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ARTICLE TYPE

Enhanced Performance of P-type Dye Sensitized Solar Cells Based on Mesoporous $Ni_{1-x}Mg_xO$ Ternary Oxides Films

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A series of $Ni_{1-x}Mg_xO$ (x = 0-0.2) oxides mesoporous films with p-type semi-conductivity prepared by surfactant directed self-assembly method have been successfully applied as photocathodes in p-type dye sensitized solar cell (DSC) system. By gradually increasing Mg content from 0 to 20% in the ternary oxides, the effective light harvesting efficiency increases monotonically which is associated with the increased dye absorbing amount and improved optical transmittance, meanwhile the flat-band potential gradually increases, implying a continuous negative shift of valance band position of the p-type semiconductors. The latter is closely related to the charge injection from dye to semiconductor and the photovoltage (V_{oc}) of the solar cell. The overall power conversion efficiency is optimized at the $Ni_{0.9}Mg_{0.1}O$ photocathode, which is significantly improved by about 85% from pure NiO. The enhanced performance is attributed to 34.4% increased photocurrent density (J_{sc}), 22.5% increased V_{oc}, and 13.0% increased fill factor. These improvements can be explained by increased light harvesting, enhanced charge collection, and flat-band potential positive shift. Further increasing Mg content in the ternary oxide to be $Ni_{0.8}Mg_{0.2}O$, the valance band position is too deep to hinder efficient hole injection. J_{sc} of the corresponding solar cell decrease largely. This work proves that $Ni_{0.9}Mg_{0.1}O$ is a superior alternative to NiO as photocathode material in p-type DSCs.

Introduction

The research on dye sensitized p-type semiconductor solar cells (called p-DSCs) has gained increasing attention during recent years, owing to its possibility to fabricate tandem solar cells with those n type semiconductors based DSCs (n-DSCs).[1-13] This concept of tandem solar cell has been firstly demonstrated as a real cell by Lindquist and co-workers in 1999.[14] In such a cell configuration, photoexcitation of the sensitizer in the conventional n-DSC part results in electron injection to the conduction band of n-type semiconductors (*e.g.*, TiO_2, ZnO), while at the same time the sensitizer in the p-DSC part results in hole injection to the valance band of p-type semiconductors.[15,16] The photo-oxidized or reduced dye is then regenerated by a commonly used iodide/triiodide electrolyte. According to Kirchhoff's circuit law, the photovoltage of this tandem device is the sum of that of n-DSC part and p-DSC part, while the photocurrent is limited by the smaller one of the two half cells, which is generally the p-DSC part.[15,17] Theoretically, the performance of this pn tandem DSC can surpass either of the single junction DSCs.[1-3,18] However, p-DSCs up to date have not achieved satisfactory performance. The reported best efficiency was only about 0.5%.[9-11] The poor performance of p-DSC is the major obstacle towards the high efficiency pn tandem DSC. Currently, to exploit superior p-type sensitizers and semiconductors are of equal and critical importance to high performance p-DSCs.

The development of novel sensitizers (dyes or quantum dots) in p-DSCs has achieved solid progress.[6,7,9,19] For example, Hagfeldt and Sun *et al*. synthesized an anchor functionalized triphenylamine based dye (P1 dye) for p-DSC,[6,7] resulting in a record incident photon-to-current efficiency (IPCE) of 35% in 2008. Through optimizing mesoporous NiO film' morphology by surfactant direct self-assembly method, their p-DSC has achieved IPCE up to 64% and overall efficiency up to 0.15%.[8]

Our group recently has reported many alternative transparent p-type semiconductors, such as $CuCrO_2$, Mg doped $CuCrO_2$, $CuGaO_2$, K doped ZnO nanocrystals, and achieved competitive performance of corresponding p-DSCs.[19-23] But the most commonly used NiO due to its good stability and easier control on the component, it is still worthy to further improve the quality of NiO films, in order to achieve improved transparency, charge collection property and especially deeper valance band. The first two parameters are closely associated with the photocurrent density (J_{sc}) of the solar cell and the last one decides the maximum photovoltage (V_{oc}) of the solar cell.

In this study, a series of $Ni_{1-x}Mg_xO$ (x = 0-0.2) mesoporous films have been prepared by a common surfactant directed self-assembly method, and have been critically compared as photocathodes in p-DSCs. Judicious design of Mg content in the $Ni_{1-x}Mg_xO$ ternary oxides plays a critical role in optimizing the solar cells' performance. P1 dye was employed as the sensitizer, in comparison to the later reported p-type dyes,[9] its smaller molecular size should benefit for better penetration through the relatively narrow pore channel of the surfactant templated mesoporous films. The $Ni_{0.9}Mg_{0.1}O$ photocathode has achieved an overall efficiency of 0.19%, with V_{oc} of 109 mV, J_{sc} of 5.16 mA cm^{-2} and fill factor (*FF*) of 0.34; whereas the pure NiO reference has achieved 0.10% efficiency, with V_{oc} of 89 mV, J_{sc} of 3.84 mA cm^{-2}, *FF* of 0.30. The inherent reasons responsible for such performance change have been discussed and clarified.

Experimental

All chemicals without annotation were purchased from Sigma Aldrich at analytical grade and used without further purification. The series of mesoporous $Ni_{1-x}Mg_xO$ (x = 0, 0.05, 0.1, 0.2) films were prepared via the same method modified from the literature.[8] Briefly, 1.0 g triblock co-polymer F108 and 1.8 g $NiCl_2{\cdot}6H_2O$ with a certain Ni/Mg mole ratio were added to 3.0 g water and 6.0 g ethanol mixed solution under stirring for three days. $MgCl_2{\cdot}6H_2O$ was used as Mg source. The precursor was deposited on FTO glass by doctor-blade method. The wet film was dried slowly, gradually heat up to 450 °C at the rate of 3 °C min^{-1} and kept at 450 °C for 30 min. The procedure was repeated by three times to achieve the desired thickness. After the last sintering step and the film cooling down to 80°C, it was immersed in a P1 dye acetonitrile solution (0.3mM) and kept at room temperature for 18h. DSCs were made by sandwiching the Pt counter electrodes and the P1 dye sensitized $Ni_{1-x}Mg_xO$ photocathodes using Surlyn film (25μm) as the spacers. The electrolyte containing 1 M LiI/0.1 M I_2 in acetonitrile was introduced into the cells via vacuum backfilling.

The morphology of the $Ni_{1-x}Mg_xO$ films was characterized using scanning electron microscopy (SEM, FEI Sirion 200). X-ray diffraction (XRD) patterns were obtained with a PAN alytical B.V. X-ray diffraction system. The film thickness was determined by VeecoDektak 150 surface profiler. The UV-Vis spectroscopy was recorded on a Perkin-Elmer UV/Vis spectrophotometer (model Lambda 950). The photocurrent density-voltage (*J-V)* curves were measured by using a Newport AM1.5G solar simulator (model 91192) at the light intensity of 100 mW cm^{-2}, calibrated by a standard silicon reference cell. The active areas of DSCs were set at 0.16 cm^2, determined by a square mask. IPCE was measured on the basis of a Newport Apex Monochromator illuminator (model 70104). Mott-Schottky plots ($1/C^2$ vs. E) were measured on an electrochemical workstation (model CHI760D, Shanghai Chenhua Instruments) at a bias potential sweeping from 0 V to 1 V with a rate of 10 mV s^{-1} and at 1000 Hz. A saturated calomel electrode (SCE) was used as the reference and connected to the aqueous KOH (0.5 M) solution via a salt bridge. Transient photocurrent/photovoltage decays were performed on a homemade photo-electrochemical system. A white light bias on the sample was generated from an array of diodes. Red light pulse diodes (0.05 s square pulse width, 100 ns rise and fall time) controlled by a fast solid-state switch were used as the perturbation source. The voltage dynamics were recorded on a PC-interfaced Keithley 2602A source meter with a 100 µs response time. The perturbation light source was set to a suitably low level in order for the voltage decay kinetics to be monoexponential. By varying the white light bias intensity, the recombination rate constant and hole diffusion rate constant could be estimated over a range of applied biases.

Results and discussion

It is known that both NiO and MgO are with rock-salt structure. Their lattice mismatch is as small as 0.8%.[24] This provides the possibility for the formation of infinite solid solution of $Ni_{1-x}Mg_xO$. Fig. 1 shows the XRD patterns of the $Ni_{1-x}Mg_xO$ (x = 0, 0.05, 0.1, 0.15, 0.2) films coated on FTO glasses. It can be clear identified that the ternary oxides are with the same crystal structure of pure NiO. The monotonous blue-shift of peak position, when x increases from 0 to 0.2 (as shown in the insert of Fig. 1), is consistent with the lattice expending due to gradual substitution of smaller Ni^{2+} by larger Mg^{2+}.

Fig. 2a, b show the SEM images of the pure NiO, $Ni_{0.9}Mg_{0.1}O$ film respectively. It is clear that the particle size of 10-15 nm and the porosity of the two films keep nearly unchanged. The results reflect that the surfactant directed self-assembly method is commonly valid to control the film morphologies irrelevant to the film composition. The high porosity of the films is generated by the decomposition of the surfactant micelles (block copolymer, Pluronic F108). Such organized porosity can facilitate dye absorption and electrolyte penetration. To analyse the chemical composition of the designed $Ni_{0.9}Mg_{0.1}O$ film, elemental EDX mapping was employed to characterize the sintered film on Si wafer substrate. As shown in Fig. 2c-e, both Mg, and Ni elements are distributed homogeneously and the

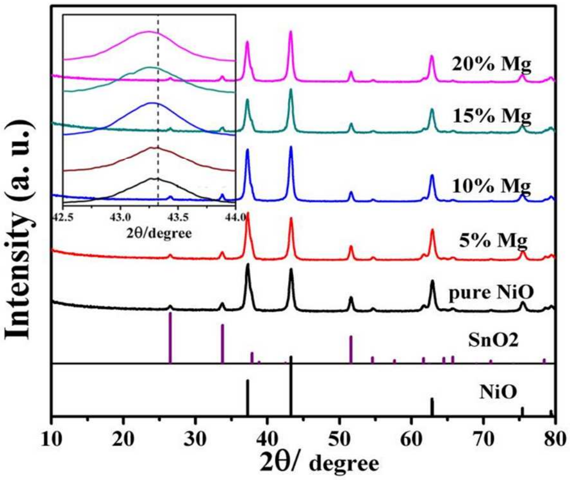

Fig. 1 XRD patterns of pure NiO and $Ni_{1-x}Mg_xO$ (x=0.05, 0.1, 0.15, 0.2) films coated on FTO glasses.

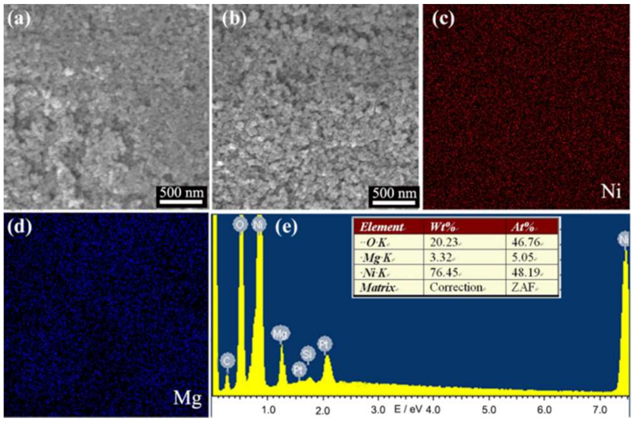

Fig.2 SEM image of a) pure NiO, b) $Ni_{0.9}Mg_{0.1}O$ films. c-d) EDS mapping results of $Ni_{0.9}Mg_{0.1}O$ films of Ni and Mg elements and e) its corresponding elemental analysis report.

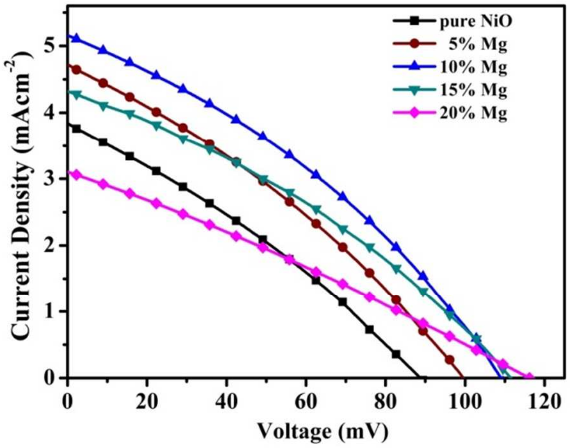

Fig. 3 *J-V* characteristic curves of the p-type DSCs based on pure NiO, and $Ni_{1-x}Mg_xO$ ternary oxides with x = 0.05, 0.1, 0.15, 0.2 respectively.

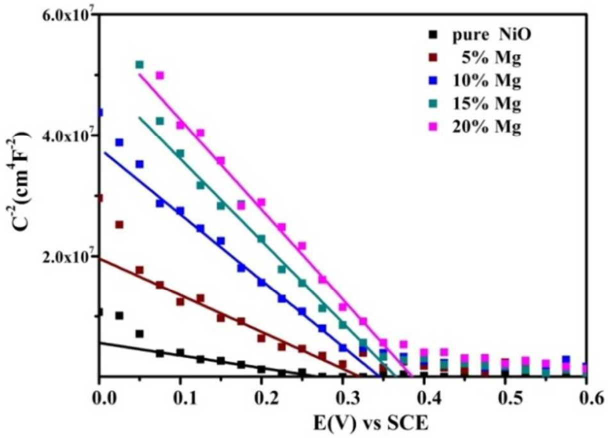

Fig. 4 Mott-Schottky plots of pure NiO and $Ni_{1-x}Mg_xO$ ternary oxides films.

element percentages of Mg (5.05%), Ni (48.19%), and O (46.76%) are almost consistent with the concentrations of their source materials in the precursor and well consistent with their designed stoichiometric proportions. $Ni_{1-x}Mg_xO$ is easy to form homogeneous solid solutions, which have been widely reported previously.[25, 26]

J-V curves of the p-DSCs using the series of mesoporous $Ni_{1-x}Mg_xO$ (x = 0, 0.05, 0.1, 0.15, 0.2) films as photocathodes are shown in Fig. 3. The resultant photovoltaic parameters are summarized in Table 1. An optimal efficiency of 0.19% was obtained by the $Ni_{0.9}Mg_{0.1}O$ photocathode. It is noteworthy that the $Ni_{0.9}Mg_{0.1}O$ based DSC possesses 85% higher efficiency than the NiO reference, ascribed to much higher J_{sc} (5.16 mA cm^{-2} versus 3.84 mA cm^{-2}), decently higher V_{oc} (109 mV versus 89 mV) and *FF* (0.34 versus 0.30) of the former. For a series of $Ni_{1-x}Mg_xO$ films, it is observed that by increasing Mg content, J_{sc} at first increases and reaches a maximum of 5.16 mA cm^{-2} with x = 0.1, and then gradually decreases; and *FF* shows the same tendency. While V_{oc} increases from 89 mV to 116 mV monotonically as x increases from 0 to 0.2.

In order to clarify the reasons leading to higher V_{oc} for the solar cells based on ternary oxides films. The Mott-Schottky analysis has been employed to measure the flat band potential (V_{fb}) of the $Ni_{1-x}Mg_xO$ films.[21, 27-30] The approximate V_{fb} can be obtained by fitting linear in the depletion zone of Mott-Schottky plot to get the intercept on the abscissa; and the concentration of charge carrier can be calculated from the slope of linear fits. From Fig. 4, the fitted linear plots have negative value, confirming that NiO and $Ni_{1-x}Mg_xO$ films are all with p-type semiconductivity.[21, 31] The results in Fig. 4 indicate a positive shift of V_{fb} with increasing Mg content. The V_{fb} of the pure NiO electrode is about 0.27V (vs. SCE), whereas the V_{fb} of the $Ni_{0.8}Mg_{0.2}O$ electrode increases a lot to 0.39V. This positive shift of V_{fb} should be associated with the shift of valance band positions of the $Ni_{1-x}Mg_xO$ ternary oxides, which according to the literature could be explained by the Vegard's law.[24] It is known that V_{oc} of the DSC device is determined by the difference between the valance band of $Ni_{1-x}Mg_xO$ and the redox potential of the I^-/I^{3-} couple.[21, 32] Therefore, it is reasonable that V_{oc} of DSCs increases due to positive shift of V_{fb} as Mg content increases.

Table 1 Performance parameters of the DSCs based on pure NiO and ternary Ni_{1-x} Mg_xO oxides.

Sample	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*FF*	η (%)
Pure NiO	89	3.84	0.30	0.10
5% Mg	100	4.72	0.32	0.15
10% Mg	109	5.16	0.34	0.19
15% Mg	112	4.32	0.33	0.16
20% Mg	116	3.10	0.28	0.10

Regarding to the J_{sc} difference of the DSCs based on the series of $Ni_{1-x}Mg_xO$ (x = 0-0.2) films, their IPCE differences as shown in Fig. 5a can explain. The maximum IPCE at about 510 nm for the $Ni_{0.9}Mg_{0.1}O$ based DSC is 44%, much higher than that of pure NiO (32%), $Ni_{0.95}Mg_{0.05}O$ (40%), $Ni_{0.85}Mg_{0.15}O$ (36%), and $Ni_{0.8}Mg_{0.2}O$ (27%). It is known that light harvesting efficiency (*LHE*), injection efficiency from dye to semiconductor (Φ_{inj}), and charge collection efficiency (η_{cc}) all have contribution to the total IPCE, which determines J_{sc} according to equation, IPCE = $LHE \times \Phi_{inj} \times \eta_{cc}$.[22, 23] The maximum IPCE and therefore J_{sc} achieved at x = 0.1 among the series of $Ni_{1-x}Mg_xO$ (x = 0-0.2) photocathodes could be explained as follows by balanced evaluation on those three factors. First, with respect to *LHE*, the optical transparency of the $Ni_{1-x}Mg_xO$ films increases as the Mg content increases (as

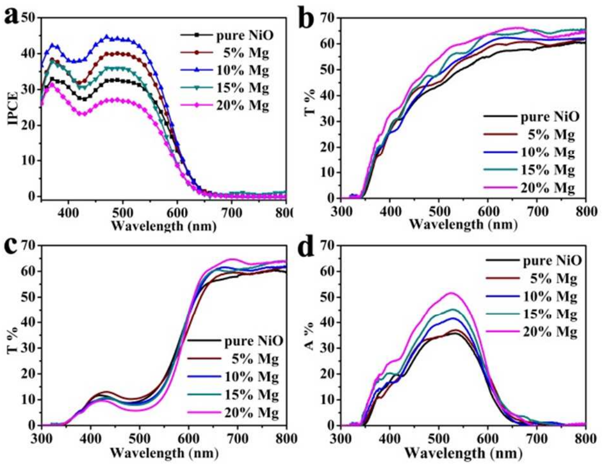

Fig.5 (a) IPCE spectra of the DSCs based on the $Ni_{1-x}Mg_xO$ (x = 0-0.2) films. Optical transmittance spectra of the b) undyed and c) dyed of $Ni_{1-x}Mg_xO$ ternary films. d) The absorptivity obtained by subtracting the dyed films' transmittance from the undyed.

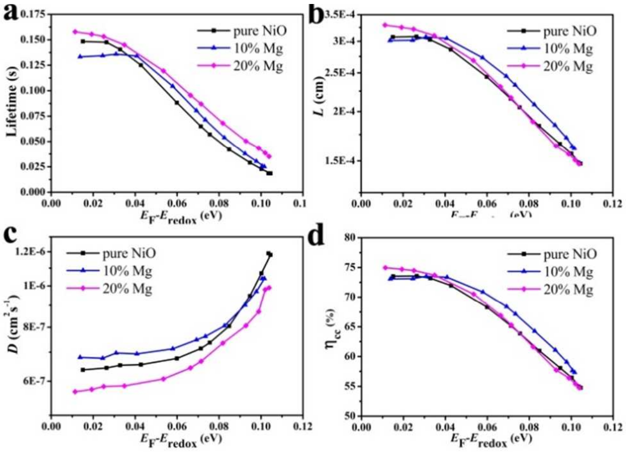

Fig.6 The photocurrent/photovltage transient decay plots of p-DSCs with the dependencies of a) hole lifetime, b) effective hole diffusion length (*L*), c) hole diffusion coefficient (*D*), d) the calculated charge collection efficiency (η_{cc}) on "E_F-E_{redox}" (the potential offset between the quasi Femi level of the semiconductor and the redox potential of the electrolyte) for p-DSSCs based on pure NiO and $Ni_{0.9}Mg_{0.1}O$ film. The charge collection efficiency is calculated according to the equation: $\eta_{cc}= L(1-e^{-d/L})/d$, where *d* is the film thickness.

shown in Fig. 5b), which can lead to steadily improvement on *LHE*. The higher transmittance should due to the partial remove of Ni^{2+} with intrinsic light absorption due to oscillator strength *d*–*d* interband transitions. The gradually increased optical band gap of $Ni_{1-x}Mg_xO$ compared with NiO could be another reason;[24] besides, it is found that the dye adsorbing amount gradually increases as the Mg content increases (as reflected by the transmittance difference between the films before and after dye absorbing, Fig. 5c, d), which should be owing to the enhanced surface basicity of the films with more Mg surface atoms. Therefore, *LHE*s for the $Ni_{1-x}Mg_xO$ series photocathodes should monotonously increase as the increasing x from 0 to 0.2. Second, with respect to the charge collection efficiency of the compared photocathodes, as evaluated by the transient photovoltage/photocurrent decay techniques, the $Ni_{0.9}Mg_{0.1}O$ film is found to be improved a little bit than that of pure NiO film in almost the whole applied potential range, which is due to slightly prolonged recombination time (Fig. 6a) and increased hole diffusion coefficient (Fig. 6c). These results can basically explain the improved *FF* of DSC based on $Ni_{0.9}Mg_{0.1}O$ than that of NiO. Higher η_{cc} together with the improved *LHE* can well plain the higher IPCE and J_{sc} of DSC based on $Ni_{0.9}Mg_{0.1}O$ than that of NiO. Interestingly, the detected charge collection property of $Ni_{0.8}Mg_{0.2}O$ film is comparable to that of $Ni_{0.9}Mg_{0.1}O$ (Fig. 6b, d), however, its measured IPCE and J_{sc} are much inferior. In view of that *LHE* of $Ni_{0.8}Mg_{0.2}O$ is even higher than $Ni_{0.9}Mg_{0.1}O$, this contradiction should be explained by other reason. Plausibly, the driving force for hole injection, determined by the difference between the valance band of $Ni_{1-x}Mg_xO$ films and the HOMO level of P1 dye, is decreased as Mg content increases. The largely decreased hole injection efficiency from $Ni_{0.9}Mg_{0.1}O$ to $Ni_{0.8}Mg_{0.2}O$ may surpass the other two factors (i.e., *LHE* and η_{cc}) and dominate the lowest IPCE and J_{sc} of the corresponding solar cell.

Furthermore, the transient results in Fig. 6c also reflect that slight increasing the Mg doping level from NiO to $Ni_{0.9}Mg_{0.1}O$ will not affect or even can increase the charge transport property of the film. But further increasing the doping level to $Ni_{0.8}Mg_{0.2}O$, hole diffusion inside the mesoporous film may be with increased difficulty. The gradually increased lifetime from NiO, $Ni_{0.9}Mg_{0.1}O$ to $Ni_{0.8}Mg_{0.2}O$ (Fig. 6c) is possibly due to the increased adsorbing density of dye molecular on the more basic surface of the semiconductors.

Conclusion

In summary, a series of ternary $Ni_{1-x}Mg_xO$ mesoporous films have been critically compared as photocathodes in p-DSCs. The surfactant directed self-assembly method for film preparation is facile to control the film's morphology and composition. These allow fair comparisons on physicochemical properties of the $Ni_{1-x}Mg_xO$ series films associated with Mg content tuning. It is found as x value increases from 0 to 0.2, the ternary film becomes more transparent and tends to adsorb more dye, which both lead to higher *LHE* of the solar cell. Flat band potential also shifts monotonously as x increases, which has two different impacts on the solar cell performance: first, V_{oc} increases monotonously as x increases which is due to the potential difference between valance band of p-type semiconductor and redox potential of electrolyte becomes larger; second, the hole injection becomes a hindering factor when x = 0.2, because of too small driving force for hole injection, the consequence of which is the limited J_{sc} of the $Ni_{0.8}Mg_{0.2}O$ based DSC. By balanced optimization of the above mentioned several factors, the maximum overall PCE of 0.19% was finally achieved by the $Ni_{0.9}Mg_{0.1}O$ film, which is improved by 85% in comparison to the NiO based DSC with an efficiency of 0.10%. Transient photovoltage/photocurrent decays measurements reflect that the $Ni_{0.9}Mg_{0.1}O$ film based DSC are superior in both facilitating hole transport and retarding interface recombination. Therefore, through this work, it is found that $Ni_{0.9}Mg_{0.1}O$ film is a promising photocathode material alternative to pure NiO in p-DSCs.

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Notes and references

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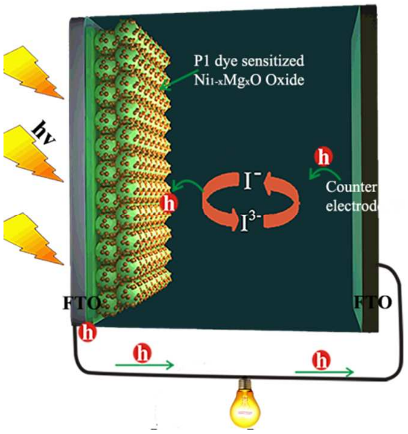
* Colour graphic:



Mesoporous $Ni_{1-x}Mg_xO$ ternary oxides used as highly efficient photocathodes in p type dye-sensitized solar cells.