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COMMUNICATION

First dye-sensitized solar cell with p-type LaOCuS nanoparticles as photocathode

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The layered LaOCuS oxysulfide is a well known wide band gap p-type semiconductors with strong interests for transparent electronics. We report here that nanoparticles of
10 **this material can also be used as a substitute for the widely used NiO compound to fabricate photocathodes for p-type dye sensitized solar cells.**

Transparent conducting oxides (TCOs) have the exceptional propensity to couple two antagonist properties: a high electrical
15 conductivity and a high optical transparency. Such characteristics open up the door to numerous optoelectronic applications such as electrochromic glasses, touchscreen, anti-glare, flat panel displays, anti-static shields, low emissivity glasses, defrosting windows, electrochromic glasses and photovoltaics.[1] Commonly
20 used TCOs are n-type materials belonging to the ZnO-SnO$_2$-In$_2$O$_3$-Ga$_2$O$_3$-CdO classes of compounds. They have successfully reached the level of industrial development as they can be found in many everyday life devices. Nevertheless, new applications in optoelectronics require p-type TCOs such as CuAlO$_2$,[2] CuGaO$_2$,[3]
25 SrCu$_2$O$_2$,[4] which have recently emerged in the literature. These p-type metal oxides are also the candidates for a new generation of dye-sensitized solar cell (p-DSSC), which is much less investigated than conventional Grätzel cells (**Fig. 1**).[5] The most used and most investigated p-type semiconductor (p-SC) for this
30 technology is undoubtedly NiO, while recently doped and undoped CuAlO$_2$,[6] CuGaO$_2$,[7] CuCrO$_2$,[8] NiCo$_2$O$_4$[9] have been proposed to replace it. p-DSSCs are based on a reverse operation principle as Grätzel cell, in which the photoanode (consisting of a n-type semiconductor such as TiO$_2$,[10] ZnO[11]) is replaced by a
35 photocathode made of a dye-sensitized p-type semiconductor (p-SC, e.g. NiO[12]). Upon light excitation an hole is injected from the dye excited state (S*) into the valence band of the p-SC and the reduced dye (S⁻) donates its electron to a redox shuttle, which diffuses to the Pt counter electrode (Figure 1). p-DSSCs have still
40 quite low performances compared to Grätzel cells with a recent record 2.51% photovoltaic conversion (η) currently held by Perera et al.[13] It is accepted that the photovoltaic performances of p-DSSCs can be greatly enhanced if NiO could be replaced by a new p-SC displaying higher transparency, higher hole mobility
45 and deeper valence band potential.[5] In this context, we have investigated LaOCuS oxysulfide as a potential material to prepare p-DSSCs. Indeed, LaOCuS exhibits a higher conductivity, a slighly higher charge mobility (~0.6 cm^2.V^{-1}s^{-1})[14] and a higher transparency in the visible range (60-70%)[15] (see Fig. **S1** in
50 Suplementary Material) than NiO, making it an attractive susbtitute for NiO for this application. Here, we report the first investigations on this material for application in p-DSSCs .
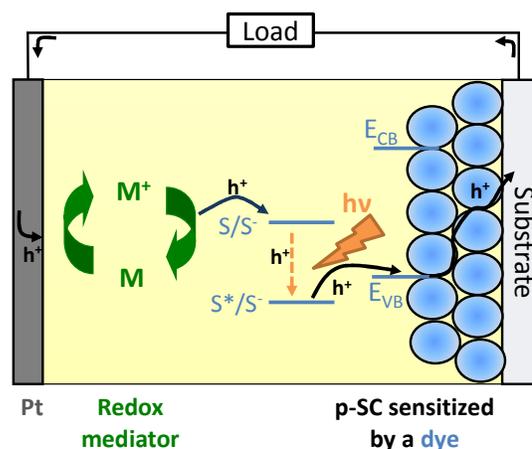

Fig. 1. Schematic operating principle of a p-type dye sensitized
55 solar cell. S=sensitizer, M=redox mediator.

Light grey LaOCuS nanoparticles were synthesized according to the slighltly modified method of Doussier *et al.*[16] where the dehydratation conditions of the LaCl$_3$,7H$_2$O precursor were
60 optimized (namely, 75h at 100°C in an oven). Scanning electron micrographs on as-obtained samples evidenced plate-shaped crystals with typical size 40 nm side and 5-10 nm thick (see **Fig S2** in Supplementary Material). This is inherited from the layered structure of the material commonly described as built upon the
65 regular stacking of [Cu$_2$S$_2$] and [La$_2$O$_2$] infinite layers. The specific surface area, determined by the Brunauer–Emmett–Teller (BET) method, was calculated at 44(1) m^2.g^{-1}, i.e. three times lower than Inframat© black NiO's (158(1) m^2.g^{-1})[7a] which is the reference material in the domain of p-type DSSCs.
70 Electrochemical impedance spectroscopy (EIS) measurements were carried out on pressed (100 bars) and sintered (3 hours at 450°C under nitrogen atmosphere) pellets to determine the flat band potential of LaOCuS in aqueous solution with LiClO$_4$ (1 M) as supporting electrolyte at pH of 6.3. Impedance spectra were
75 obtained under an AC voltage (5 mV in amplitude and a frequency range of 1 Hz to 100 kHz) in a potential range from -0.2 to +0.5 V vs. SCE, and were analysed in order to determine flat band potential (E$_{fb}$) using the Mott-Schottky method at relatively high frequencies (1–10 kHz). The faradic surface
80 phenomena were neglected because they are much slower than the charge-discharge ones (capacitive phenomena) at the semiconductor/electrolyte interface. The whole interface semiconductor/electrolyte capacitance (C) was determined according to the imposed potential (E) by modelling the whole

electrochemical cell with a simplified Randles-equivalent circuit (**Fig. 2a**). This is composed of a series resistance R_S (mainly resistance of the electrolyte and a contact resistance at the interfaces between the copper foil and the pellet, and in between

5 the pellets) and a constant phase element CPE accounting for the non-ideality of the capacitance defined as $Z_{CPE} = 1/(Q(j\omega)^\alpha)$. Q, α, and ω stand respectively for the pseudo-capacitance (perfect capacitor, F/s^α unit, the deviation towards an ideal capacitance (α different of 1) and the angular frequency. In the following, C

10 values vs. E were calculated using the $C = (Rs^{1-\alpha}Q)^{1/\alpha}$ formula [17]. Assuming that $C^{-2} \approx C_{SC}^{-2}$ with C_{SC} the space charge capacity within the space charge layer of the semiconductor, the Mott-Schottky graph was plotted (**Fig. 2b**) according to the eponymous relation for SC,

15
$$\frac{1}{C_{SC}^2} = -\frac{2}{\varepsilon\varepsilon_0 eA^2 N_A}(E - E_{fb} + \frac{kT}{e}) \qquad (1)$$

where A is the interfacial surface area between the semiconductor electrode and the electrolyte, k the Boltzmann constant, T the temperature, e the electron charge, ε_0 the vacuum permittivity and ε the relative permittivity of the semiconductor.

20 The $1/C^2$ vs. E curve is a perfect straight line with a negative slope in agreement with the p-type nature of LaOCuS powdered sample. The flat band potential (E_{fb}) of LaOCuS, was extrapolated from the linear region, and is estimated at 0.26 V/SCE, i.e. 0.07 V lower than that of NiO measured in the

25 identical conditions (see Fig. S3 in Suplementary Material).[7a] At high voltages (i.e. E higher than 0.05 V/SCE), the $1/C^2$ vs. E curve deviates from the linear behaviour. This is attributed to the surface state contribution in Helmholtz layer. Indeed, the inverse of the Helmholtz capacity is not negligible anymore and the

30 Mott-Schottky relation cannot be directly used ($C^{-2} \neq C_{SC}^{-2}$). It leads to the definition of a "pseudo" flat band potential $E_{fb}' = 0.4$ V/SCE (i.e. 0.07 V higher than NiO) directly correlated to the real flat band potential: $E_{fb} = E_{fb}' + \Delta E$. This deviation certainly originates from an ohmic drop ($\Delta E = -0.13$ V) through the

35 Helmholtz layer. Indeed, it was noticed that the series resistance changes with the applied potential in the 0.1-0.4 volt domain. This is most probably related to the adsorption of chemical species on LaOCuS surface or to the progressive dissolution of the inorganic material in contact with water. This would explain

40 the evolution of the C/V curve in the aforementioned voltage domain under cycling and this hypothesis is consistent with the recovery of the initial behavior once the surface was refreshed by polishing.

These intrinsic aforementioned properties of LaOCuS and its flat

45 band potential prompted us to prepare solar cells with LaOCuS particles to assess the possibility to use oxysulfide material as substitute of NiO in p-DSSCs. The LaOCuS nanoparticles were first dispersed in an organic paste as already described[7b] and spread by the doctor Blade method on FTO substrates. The

50 resulting films were sintered at 400°C for 30 min under argon atmosphere in order to remove organic compounds and to neck the particles in order to create a hole percolation pathway. Scanning electron micrographs of a LaOCuS films are displayed in **Fig. 3**. The plan view revealed a large roughness of the surface

55 of the mesoporous films while examination of the cross section led to an average thickness of about 3 μm. Dye sensitized photocathodes were then prepared by coating the above films with the PMI-NDI dyad (a push-pull sensitizer, **Fig. 3c**).[18]
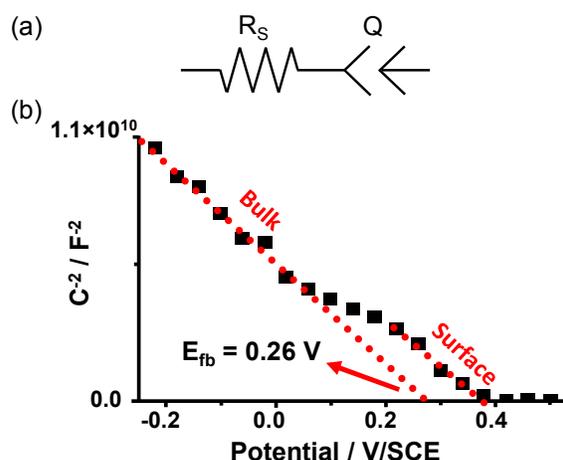
60 **Fig. 2.** Randles equivalent circuit of the SC-electrolyte interface (a) and Mott-Schottky plots for a LaOCuS pellet (electrolyte: LiClO₄ in water; pH= 6.3)(b).

This was realized by immersing the LaOCuS electrodes into a

65 solution of PMI-NDI (0.3 mM in acetone) for 48 hours. The light red colour of the film attests to the adhesion of the dye on the surface of LaOCuS; the surface concentration is nevertheless low. The components were then assembled as described elsewhere[7b] to form the solar cell shown in **Fig. 3e**. The photocathode/polymer

70 spacer (25 μm, Surlyn)/platinum-coated FTO glass were stacked together and sealed by heating under pressure, the interspaced layer was filled *via* a drilled hole (by vacuum backfilling technique)[19] with cobalt-based redox mediator (**Fig. 3e**), namely a
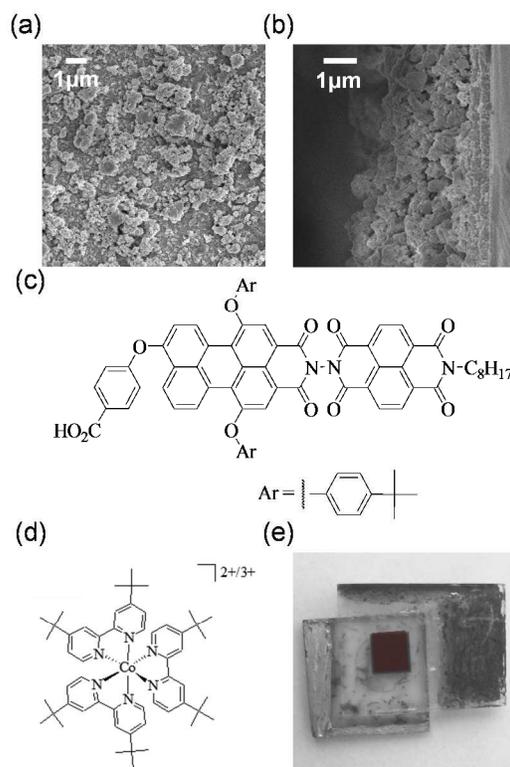
75 **Fig.3**. Plan-view (a) and cross-sectional (b) SEM micrographs of LaOCuS on FTO, structure of the PMI-NDI sensitizer (c), cobalt complex redox mediator (d) and picture of the p-DSSC (e).

mixture of 0.1 M tris(4,4′-bis-tert-butyl-2,2′-bipyridine)cobalt(II/III) (redox potential around 0.11 V/SCE) and 0.1 M LiClO$_4$ in propylene carbonate and the hole was isolated with a glass disk by sealing with a hot melt polymer gasket (60
5 μm, Surlyn). The use of the I$^-$/I$_3^-$ redox mediator was not considered here due to its reactivity with LaOCuS.

Current-voltage characteristics recorded in the dark and under AM1.5 illumination (1000W/m^2) for two p-DSSCs prepared from different LaOCuS batches are depicted in **Fig. 4**. The
10 examination of the J/V curves clearly evidence the photovoltaic effect of LaOCuS photocathodes. No photocurrent was observed in absence of light, while a J$_{SC}$ of about 0.039 mA/cm^2 is measured under illumination supports effective hole photoinjection in LaOCuS valence band from the dye as it occurs
15 in NiO based p-DSSCs. However, at this stage the J$_{sc}$ value remains much lower than that measured with NiO-based DSSCs in the same conditions. This is certainly related to the weaker specific surface area of LaOCuS film and consequently to the lower quantity of dye chemisorbed on its surface. In addition, it is
20 conceivable that the carboxylic binding group on the dye has a lower affinity for LaOCuS than NiO inducing a lower dye coverage of the film.
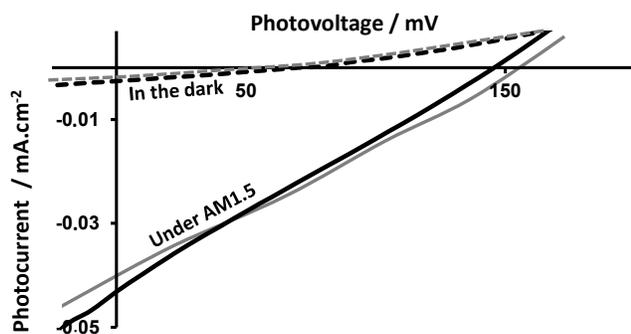
Photovoltage / mV

25
Fig.4. Current/voltage characteristics of two solar cells recorded in the dark (dash line) and under AM1.5 illumination (straight line) with LaOCuS photocathode, PMI-NDI dyad as sensitizer, and tris(4,4′-bis-tert-butyl-2,2′-bipyridine)cobalt(II/III)/LiClO$_4$ in
30 propylene carbonate as redox mediator.

The open circuit voltage (V$_{OC}$ ≈ 150 mV) is also lower than the best values obtained with NiO-based devices (285-375 mV) prepared with identical components.[7a,20] Since the flat band
35 potential of NiO and LaOCuS are close, this points to high losses by electron-hole recombinations in the present system decreasing the Fermi level of the SC under illumination.

To sum up, we have demonstrated the successful implementation of an oxysulfide material: LaOCuS as photocathode in p-DSSCs.
40 The position of its valence band potential is very similar to that of NiO allowing effective hole injection from the photo-excited PMI-NDI sensitizer. However, the attained photovoltaic characteristics of LaOCuS based solar cells (V$_{OC}$ ≈ 150 mV, J$_{sc}$ ≈ 0.039 mA/cm^2, ff ≈ 26%, η ≈ 0.002%) (see Table S1 in
45 Suplementary Material for comparison with a NiO-based DSSC fabricated with the same dye and electrolyte) could be greatly improved with films of higher surface areas and with dyes having higher binding affinities for this semiconductor. In that respect LaOCuS based p-type DSSCs might become valuable alternative
50 to NiO-based devices.

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55 ## Notes and references

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