A Sulfide/Polysulfide-Based Ionic Liquid Electrolyte for Quantum Dot-Sensitized Solar Cells

Vasko Jovanovski,[†,‡] Victoria González-Pedro,[§] Sixto Giménez,[§] Eneko Azaceta,[†] Germán Cabañero,[†] Hans Grande,[†] Ramon Tena-Zaera,*[,†] Iván Mora-Seró,*[,§] and Juan Bisquert[§]

[†]CIDETEC-IK4, Paseo Miramón 196, 20009 Donostia/San Sebastian, Spain
[‡]Analytical Chemistry Laboratory, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
[§]Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain

S *Supporting Information*

ABSTRACT: Further development of quantum dot-sensitized solar cells (QDSCs) will require long-term stability in addition to the continuous increase of photovoltaic (PV) conversion efficiency achieved in the last years. We report a robust S^{2-}/S_n^{2-} electrolyte that has been specifically designed for compatibility with CdSe quantum dots in sensitized solar cells. The new pyrrolidinium ionic liquid reaches 1.86% efficiency and a short-circuit current close to 14 mA·cm^{-2} under air-mass 1.5 global illumination and improves the device lifetime with good photoanode stability over 240 h. PV characterization showed that the solar cell limitations relate to poor catalysis of regeneration at the counter electrode and high recombination. Further improvement of these factors in the robust electrolyte configuration may thus have a significant impact for advancing the state-of-the-art in QDSCs.

The demand for clean energy technologies has spurred academic and technological interest in new and efficient ways to generate electricity from renewable natural resources. Among innovative photovoltaic (PV) approaches, semiconductor-sensitized solar cells (SSSCs), including quantum dot-sensitized solar cells (QDSCs), have exhibited a rapid evolution in energy conversion efficiency in the past few years and are now attracting growing research interest. Since SSSCs possess strong similarities to dye-sensitized solar cells (DSCs), the impressive background gained in the last two decades on the latter may serve to accelerate the advancement of SSSCs. However, electrolytes containing I^-/I_3^-, which show the highest performance in DSCs, cannot be used in SSSCs because of their corrosive character. Electrolytes containing alternative redox pairs, such as S^{2-}/S_n^{2-} and $[Co(o$-phen$)_3]^{2+/3+}$, have thus been proposed for SSSCs. Here, a pyrrolidinium ionic liquid (IL)-based electrolyte containing S^{2-}/S_n^{2-} is introduced to be used in CdSe QDSCs, improving the device lifetime and reaching a conversion efficiency of 1.86% and short-circuit currents close to 14 mA·cm^{-2} under air-mass 1.5 global illumination, with good photoanode stability over 240 h. Moreover, the present IL electrolyte may be used in other devices such as chalcogenide-based photoelectrochemical solar cells to solve their stability limitations. The present results

may thus have a significant impact not only for enhancing the strengths of new PV approaches but also for solving the weaknesses of old concepts.

Metal oxide-based sensitized solar cells have attracted considerable attention in the recent past. ILs became a vital part of electrolytes in DSCs,[1,2] also showing promise for other electrochemical devices where nonvolatility, nonflammability, and high ionic conductivity are in high demand. Research areas where ILs have become invaluable also include lithium batteries, fuel cells, double-layer capacitors, and actuators.[3] The I^-/I_3^- redox couple has played a central role in charge transport in DSCs, first dissolved in organic solvents[4] and later in ILs.[1,2] The inorganic semiconductor sensitizers[5–9] are now emerging as appealing alternatives to organic dyes because they exhibit a relatively high molar extinction coefficient and efficiently absorb a broader portion of the solar spectrum. QDs are also especially interesting because of their potential multiple exciton generation,[10] opening wide possibilities for further enhancement of the conversion efficiency. However, the I^-/I_3^- electrolytes cannot be used for solar cells sensitized with inorganic semiconductor light absorbers[11] such as chalcogenide QDs because of the highly corrosive nature of polyiodide species,[11,12] unless they are protected with a TiO_2 coating.[13] Therefore, alternative redox couples such as $Fe(CN)_6^{4-/3-}$ [14] and S^{2-}/S_n^{2-} [7,9,15] in aqueous media and $[Co(o$-phen$)_3]^{2+/3+}$ [16] in organic media have been proposed as alternative electrolytes. Although the aqueous S^{2-}/S_n^{2-} electrolyte is the most frequently used when investigating QDSCs,[7,9,15] this redox couple remains poorly defined because of the complex chemistry of sulfur species in water, leading to gradual disproportionation reactions generating sulfide and oxosulfur species (SO_3^{2-}, SO_4^{2-}) and thus consuming the redox couple. Moreover, the eventual corrosion of the chalcogenide compounds in aqueous electrolytes was pointed out as a major problem of photoelectrochemical cells based on single-crystal or polycrystalline layers of CdSe.[17] IL-based electrolytes containing redox couples compatible with inorganic sensitizers thus appear to be highly attractive not only for enhancing the robustness and performance of innovative solar cell architectures such as QDSCs but also to surpass the limitations of old concepts and therefore revive their strong potentials.
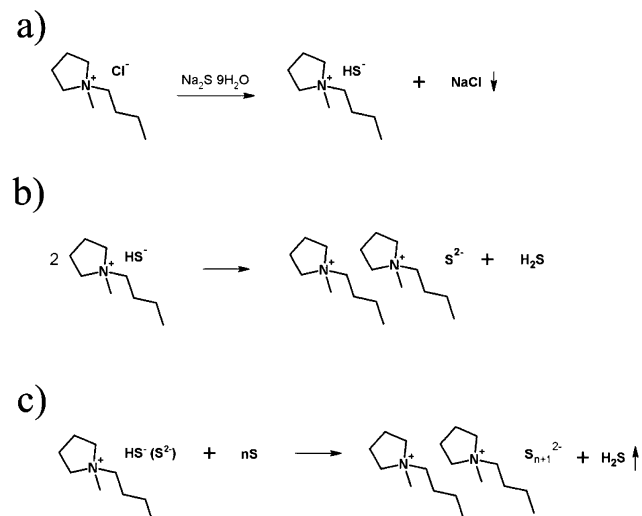
 20156

In view of the above, the first-ever pyrrolidinium IL comprising sulfide anion was synthesized and tested as a key component of a redox electrolyte for QDSCs.[18] It was prepared by anion exchange of 1-butyl-1-methylpyrrolidinium chloride and $Na_2S \cdot 9H_2O$ in methanol/acetonitrile (Scheme 1a). Since

Scheme 1. (a) Synthesis of 1-Butyl-1-methylpyrrolidinium Sulfide; (b) Equilibrium Scenario for HS^- and S^{2-}; (c) Formation of the IL S^{2-}/S_n^{2-} Redox Couple

a)

b)

c)

Figure 1. Cyclic voltammetry of 1-butyl-1-methylpyrrolidinium sulfide: (a) pure, (b) containing an equimolar amount of sulfur, and (c) diluted with 2 equiv of a 1:1 acetonitrile/valeronitrile solvent mixture.

Table 1. Ionic Conductivities (λ) and Diffusion Coefficients (D) of IL Electrolytes^a

	electrolyte composition		
parameter	IL	IL + sulfur	IL + sulfur + solvent
λ (mS/cm)	7.4	6.4	8.9
D (cm^2/s)	4.7×10^{-8}	4.9×10^{-8}	2.9×10^{-7}

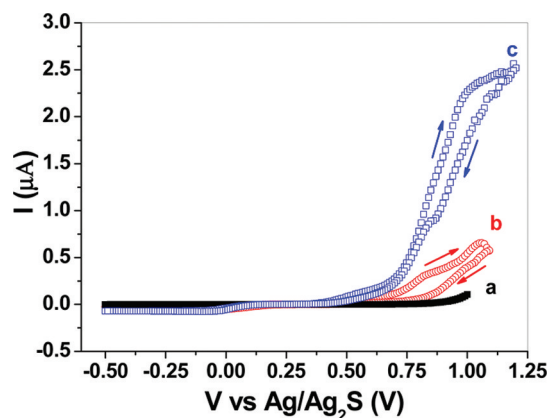^{a}Compositions are the same as in Figure 1. The solvent was 1:1 (v/v) acetonitrile/valeronitrile.

the highly predominant sulfide species in protic solutions is HS^-,[19] exchange of monovalent Cl^- takes place with monovalent HS^-. The driving force for this exchange is formation of NaCl, which precipitates from the aforementioned solution. This solvent mixture proved best for removing traces of chloride originating from the initial IL. The novel sulfide IL was then isolated in vacuo and analyzed. More details can be found in the Supporting Information (SI).

The analysis of the cation is unambiguous (Figure S1 in the SI), whereas it is believed that the anion is composed of an equilibrium between HS^- and S^{2-} (Scheme 1b). The types of anion and especially the ratio between them are rather difficult to determine with precision. Molecular sulfur was dissolved in the sulfide IL, leading to the formation of the S^{2-}/S_n^{2-} redox IL. The dissolution of molecular sulfur was accompanied with the formation of H_2S gas, indicating the instability of HS_n^- and the formation of S_n^{2-} (Scheme 1c).

The novel IL S^{2-}/S_n^{2-} redox couple was studied electrochemically and with several spectroscopic techniques. Cyclic voltammetry (Figure 1) showed that the oxidation potential of the sulfide IL (curve a) was at 1.0 V vs Ag/Ag_2S, which is comparable to the oxidation potential of 1-methyl-3-propylimidazolium iodide (0.9 V vs Ag/AgI)[20] measured in the same manner using a Pt microelectrode. The oxidation potential of the IL with an equimolar sulfur ratio was shifted to 0.8 V with a severe increase in current, signaling the formation of a redox couple as shown in Figure 1, curve b. A further drastic increase in the current was observed after the addition of the solvent mixture (1:1 v/v acetonitrile/valeronitrile), as depicted in Figure 1, curve c.

Measurements of the ionic conductivity (λ) revealed unusually high conductivity for the rather viscous initial sulfide IL (Table 1). For comparison, λ was ~4 times higher than for the analogous iodide IL.[21] The high λ for the sulfide IL could

be attributed to the high proton conductivity[22] via the Grotthus mechanism by proton hopping from one sulfur to another (H−S$^-$⋯H). The loss of HS^- anions in the form of H_2S and the formation of S^{2-} (Scheme 1b) could be the main reason for the drop in λ after the addition of sulfur (Table 1).

To corroborate this assumption, diffusion coefficients (D) of sulfide-related species were estimated (see the SI). They confirmed that sulfide was not behind high conductivity of the sulfide IL, as D was nearly 3 times lower than for the iodide IL.[23] With the addition of an equimolar amount of molecular sulfur, D was nearly unaffected (increased by only 4%). This observation reinforces the hypothesis that loss of HS^- is a main cause of the decrease in λ for the S^{2-}/S_n^{2-} redox IL with respect to the sulfide IL. However, with the addition of solvent, D increased dramatically (nearly 6-fold; Table 1). By correlating the λ and D values, we can conclude that the ionic conduction in the sulfide IL occurs mainly via the Grotthus mechanism. However, upon addition of sulfur, the contribution of sulfide-related species becomes significant, especially in electrolytes containing organic solvents.

PV characterization of CdSe-sensitized solar cells using the S^{2-}/S_n^{2-} redox IL-based electrolyte was carried out, and the results are summarized in Figure 2 and Table 2. TiO_2 photoanodes were used to prepare the solar cells. TiO_2 was sensitized with CdSe grown by successive ionic layer adsorption and reaction (SILAR), with a final coating of ZnS. Platinized conductive glass was used as the counter electrode, allowing the sealing of the cell. The S^{2-}/S_n^{2-} redox IL was tested in its pure form (pure, i.e., sulfide IL + sulfur) and diluted 1:2 (w/v) or 1.7 M in 1:1 (v/v) acetonitrile/valeronitrile (1−2). A dramatic 44% increase in PV conversion efficiency was obtained after dilution of the IL (1.86% vs 1.29% for the pure IL). This increase streams from the higher open-circuit voltage (V_{oc}) (0.42 vs 0.38
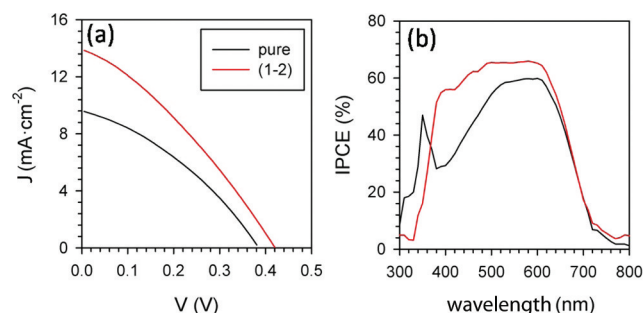
Figure 2. (a) Current density–voltage (J–V) curves under 1 sun illumination and (b) incident photon to current conversion efficiency (IPCE) for SSSCs using the IL in its pure form and diluted with 2 equiv of 1:1 (v/v) acetonitrile/valeronitrile.

Table 2. PV Parameters of the Solar Cells Tested with the Pure IL and the IL Diluted in 1:1 Acetonitrile/Valeronitrile[a]

	V_{oc} (V)	J_{sc} (mA/cm^2)	J_{sc}^{IPCE} (mA/cm^2)	FF	η (%)
pure	0.38	9.57	9.01	0.35	1.29
1–2	0.42	13.85	10.51	0.32	1.86

[a]Abbreviations: V_{oc}, open-circuit voltage; J_{sc}, short-circuit current density; FF, fill factor; η, efficiency. The theoretical short-circuit current obtained after integration of the IPCE with the AM1.5 spectrum (J_{sc}^{IPCE}) is also included.

V) and especially from the higher short-circuit current density (J_{sc}) (13.85 vs 9.57 mA/cm^2).

In addition to the J–V measurements, J_{sc} was also estimated by integrating the spectral response of the device, characterized through the incident photon to current conversion efficiency (IPCE) measured under relatively low illumination (Figure 2b). Although relatively higher estimated and measured J_{sc} values were obtained for diluted electrolytes, the differences are lower for the J_{sc} estimated from the IPCE. This observation suggests that diffusion limitations may be significant in the pure S^{2-}/S_n^{2-} redox IL under 1 sun illumination. The discrepancy between the estimated and measured J_{sc} values can be attributed to two different effects. A light reflecting surface after the cell was used for J–V measurements. In addition, since the illumination intensity was considerably higher for measurement of the J–V curves, the role of thermal effects on the properties of the IL, particularly viscosity and hence diffusion of ionic species, was also important in the photocurrent increase. In fact, J_{sc} increased with a light soaking. The photocurrents reported in Table 1 were obtained after 20 min of light soaking. In this context, it is worth mentioning that $D > 3 \times 10^{-7}$ cm^2/s was measured for the pure S^{2-}/S_n^{2-} redox IL at 50 °C, which may be close to the device temperature under the simulated sunlight.

To understand further the PV performance of the tested solar cells, impedance spectroscopy (IS) characterization was carried out. This technique allows the separation of the individual contributions of the different elements of the PV device (sensitized electrode, counter electrode, diffusion in the electrolyte, and resistance at the contacts for each applied voltage bias, V_{app}).[24] The chemical capacitance (C_μ) and recombination resistance (R_{rec}) were extracted from IS measurements using a previously developed model.[8,24,25] In Figure 3a, C_μ is plotted against the voltage drop at the sensitized electrode, V_F, determined by subtracting from V_{app} the voltage drop at the series resistance ($V_F = V_{app} - V_{series}$).
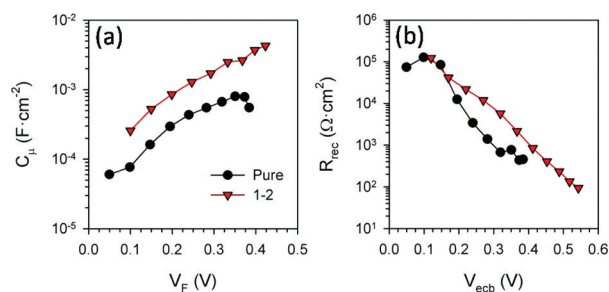
Figure 3. (a) Chemical capacitance (C_μ) vs electrode potential (V_F) and (b) recombination resistance (R_{rec}) vs equivalent conduction band potential (V_{ecb}) for QDSCs using the pyrrolidinium IL in its pure form and diluted with 2 equiv of 1:1 acetonitrile/valeronitrile.

The slope of C_μ reflects the exponential density of states of TiO$_2$.[24,26] Since no significant shift in the potential onset of the oxidation waves from the pure and diluted S^{2-}/S_n^{2-} redox IL was detected by cyclic voltammetry (Figure S2), the 0.12 V offset between the two capacitance curves (Figure S3) points out the downshift of the conduction band of TiO$_2$ after electrolyte dilution. This behavior was observed previously after surface modification of TiO$_2$ by coating with ZnS or molecular dipoles[27] and with increasing number of CdSe SILAR cycles.[8] To compare the R_{rec} values on the basis of a similar electron density [i.e., the same distance between the electron Fermi level (E_F) and the conduction band (CB) of TiO$_2$ (E_{CB})], the C_μ curves were overlapped by applying a +0.12 V shift to the curve of the 1–2 sample (Figure S3), and the same shift was applied for R_{rec} (Figure 3b), where the voltage scale is V_{ecb} (the potential for an equivalent conduction band).[24] The downward displacement of the TiO$_2$ CB increases the photoelectron injection driving force, producing a higher photocurrent in the case of the diluted electrolyte. On the other hand, the higher R_{rec} observed in Figure 3b for the diluted IL is responsible for the higher V_{oc} obtained (Figure 2a and Table 2).[8]

Comparing the results obtained for the IL with the previous ones using an aqueous polysulfide electrolyte, we observe similar photocurrents but a decrease in FF and V_{oc}.[8] The lower FF is a consequence of the platinized counter electrode used in this case, which is simpler to seal than the brass foil used to produce Cu$_2$S counter electrodes.[28] The lower V_{oc} may be due to a high recombination process[8] but also affected by the small (~80 mV) shift in the redox level of the S^{2-}/S_n^{2-} IL versus the analogous aqueous system (Figure S4).

The great interest in ILs for the preparation of sensitized solar cells is to obtain cells with higher long-term stability. The stability of the solar cells with the S^{2-}/S_n^{2-} redox IL-based electrolytes was tested, and no significant drop was measured for J_{sc} and V_{oc} over 10 days (240 h) for solar cells with the pure and diluted electrolyte (Figure S5). This indicates excellent stability for the TiO$_2$/CdSe photoanode. As far as we know, this is the highest reported stability for polysulfide-based electrodes in QDSCs. The measured drops in conversion efficiency of the full device were similar for the two electrolytes (35% decrease) and can be ascribed mainly to the decrease in FF, especially in the case of the diluted sample. This is due to an increase of the charge transfer (CT) resistance at the Pt counter electrode interface, which is related to electrode contamination. It is well-known that the photocatalytic activity of Pt with polysulfide-based electrolytes is poor.[28–30] Consequently, the use of a different counter electrode material (e.g., Cu$_2$S,[28] PbS,[31] Cu$_2$S–reduced graphene oxide compo-

site[32]) should lead to significantly higher stability of the full device, but in that case, technical problems for sealing the device would have to be solved. In this sense, is mandatory to develop efficient counter electrodes from the CT point of view and with the capability of easy sealing.[33]

In conclusion, we have designed and synthesized a novel pyrrolidinium-based IL for its application as a stable electrolyte in QDSCs. The PV efficiency of CdSe solar cells reached a promising 1.86% under 1 sun illumination, with excellent photoanode stability over 10 days, which could be further improved by optimizing the configuration of the cell. This could be done by reducing the series resistance using a less resistive counter electrode and by increasing V_{oc} by introducing more open TiO_2 structures.[34]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, ^1H NMR spectra, cyclic voltammetry, diffusion coefficient estimation, IS, Comparison to aqueous S^{2-}/S_n^{2-} redox couple, and solar cell stability. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

rtena@cidetec.es; sero@fca.uji.es

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■ REFERENCES

(1) Bai, Y.; Cao, Y. M.; Zhang, J.; Wang, M.; Li, R. Z.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Nat. Mater.* **2008**, *7*, 626.

(2) Papageorgiou, N.; Athanassov, Y.; Armand, M.; Bonhote, P.; Pettersson, H.; Azam, A.; Grätzel, M. *J. Electrochem. Soc.* **1996**, *143*, 3099.

(3) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621.

(4) Oregan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(5) Levy-Clement, C.; Tena-Zaera, R.; Ryan, M. A.; Katty, A.; Hodes, G. *Adv. Mater.* **2005**, *17*, 1512.

(6) Chang, J. A.; Rhee, J. H.; Im, S. H.; Lee, Y. H.; Kim, H. J.; Seok, S. I.; Nazeeruddin, M. K.; Grätzel, M. *Nano Lett.* **2010**, *10*, 2609.

(7) Kamat, P. V. *J. Phys. Chem. C* **2008**, *112*, 18737.

(8) Gonzalez-Pedro, V.; Xu, X. Q.; Mora-Sero, I.; Bisquert, J. *ACS Nano* **2010**, *4*, 5783.

(9) Mora-Sero, I.; Bisquert, J. *J. Phys. Chem. Lett.* **2010**, *1*, 3046.

(10) Sambur, J. B.; Novet, T.; Parkinson, B. A. *Science* **2010**, *330*, 63.

(11) Hodes, G. *J. Phys. Chem. C* **2008**, *112*, 17778.

(12) Zaban, A.; Micic, O. I.; Gregg, B. A.; Nozik, A. J. *Langmuir* **1998**, *14*, 3153.

(13) Shalom, M.; Albero, J.; Tachan, Z.; Martínez-Ferrero, E.; Zaban, A.; Palomares, E. *J. Phys. Chem. Lett.* **2010**, *1*, 1134.

(14) Tena-Zaera, R.; Katty, A.; Bastide, S.; Levy-Clement, C. *Chem. Mater.* **2007**, *19*, 1626.

(15) Chakrapani, V.; Baker, D.; Kamat, P. V. *J. Am. Chem. Soc.* **2011**, *133*, 9607.

(16) Lee, H. J.; Yum, J. H.; Leventis, H. C.; Zakeeruddin, S. M.; Haque, S. A.; Chen, P.; Seok, S. I.; Grätzel, M.; Nazeeruddin, M. K. *J. Phys. Chem. C* **2008**, *112*, 11600.

(17) Licht, S.; Peramunage, D. *Nature* **1990**, *345*, 330.

(18) Jovanovski, V.; Marcilla, R.; Mecerreyes, D.; Cabanero, G.; Tena-Zaera, R.; Mora-Seró, I. Bisquert, J. Eur. Pat. No. 10382132.8-2119 and PCT/EP/2011/058143, 2010.

(19) Eckert, W. *J. Electrochem. Soc.* **1998**, *145*, 77.

(20) Jovanovski, V.; Orel, B.; Jerman, I.; Hocevar, S. B.; Ogorevc, B. *Electrochem. Commun.* **2007**, *9*, 2062.

(21) Jerman, I.; Jovanovski, V.; Surca Vuk, A.; Hocevar, S. B.; Gaberscek, M.; Jesih, A.; Orel, B. *Electrochim. Acta* **2008**, *53*, 2281.

(22) Sun, J. Z.; MacFarlane, D. R.; Forsyth, M. *J. Mater. Chem.* **2001**, *11*, 2940.

(23) Jovanovski, V.; Orel, B.; Jese, R.; Vuk, A. S.; Mali, G.; Hocevar, S. B.; Grdadolnik, J.; Stathatos, E.; Lianos, P. *J. Phys. Chem. B* **2005**, *109*, 14387.

(24) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Mora-Sero, I.; Bisquert, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9083.

(25) Mora-Sero, I.; Gimenez, S.; Fabregat-Santiago, F.; Gomez, R.; Shen, Q.; Toyoda, T.; Bisquert, J. *Acc. Chem. Res.* **2009**, *42*, 1848.

(26) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.

(27) Barea, E. M.; Shalom, M.; Gimenez, S.; Hod, I.; Mora-Sero, I.; Zaban, A.; Bisquert, J. *J. Am. Chem. Soc.* **2010**, *132*, 6834.

(28) Gimenez, S.; Mora-Sero, I.; Macor, L.; Guijarro, N.; Lana-Villarreal, T.; Gomez, R.; Diguna, L. J.; Shen, Q.; Toyoda, T.; Bisquert, J. *Nanotechnology* **2009**, *20*, No. 295204.

(29) Hodes, G.; Manassen, J.; Cahen, D. *J. Electrochem. Soc.* **1980**, *127*, 544.

(30) Licht, S.; Khaselev, O.; Ramakrishnan, P. A.; Soga, T.; Umeno, M. *J. Phys. Chem. B* **1998**, *102*, 2536.

(31) Tachan, Z.; Shalom, M.; Hod, I.; Rühle, S.; Tirosh, S.; Zaban, A. *J. Phys. Chem. C* **2011**, *115*, 6162.

(32) Radich, J. G.; Dwyer, R.; Kamat, P. V. *J. Phys. Chem. Lett.* **2011**, *2*, 2453.

(33) Deng, M.; Huang, S.; Zhang, Q.; Li, D.; Luo, Y.; Shen, Q.; Toyoda, T.; Meng, Q. *Chem. Lett.* **2010**, *39*, 1168.

(34) Sudhagar, P.; Song, T.; Lee, D. H.; Mora-Seró, I.; Bisquert, J.; Laudenslager, M.; Sigmund, W. M.; Park, W. I.; Paik, U.; Kang, Y. S. *J. Phys. Chem. Lett.* **2011**, *2*, 1984.

20159

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