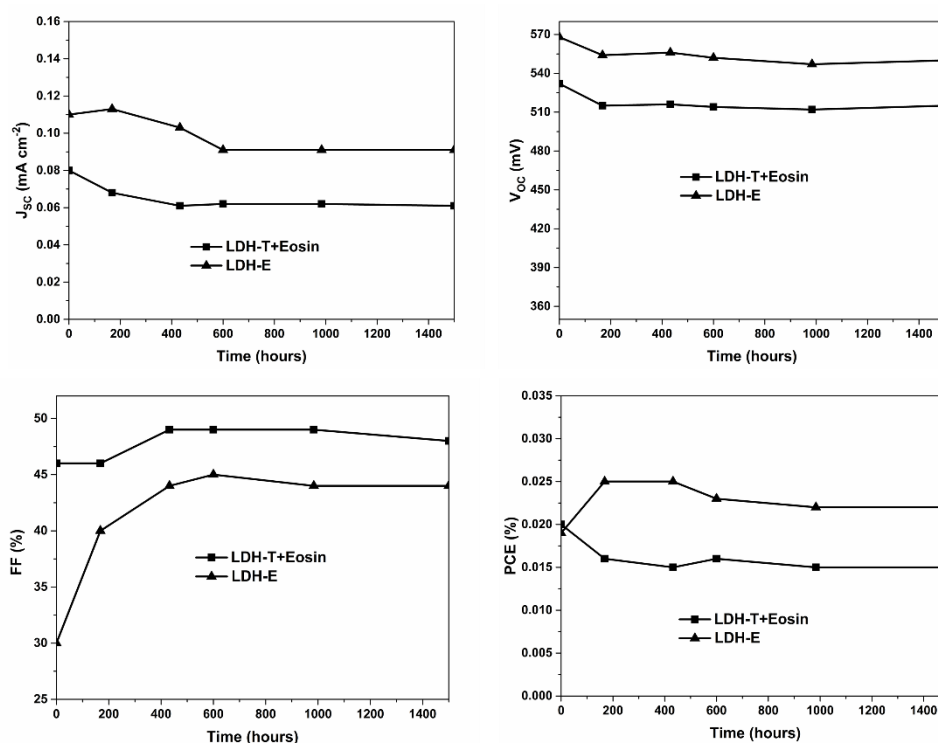


Figure 8. Photovoltaic parameters extrapolated during long-term stability tests (1500 hours).

The results reported in Figure 8 show a higher PCE stability for the DSSCs based on LDH-E than the one based on LDH-T+Eosin. Considering the FF, the device based on LDH-E shows an increase of this parameter during the storage time that finally increases the overall PCE during this time. The same behavior was obtained for J_{sc} that slightly increases for LDH-E devices during the first 200 hours, while it decreases for the LDH-T+Eosin system. These results indicate that an equilibrium occurs between Eosin Y-based photoanodes and the electrolyte after the production of the devices that finally improves their properties. Finally, only the LDH-E photoanode was able to maintain a very stable V_{oc} value up to 1500 hours due to the low amount of recombination inside the cell. The simplified schemes of the working mechanism of the DSSCs based on LDH-T+Eosin and LDH-E are reported in Figure 9.

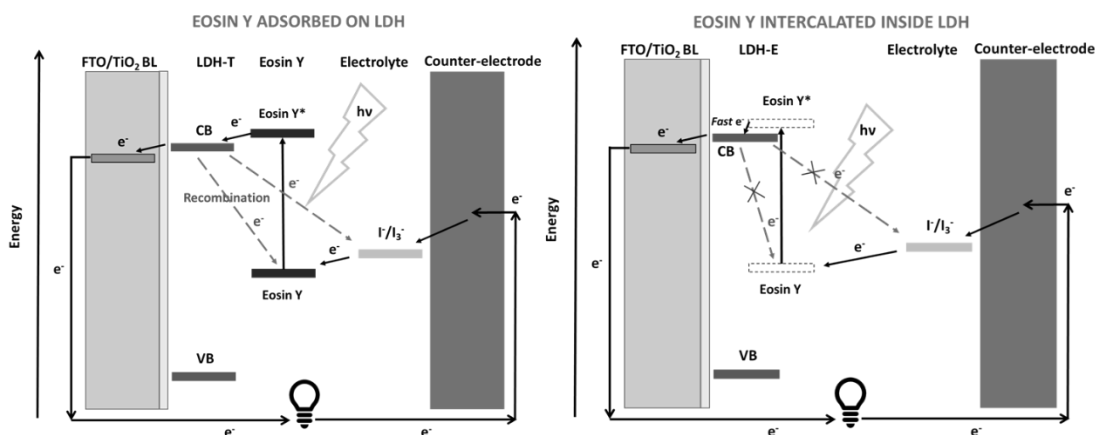


Figure 9. Schematic representation of the working mechanism for DSSCs based on (A) sensitized LDH with Eosin Y (LDH-T+Eosin) and (B) Eosin Y intercalated into LDH (LDH-E).

When Eosin Y is adsorbed on LDH (LDH-T+Eosin, Figure 9A) photons are absorbed by Eosin Y upon illumination and the photo-generated electrons are injected from the excited state of the dye to the LDH conduction band (CB) and flow thorough the external circuit to the counter-electrode. The dye returns to its ground state by electron transfer from the electrolyte (iodide/triiodide redox system) and finally, an electron transfer occurs from the counter-electrode to the electrolyte to close the circuit. However, EIS analyses and dark current curves show high recombination rate between the photo-generated electrons into CB and the ground state of the dye and electrolyte. When LDH-E photoanode is used, (Figure 9B) the intercalation of Eosin Y molecule inside the LDH structure reduces these recombinations and improve the injection rate of the photo-generated electrons, thus leading the highest Voc and current density and to a more stable device. Based on the improved photo-electron injection from the dye to the LDH sheets, we assume that LDH-E can be represented as a hybrid material able to adsorb light (as reported in Figure 5 with Reflectance spectra) and fastly moving charges.

4. Conclusion

LDH-E was synthesized by a facile one-pot method based on coprecipitation and applied as photoanode in DSSCs. For comparison, an analogous terephthalate intercalated ZnAl LDH was also produced and sensitized with Eosin Y, following a more classical approach for photoanode preparation. Characterization of LDH confirmed the insertion of Eosin Y in the interlayer of its structure, as also shown by TEM analysis. TGA indicated that the interlayered structure was stable up to over 200°C. Eosin Y intercalation into the ZnAl LDH structure increased the stability and efficiency of the DSSCs based on this material. The best performances were obtained for the devices based on LDH-E photoanode due to the key role of Eosin Y inside LDH that decreases the amount of charge recombination phenomena thus increasing the V_{OC} of the correspondent DSSC.

For the same reasons, the stability of the DSSCs based on LDH-E photoanode is increased. These results open the possibility to apply this class of materials in the energy production field, in particular as photoanode for DSSCs. However, the PCE should be improved working on both the increase of the LDH crystallinity and the film adhesion onto the substrates.

375

376 Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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380 5. References

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