

# A Quasi-Solid-State Dye-Sensitized Solar Cell Based on a Sol–Gel Nanocomposite Electrolyte Containing Ionic Liquid

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Received November 12, 2002. Revised Manuscript Received February 7, 2003

TiO<sub>2</sub> dye-sensitized quasi-solid-state solar cells have been constructed by employing a nanocomposite organic/inorganic gel electrolyte made by the sol–gel method. The nanocomposite gel is based on silica while its organic subphase is a mixture of a surfactant (Triton X-100), an organic solvent (propylene carbonate), iodine, and 1-methyl-3-propylimidazolium iodide, which is an ionic liquid (molten salt). The last two components produce a I<sub>3</sub><sup>−</sup>/I<sup>−</sup> redox couple. Improved results were obtained by also adding *N*-methylbenzimidazole. Time-resolved luminescence quenching analysis, dark dc conductivity measurements, and cell efficiency measurements were used to determine the optimal composition of the gel for maximum cell efficiency, which in the present case was 5.4%.

## Introduction

Dye-sensitized photoelectrochemical cells have established themselves as the most promising low-cost alternative for the photovoltaic conversion of solar energy. Briefly, this device is composed of three adjacent thin layers sandwiched between two transparent conductive oxide (TCO) electrodes: a high band-gap nanocrystalline semiconductor coated with a dye sensitizer for absorption in the visible region, a platinized counter electrode to collect the electrons, and a redox electrolyte. The electrolyte provides the internal electric conductivity by diffusing among semiconductor nanoparticles; it sets the potential barrier necessary for photovoltaic conversion and transfers charge for regenerating the system by reducing the oxidized sensitizer. Oxidation of the dye occurs upon photon absorption followed by very rapid injection of the excited electron into the conduction band (CB) of the semiconductor.

Since the original model cell<sup>1</sup> reported in 1991, the study of this device has attracted an ever-growing interest from scientists of different disciplines around the world. These studies have established certain materials as the uncontested components of the cell. Thus, TCO can be indium-doped tin oxide (ITO), but better results are frequently reported with fluorine-doped SnO<sub>2</sub> (FTO).<sup>2</sup> Although several metal oxides are studied from time to time as the high band-gap semiconductor,<sup>3,4</sup> the material of choice is nanocrystalline

TiO<sub>2</sub>, while ruthenium bipyridyl derivatives are the best choice of a dye sensitizer. Thus, in the most popular case of *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), [RuL<sub>2</sub>(NCS)<sub>2</sub>], its LUMO level is conveniently located close and above<sup>5</sup> the CB edge of TiO<sub>2</sub> and its excited-state lifetime is long enough so that injection of an excited electron into the semiconductor CB is quantitative. Thus, the vast majority of recent research focuses on the other major components of the cell, that is, the electrolyte, its chemical composition, and its physical state. The electrolyte contains I<sub>3</sub><sup>−</sup>/I<sup>−</sup> as a redox couple. This couple makes a convenient combination<sup>5</sup> with TiO<sub>2</sub> and RuL<sub>2</sub>(NCS)<sub>2</sub> and it has also become a standard and uncontested choice.<sup>1–10</sup> It is obtained by simultaneously dissolving iodine and an iodide salt in a solvent solubilizing both, for example, several organic solvents such as propylene carbonate (PC) or acetonitrile (ACN).<sup>2,11,12</sup> Recently, cobalt com-

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plexes also became popular as alternative redox couples for dye-sensitized solar cells.<sup>13</sup>

The use of solvents in a solar cell has created a lot of skepticism regarding sealing problems, photochemical stability, and solubilization capacity of the redox couple. This latter question will be further commented on below. For this reason, substituting liquid electrolyte by a solid gel electrolyte has been considered as offering several advantages compared with the original wet cells. Dye-sensitized solid-state solar cell (DSSC) was first constructed by employing a polymeric matrix electrolyte. Such cells seemed to solve several practical problems; however, questions on photochemical stability still remained open. In addition, these were low-efficiency cells due to small ionic conductivity.<sup>14–16</sup> A promising alternative has been recently proposed by using nanocomposite gel electrolytes made by the sol–gel method.<sup>6,7</sup> These materials have many advantages. They are composed of two subphases, one organic and the other inorganic (silica) mixed in the nanoscale. The inorganic subphase provides the gelling agent and simultaneously works as a gluing material holding the working and the counter electrode together, without additional aids. The organic subphase is made of a mixture of chemical substances providing ionic conductivity. Such nanocomposite gels can accommodate appropriate solvents within the organic subphase (in other words, within the pores left by the inorganic network) so that ionic conductivity can be raised to a satisfactory degree. Preliminary data suggest greater stability of the organic solvent when incorporated into a nanocomposite gel. In the present work such gels were used to construct the DSSCs.

No matter whether one uses a liquid or a gel electrolyte, organic solvents are relatively bad solvents for alkaline iodide salts. Crystallization, for example, of KI has been a source of deterioration of the cell.<sup>17,18</sup> For this reason, it has been proposed to substitute metal cations by organic cations containing quaternary ammonium groups.<sup>18–21</sup> Some of these substances, for example, dialkylimidazolium iodides, have low melting points and they are liquid at room-temperature conditions (ionic liquids). Therefore, they are, in principle, immune to crystallization problems. Incorporating ionic

liquids into these nanocomposite gel electrolytes is also the object of the present work.

With the above information in mind, we have constructed DSSCs using ionic liquid electrolytes incorporated into nanocomposite sol–gel films and measured their efficiency at different matrix compositions. The obtained cell performances were very promising and satisfactory.

## Experimental Section

**Materials.** Titanium(IV) isopropoxide, tetramethoxysilane [TMOS], polyoxyethylene(10) isooctylphenyl ether [Triton X-100], propylene carbonate [PC], *N*-methylbenzimidazole [NMBI], iodine, tris(2,2'-bipyridine)ruthenium dichloride hexahydrate [Ru(bpy)<sub>3</sub><sup>2+</sup>], pyrene, coumarine-153 [C-153], and methyl viologen [MV<sup>2+</sup>] were purchased from Aldrich and used as received. *cis*-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) [RuL<sub>2</sub>(NCS)<sub>2</sub>] was provided by Solaronix SA (Switzerland). 1-Methyl-3-propylimidazoliumiodide [MPII] was synthesized according to ref 23. The rest of the reagents were from Merck, while Millipore water was used in all experiments. Transparent conductive oxide (TCO) electrodes were cut from a FTO-coated glass (8 Ω/square) purchased from Hartford Glass Co., USA.

**Preparation of TiO<sub>2</sub> Mesoporous Films.**<sup>6,7,22</sup> A reverse micellar solution of 0.2 M Triton X-100 and 0.4 M water was prepared in cyclohexane. To this solution we added 0.2 M titanium isopropoxide under vigorous stirring and at ambient conditions. Other concentrations of the above components have also been tried but optimal results were obtained with the present combination. Hydrolysis and condensation of titanium isopropoxide begins as soon as it is introduced in the reverse micellar solution, but it takes about an hour before the solution becomes a visible gel. The thus-prepared composite material can be deposited as thin film on a FTO-coated glass by the dip-coating method. A slide was cut from an 8 Ω/square FTO-coated glass, sonicated for 20 min in ethanol, and finally, copiously washed with Millipore water and dried in a stream of N<sub>2</sub>. The thus-prepared slide was dipped into the gelling solution at an early stage of gelation and was quickly withdrawn at a speed of 2 cm/s. The composite organic–inorganic film was left to dry in air and the dipping was repeated two more times. The film was deposited on only the FTO-coated side of the glass. The other side was covered with tape. After three dippings, the back tape was peeled off and the glass surface was locally washed with acetone. Then, the film was slowly heated in air, up to 450 °C, at a rate of 3.5 °C/min. The film was finally sintered at 450 °C for about 15 min more. The procedure was repeated two additional times so that 3 × 3 depositions were made. The obtained film was transparent. With successive coatings, thicker films could be made; however, thickness grows at the expense of transparency. The diameter of the nanoparticles making the nanocrystalline TiO<sub>2</sub>, as estimated by using AFM images, was around 30 nm. X-ray scattering showed that the film consists of anatase.

**Solar Cell Fabrication.** When the TiO<sub>2</sub> film was taken out of the furnace and while it was still hot, it was dipped into a 1 mM ethanolic solution of RuL<sub>2</sub>(NCS)<sub>2</sub> and was left there for about 16 h. Then, the dye-coated electrode was copiously washed with ethanol and dried in a stream of N<sub>2</sub>.

On the top of the TiO<sub>2</sub>/dye layer, a thin nanocomposite organic/inorganic film containing I<sub>3</sub><sup>-</sup>/I<sup>-</sup> was deposited by the sol–gel method under the following procedure, which was carried out at ambient conditions. Two milliliters of PC was mixed with 0.5 mL of Triton X-100, giving a transparent solution. The molar fraction of PC and Triton X-100 varied in different experiments; however, the above 4:1 ratio was found

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optimal. Then, we added the following reagents by strictly observing order and maintaining continuous stirring: 0.65 mL of glacial acetic acid; 0.35 mL of TMOS; 0.5 M MPII; 0.04 mM NMBI and iodine at various concentrations. The quantity of MPII and NMBI were also varied but optimal results were obtained at the above concentrations. The gelation procedure starts as soon as TMOS has been added to the solution. Gelation is carried out by acetic acid solvolysis.<sup>7,24</sup> It is a multistep reaction leading to the formation of a  $-\text{O}-\text{Si}-\text{O}-\text{Si}-$  network. The material was an apparent gel about 12 h after mixing of the reagents. The solution was still fluid 5 h after mixing and ready for application. Other waiting times were also tried but 5 h was considered optimal.

On top of the titania film we placed a single drop of the electrolyte mixture and squeezed it with a platinized FTO-coated glass. Si-O bridges help bind the counter electrode so that the nanocomposite  $\text{SiO}_2/\text{Triton}/\text{PC}$  material additionally acts in holding the parts of the cell together in a stable thin sandwich configuration.

**$\text{SiO}_2/\text{Triton}/\text{PC}$  Films Used for Time-Resolved Luminescence Probing Studies.** The films used for luminescence probing were deposited on plain glass and did not contain the redox couple, but they were enriched with a luminophore/quencher couple, either pyrene/C-153 or  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ . Triton X-100 and PC were mixed at different molar fractions, always giving a total volume of 2.5 mL, and the fluorophore/quencher couple was solubilized in this mixture. Then, we added 0.65 mL of glacial acetic acid and, finally, 0.35 mL of TMOS. After 5 h, pre-cleaned glass slides were dipped into the gelling sol and the obtained films were left to dry overnight under ambient conditions.

**Methods.** Incident photon to current efficiency (IPCE%) values were measured by illumination of the samples with a 250-W Phillips tungsten halogen lamp through a filter monochromator (Oriel-7155). The lamp spectrum satisfactorily simulates solar radiation at the surface of the earth. The number of incident photons was calculated by employing a radiant power/energy meter (Oriel-70260).  $I-V$  curves have been recorded by connecting the cell to an external variable resistor and by measuring the current flowing through the resistor and the corresponding voltage across the resistor. The cell dimension for all the above measurements was  $1 \text{ cm}^2$ . Dark dc conductivity measurements were made by sandwiching the  $\text{SiO}_2/\text{Triton}/\text{PC}/\text{I}_3^-/\text{I}^-$  electrolyte between two TCO slides. Time-resolved luminescence decay profiles were recorded with the single-photon-counting technique using a IBH nanosecond hydrogen flash lamp and ORTEC electronics.

## Results and Discussion

The principal idea in the present work was to combine a sol-gel nanocomposite material incorporating an ion-conducting fluid with a  $\text{I}_3^-/\text{I}^-$  redox couple based on an ionic liquid. We have tried various possibilities for the composition of the organic subphase of the gel but we have finally opted for a mixture of PC with Triton X-100, both necessary to make stable nanocomposite ion-conducting films. The first task to be carried out was to define an optimal composition of the gel so that stable and transparent films could be made and ion-transporting capacity could be maximized. Our experience with previous work<sup>6</sup> has shown that percolation conditions should be satisfied in a nanocomposite material to obtain appreciable values of ionic conductivity. If the ion-transporting subphase in a nanocomposite organic/inorganic material does not percolate, it is impossible to carry ions throughout the material. Time-resolved luminescence quenching is an efficient method for

determining percolation threshold. For this reason, this method has been used to study percolation conditions in the  $\text{SiO}_2/\text{Triton}/\text{PC}$  nanocomposite, as shown in the following paragraph.

**Optimal Composition of the Organic Subphase Determined by Time-Resolved Luminescence Quenching Studies.** Both the hydrophilic  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$  and the hydrophobic pyrene/C-153<sup>25</sup> luminophore/quencher couples are soluble in the organic PC/Triton mixture but they are expected to probe domains of substantially different polarities. Nevertheless, molecules such as pyrene and C-153 have a tendency to solubilize themselves at the polar/apolar interface so that probing by both couples is not expected to give very different results in the present case, but they were both examined for safer conclusions. The luminescence decay profiles of a luminophore in the presence of a quencher in a restricted medium can be expressed as a sum of stretched exponentials according to the following equation:<sup>6,25-27</sup>

$$I(t) = I_0 \exp(-t/\tau_0) \exp[-C_1(t/\tau_0)^f + C_2(t/\tau_0)^{2f}] \quad 0 < f < 1 \quad (1)$$

$C_1$ ,  $C_2$ , and  $f$  are parameters calculated by fitting eq 1 to the experimental decay profile.  $\tau_0$  is the decay time in the absence of quencher and it is measured in separate experiments. The distribution of the residuals and the autocorrelation function of the residuals were used as fitting criterion. Experience has shown that a combination of these two criteria offers parameter values with high precision (error less than 5%) and repeatability. More information about this model and of its application in the study of nanocomposite materials was previously reported.<sup>6,27</sup> The model of eq 1 applies to any quenching reaction where an excited luminophore can, in principle, be quenched by any quencher present. Thus, it applies to electron or energy transfer as well as to diffusion-controlled quenching. It is particularly fit to complex systems with unknown but, certainly, restricted geometry. The model is based on the fundamental kinetics of restricted reactions where a reactant behaves as a random walker. In a restricted environment, the number of distinct sites visited by the random walker within a time interval,  $t$ , is not proportional to  $t$  but to  $t^f$ , where  $0 < f < 1$ , hence, the noninteger power of time in eq 1. Obviously, the restrictions imposed by the reaction domain reflect on the value of  $f$ ,  $f$  being smaller in more restricted reactions. For a reaction domain possessing self-similarity, that is, a fractal, percolation conditions are satisfied for  $f > 0.67$ .<sup>28</sup> Experience has shown that most of the nanocomposite materials possess to a satisfactory degree fractal geometry so that the calculated value of  $f$  can lead to a safe determination of the percolation threshold. Indeed, different films containing a luminophore/quencher couple have been made by the above experimental procedure and the value of  $f$  has been determined by analysis with

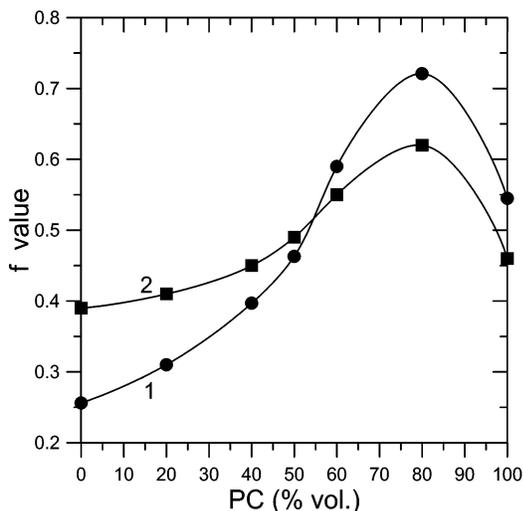
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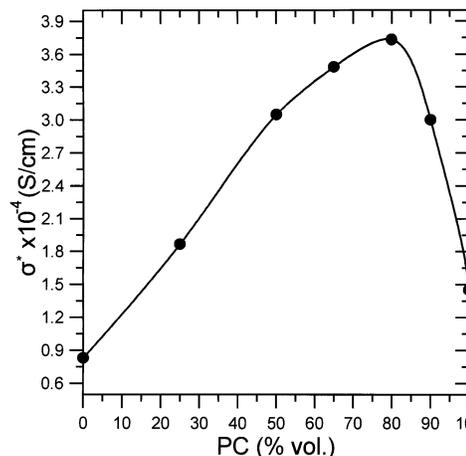


**Figure 1.**  $f$  values vs PC content calculated with eq 1 by using the luminophore quenching couple Ru(bpy)<sub>3</sub><sup>2+</sup>/MV<sup>2+</sup> (1) or pyrene/C-153 (2).

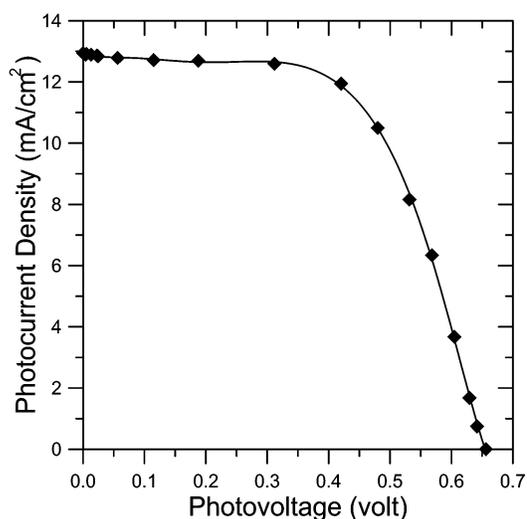
eq 1. The results are shown in Figure 1. These data show that the hydrophobic couple pyrene/C153 is, on average, more restricted, apparently, by solubilization in hydrophobic pockets, approaching but not reaching percolation threshold. In contrast, the charged couple does pass beyond the percolation threshold for a nanocomposite gel where the PC/Triton X-100 mixture contains 80% PC and 20% surfactant. The mobility of the charged species is then higher than that of the hydrophobic species in the above nanocomposite gel and this is a satisfactory result since charged species are the mobile species sought for in the present work. For both types of species, maximum mobility, that is, lower restriction, is observed at this above composition of 80%PC and 20% Triton X-10. For further increase of PC content a rapid decrease of mobility was observed. These results could define the optimum composition of the gel if they are combined with conductivity data. Such data are shown in the next paragraph.

**Conductivity Measurements.** Direct current dark conductivity measurements were made by placing the SiO<sub>2</sub>/Triton/PC/I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolyte between two TCO slides and applying constant 0.5-V electric tension. dc ionic conductivity may in some cases be problematic because of polarization and continuous current decrease. In our case, after a current drop of about 20%, following application of electric tension, the current stayed constant. The dark dc conductivity values are shown in Figure 2 and they are all recorded after current stabilization. The results show an impressive similarity with the data of the previous paragraph (cf. Figure 1). Not only these data define the composition of choice (80%PC 20% Triton X-100) in an uncontested manner but they also promote the luminescence quenching procedure as a powerful tool for studying mobility in these complex systems. The above composition is optimal in terms of mobility, but of course, satisfactory performance of the cell is expected between 50 and 90% of the PC content range.

**Photovoltaic Performance.** Having determined the composition of the organic subphase in the nanocomposite gel, we have constructed DSSCs and measured their efficiency by plotting the  $I$  vs  $V$  characteristic



**Figure 2.** Dark dc conductivity values for the SiO<sub>2</sub>/Triton/PC/I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolyte at varying PC content.

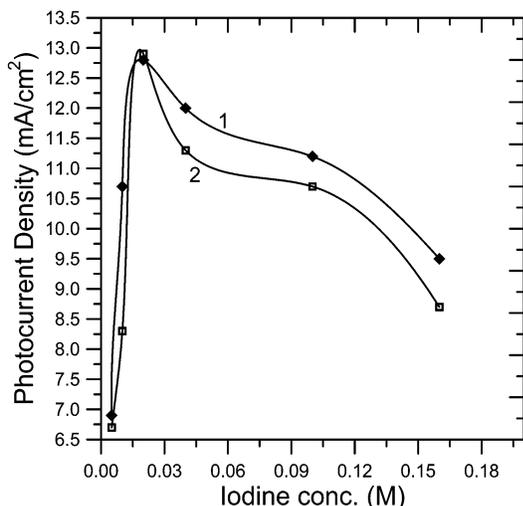


**Figure 3.**  $I$ - $V$  curve for an optimized DSSC.  $ff = 0.66$ .

curves and by calculating the overall efficiency employing the formula<sup>5</sup>

$$\eta\% = \frac{I_{sc} V_{oc} ff}{P_{inc}} 100$$

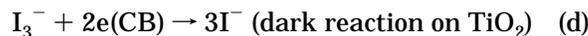
where  $I_{sc}$  is the short circuit current,  $V_{oc}$  the open circuit voltage,  $P_{inc}$  the incident light power, and  $ff$  the fill factor. A characteristic  $I$ - $V$  curve is shown in Figure 3 with maximum  $I_{sc} = 12.9$  mA,  $V_{oc} = 0.65$  V, and  $\eta\% = 5.4\%$ , for  $P_{inc} = 96$  mW/cm<sup>2</sup>. These values correspond to a gel electrolyte optimized according to the data of the previous paragraphs defining the composition of the organic subphase of the nanocomposite film. In the photocurrent action spectrum of such a cell, the incident to photon current efficiency (IPCE) value at 540 nm is 75%. In the course of these measurements we have realized that the quantity of iodine incorporated in the gel plays a crucial role in the cell performance. By keeping all other additives constant, we have varied the quantity of the added iodine and measured the cell performance. Iodine content was varied from 5 to 160 mM. During this variation  $V_{oc}$  changed in a relatively small range between 0.62 and 0.65 V. In contrast, the variation of  $I_{sc}$  was very large, as can be seen in the



**Figure 4.**  $I_{sc}$  curve vs iodine concentration for an electrolyte containing all components (1) and without NMBI (2).

plots of Figure 4. The maximum current was obtained for iodine concentration equal to 20 mM, that is, 25 times less than the concentration of MPII (500 mM). This maximum is rapidly achieved while for larger iodine concentrations the efficiency of the cell decreased. Figure 4 shows two curves, one of them corresponding to a cell containing all components while the second is recorded in the absence of NMBI. In the latter case the variation of  $V_{oc}$  was in the range 0.57–0.59 V while the  $I_{sc}$  curve gave steep and crucial behavior around 20 mM. These results show that the presence of NMBI is beneficial for both increasing  $V_{oc}$  and for smoothing the iodine concentration effects. Such behavior of NMBI was expected since this substance is a base and behaves in a way similar to 4-*tert*-butylpyridine studied in the past.<sup>2</sup> By the addition of NMBI to the electrolyte,  $V_{oc}$  increases by suppression of dark current. This is due

to adsorption of base on the  $TiO_2$  surface, which passivates the surface active recombination sites.<sup>2</sup> The behavior of the photocurrent with varying iodine concentration can be explained by considering the following redox reactions:



Increase of iodine concentration acts in favor of  $I_3^-$  according to reaction (a), given the fact that the  $I^-$  concentration is much higher than that of  $I_2$ . At the beginning and since a critical level of  $I_3^-$  is necessary for cell functioning, reactions (b) and (c) are put in effect, the photocurrent rapidly increases, and it soon achieves a maximum. For further increase of  $I_2$  and the electron-deficient  $I_3^-$  concentration, the reaction (d) becomes important,<sup>29</sup> decreasing the external current  $I_{sc}$ .

In conclusion, we have constructed a quasi-solid-state dye-sensitized solar cell based on sol-gel nanocomposite electrolyte containing ionic liquid. The overall cell efficiency was 5.4%, which is considered satisfactory for a device employing a quasi-solid electrolyte.

**Acknowledgment.** E.S. and P.L. acknowledge financial support from the program "K.KAPAΘEOΔΩPHΣ" of the University of Patras. S.M.Z., P.L., and M.G. acknowledge financial support by the Swiss National Science Foundation.

CM0213568

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