Effects of pH of a hybrid gel incorporated with 3-aminopropyltrimethoxysilane on the performance of a quasi-solid state dye-sensitized solar cell

T. Suresh[a], James Joseph[b], Kyung Mo Son[a], R. Vittal[a], Jiwon Lee[c], Kang-Jin Kim[a],*

[a]*Department of Chemistry, Korea University, Seoul 136-713, Republic of Korea*
[b]*Central Electrochemical Research Institute, Karaikudi 630 006, India*
[c]*Samsung SDI Co. Ltd., Gyeonggi-Do 449-577, Republic of Korea*

Abstract

Network hybrid gel prepared with tetraethyl orthosilicate, 3-aminopropyltrimethoxysilane (APS) and poly(ethylene glycol) was used as an electrolyte matrix in a quasi-solid state dye-sensitized solar cell (DSSC). Change in pH of this hybrid gel by varying the composition of APS was found to have remarkable effects on the photoelectrochemical performance of the cell. The hybrid gel matrix, having silane polymer backbones with free amine functionality, was characterized by FT-IR spectra and FE-SEM images, and the assembled DSSC by photocurrent-voltage and incident photon to current conversion efficiency curves. The unsealed, quasi-solid state DSSC with the hybrid gel has shown an increase in the open-circuit voltage (V_{oc}) and a steady decrease in the short-circuit photocurrent (J_{sc}), with increase in the content of APS. A maximum conversion efficiency of 4.5% was obtained for a DSSC by using 20% of APS in its hybrid gel at a light intensity of $100\,mW\,cm^{-2}$. Upon replacing the amino group of APS by bulkier aniline and benzophenoaniline groups, conversion efficiencies of the corresponding DSSCs were reduced. Variations in the V_{oc} and J_{sc} are explained in terms of shift of the flat band potential of TiO_2 and a complex formation between I_3^- and $-NH_2$ of APS of the electrolyte.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Hybrid gel; 3-Aminopropyltrimethoxysilane; Short-circuit photocurrent; Open-circuit voltage; Dye-sensitized solar cell

1. Introduction

Dye-sensitized solar cells (DSSCs) have received much attention in recent years for their low cost and high efficiency, and they are perceived as good alternative to silicon solar cells in the past one and a half decade [1–4]. Grätzel's research group achieved a cell efficiency of about 11% with a liquid electrolyte DSSC [5]. The practical usage of this type of cells is hindered owing to technological problems, such as leakage, hermitic sealing and owing to lack of long-term stability of the cells attributable to volatility of the liquid electrolytes. Replacing the liquid electrolyte in the DSSC with solid or quasi-solid electrolyte is expected to solve many technological problems. Two of the approaches to solve this problem are use of hole conducting layers, such as those of PEDOT or polypyrrole [6,7], and those of CuI or CuSCN [8,9] and use of polymer or gelled matrix to immobilize the redox electrolyte [10–12]. The former approach resulted in a very low efficiency. Polymer electrolytes based on copolymers of poly(ethylene oxide) and polyepichlorohydrin were reported to have reasonable ionic conductivities [13–15]. Beneficial effects of *in situ* photopolymerized poly [di(ethylene glycol)-2-ethyl hexyl ether acrylate] in the pores of dye-coated TiO_2 film on the photovoltaic characteristics of DSSCs were reported earlier from our laboratory [16].

Biancardo et al. [17] have addressed optimization of large scale quasi-solid state DSSCs, prepared by liquid electrolyte incorporation into the polymer matrix, polymethyl-methacrylate (PMMA). They discussed important issues like semi-transparency, quasi-solid state constructions and low-cost

*Corresponding author. Tel.: +82 2 3290 3127; fax: +82 2 3290 3121.
E-mail address: kjkim@korea.ac.kr (K.-J. Kim).

realization of serially connected modules. Cyanoacrylate (commercial glue) was used as electrolyte matrix in a quasi-solid state DSSC by Lu et al. [18], and they obtained a conversion efficiency of 4.2%. Platinum metal was substituted by PEDOT:PSS [poly(3,4-ethylenedioxythiophene):-poly(styrenesulfonate)] for preparing counter electrodes for quasi-solid state DSSCs, in which the quasi-solid state of the electrolyte was achieved by incorporating a liquid electrolyte into a polymer matrix such as PMMA using propylene carbonate as gelling solvent [19].

A nanocomposite thin film made of sol–gel silica and poly(ethylene glycol) (PEG) oligomer was used as a gel electrolyte-support for a DSSC by Stathatos et al. [20]. Recently we have reported on the performance of a DSSC based on siloxane-PEG hybrid gel electrolyte [21]. Simple condensation of PEG with silanol opens up new pathways of research on quasi-solid DSSCs, owing to the fact that the functional properties of the resulting hybrid gels can be modified by changing the hydrophobic/hydrophilic or acidic/basic nature of the silane constituent.

In the present study, we report the effects of changing the pH of a hybrid gel on the performance of the pertinent DSSC, by incorporating a base, 3-aminopropyltrimethoxysilane (APS) in the hybrid gel. The approach to incorporate aminosilane in the hybrid gel to alter the pH of a quasi-solid gel matrix, and consequent optimization of the performance of the pertinent DSSC is not reported in the literature to the best of our knowledge. Effects of tailoring the acid/base nature of a silane-PEG hybrid gel of a quasi-solid state DSSC through APS on the performance of the cell are investigated. To give a 3-D network of the gel, the APS is co-condensed with tetraethyl orthosilicate (TEOS) and PEG through the condensation of silanol moieties with glycolic OH, catalyzed by glacial acetic acid.

2. Experimental

Dye-coated TiO_2 films were prepared as working electrodes for DSSCs as follows: A thin buffer layer of non-porous TiO_2 was deposited on a cleaned FTO conducting glass, purchased from Libbey-Owens-Ford (TEC 8, 75% transmittance in the visible), from 5% titanium(IV) butoxide in ethanol by spin coating at 3000 rpm, followed by annealing of the FTO at 450 °C. A TiO_2 colloidal mixture was prepared by grinding together 1.2 g of TiO_2 (P25, Degussa), 0.5 mL of 2,3-pentanedione, 0.24 g of PEG (MW 10,000) and 1 mL of water for 10 min in a mortar. Then 0.24 g of poly(ethylene oxide) (MW > 1,000,000) was added to the content with an additional 6 mL of water, and the content was ground for another 10 min. The paste obtained was then placed in a container and stirred well for 24 h. This colloidal mixture was deposited on the above-pretreated FTO glass by the doctor blade technique, using three scotch tapes for fixing the thickness. The film was dried for 10 min at 70 °C in a hot air oven before removing the tape, and then annealed at 450 °C for 30 min. A porous TiO_2 film of about 10 μm

was produced. The TiO_2 film was cooled to room temperature, warmed again to 50–60 °C and then sensitized by immersing it in anhydrous ethanolic solution of 0.3 mM N3 dye ($RuL_2(NCS)_2$) where $L = $ 2,2′-bipyridyl-4,4′-dicarboxylic acid, Solaronix) at room temperature for 24 h; the dye-coated film was designated as TiO_2/dye film.

The hybrid gels were prepared as follows: Four 1 mL samples, each consisting of TEOS and APS, were prepared with 10%, 20%, 40% and 70% APS by volume with respect to TEOS. A sample for preparing a gel electrolyte for a reference DSSC was also taken without APS in it. Each sample was mixed with 0.2 mL of glacial acetic acid and 0.2 mL of water. Same quantity of acetic acid in all the samples ensures its neutral role with regard to the pH variations of the gels, and thereby to the variations of photovoltaic performances of the pertinent DSSCs. Each mixture was well sonicated for 10 min. Four mL of acetonitrile was added to each mixture and the sonication was continued for another 10 min. To each of these mixtures, 0.1 mL of PEG (MW 200) was added and the contents were stirred vigorously for 5 min to produce the required gel. The condensation of silanes takes place by hydrolysis or acid solvolysis, as reported by Stathatos et al. [20]. At this stage, the pHs of the thus formed gels were measured by a pH meter (Istek pH meter, Model 750P, Korea).

In order to minimize the pH changes, if any due to time gap, the above-prepared TiO_2/dye films were immediately dipped vertically in the hybrid gels for 1 min. The gel-coated TiO_2/dye films were kept in a slanting position to drain excess solvent. They were then immersed separately for 1 min in 7 mL of redox electrolyte containing 0.05 M iodine, 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.1 M LiI in 3-methoxypropionitrile. The films were again kept in a slanting position for 5 min, and the excess solvents were removed from their sides by a blotting tissue paper. Each gel-coated TiO_2/dye film electrode was sandwiched by pressing simply with a Pt-coated FTO counter electrode and then using a plastic clip. No sealant was used. After a few minutes, the siloxane gel bonded the two electrodes, making the plastic clip practically redundant. J–V curves and incident photon to current conversion efficiencies (IPCE) measurements were made with the cells as soon as they were prepared, again to minimize the pH changes that may occur due to time gap between these measurements and the pH measurements.

Sandwiched DSSCs were characterized for their photoelectrochemical behavior using a Keithley M236 source measure unit. An Oriel Xe lamp (300 W) with an AM 1.5 filter was used for illuminating the DSSCs at the light intensity of 1 sun (100 mW cm^{-2}). Incident light intensity was calibrated using a photodiode detector (Newport 818UV) and an optical power meter (Newport 1830-C). An Aminco-Bowman series 2 luminescence spectrometer model FA-256 was used to measure the light scattering from the TiO_2 films. The IPCE of the DSSCs were measured using a photon counting spectrofluorometer

(ISS PC1), equipped with a 350 W Xe lamp and a motorized monochromator. An HP 8453A diode array spectrophotometer was used for observing the spectral shifts, caused by complex formation between the iodine and the hybrid gel.

For FT-IR analysis, three 1-mL solutions, consisting of TEOS + 10% PEG, TEOS + 10% APS + 10% PEG, and TEOS + 30% APS + 10% PEG (percentages by volume), were made gels by adding to each 0.1 mL of water and 0.1 mL of glacial acetic acid, and then sonicating them. The resulting gels were then diluted, each with a few mL of ethanol. The contents were poured into clean Petri dishes, dried at 50 °C for 30 min and then kept at room temperature for 1 d. The dried contents appeared as homogeneous polymeric materials. These homogeneous polymeric solids were ground well with KBr, made pellets and characterized by a Braun MB series FT-IR spectrometer. A Hitachi S-4300 FE-SEM analyzed morphology of the TiO_2/dye film and the gel-coated TiO_2/dye films.

3. Results and discussion

The hybrid gels were characterized by FT-IR spectra and FE-SEM images. Fig. 1 shows FT-IR spectra of the dried gels. Spectrum "*a*" is for the gel with TEOS + 10% PEG, spectrum "*b*" for that with TEOS + 10% APS + 10% PEG and spectrum "*c*" for that with TEOS + 30% APS + 10% PEG. The FT-IR spectra indicate the condensation of silanol groups with ethylene glycol [22]. The Si–O–Si and Si–O–C stretching vibrations are marked at 820 and 1100 cm^{-1}, respectively. Stretching vibrations of –NH_2 in the spectra "*b*" and "*c*" (confirming the presence of APS in these gels) seem to merge with vibrations of –OH of the spectrum "*a*" to give respective broad peaks at around 3000–3500 cm^{-1}, probably due to inter-molecular hydrogen bonding of the NH_2 group with silanol or glycolic OH

in each case. Vibrations at 1475 cm^{-1} are assigned to the HC–N stretching mode, which is discernible from the CH_2 scissoring vibration at 1460 cm^{-1} in the spectrum "*a*". The appearance of the HC–N stretching mode indicates again the presence of APS in the gels corresponding to the spectra "*b*" and "*c*". The larger HC–N peak of "*c*" compared to that of "*b*" is due to the larger proportion of APS of the former compared to the proportion of APS of the latter. Based on the above observations, the hybrid gel can be represented as shown in Scheme 1, with *R* being H.

Fig. 2a and b compare cross-sectional FE-SEM images of the TiO_2/dye and gel-coated TiO_2/dye films, respectively, each obtained at a depth of 5 μm from the top of the film surface. The gel-coated TiO_2/dye film in Fig. 2b shows a homogeneous and uniform distribution of the hybrid gel within it with respect to the TiO_2/dye film in Fig. 2a, indicating that the TiO_2 particles in the gel-coated TiO_2/dye film are coated well with the hybrid gel. Increased sizes of the gel-coated TiO_2 particles are evident in Fig. 2b. This observation is also supported by the increased scattering of light by the gel-coated TiO_2/dye film, compared to that by the ordinary TiO_2/dye film, as typically shown in Fig. 3 where the gel contained 20% APS.

Fig. 4 shows the photocurrent-voltage (*J–V*) characteristics of the quasi-solid state DSSC that used 20% APS in its hybrid gel. For showing the effect of APS in the gel matrix, the *J–V* curve obtained with a quasi-solid state DSSC with a hybrid gel without APS (reference cell) is also included in the figure. It can be noted that the open-circuit voltage (V_{oc}) of the cell with APS has increased relative to that of the reference cell. Contrary to the V_{oc} increase with the incorporation of APS in the hybrid gel, the short-circuit photocurrent density (J_{sc}) shows an opposite tendency. The V_{oc} increase is consistent with the dark current decrease, which is also shown in Fig. 4.

Fig. 5 shows the effects of variation of composition of APS in the hybrid gel on the V_{oc} and J_{sc} of the unsealed, quasi-solid state DSSC. Corresponding photovoltaic parameters are summarized in Table 1, which shows the maximum solar energy conversion efficiency (η) of 4.5%, J_{sc} of 11.65 mA cm^{-2}, V_{oc} of 0.65 V and fill factor of 0.60 for 20% of APS in the hybrid gel; this conversion efficiency
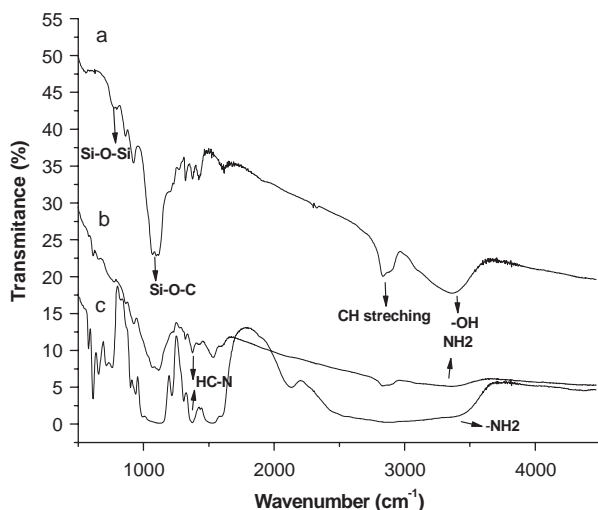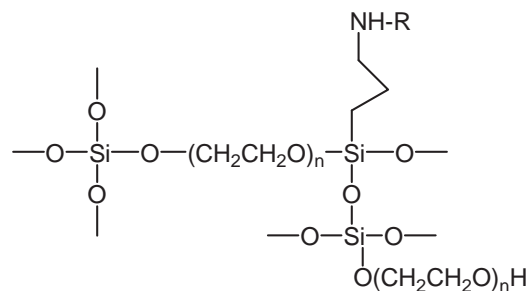

Fig. 1. FT-IR spectra of dried gels prepared with (a) TEOS + 10% PEG, (b) TEOS + 10% APS + 10% PEG and (c) TEOS + 30% APS + 10% PEG (percentages by volume).

where R = -H, -C$_6$H$_5$, -C$_6$H$_4$COC$_6$H$_5$

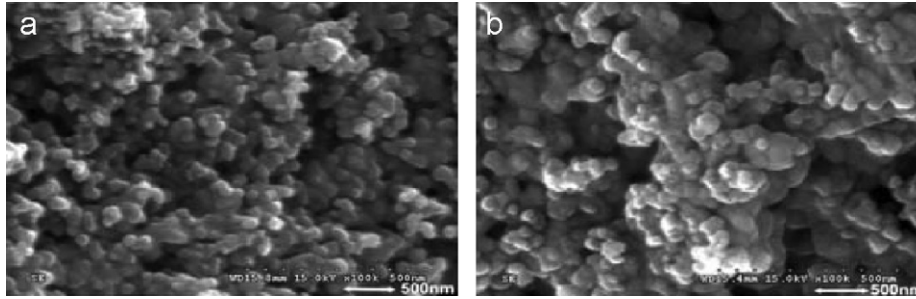Scheme 1. Schematic representation of the inorganic–organic hybrid gels.

Fig. 2. Cross-sectional FE-SEM images of (a) TiO_2/dye film, and (b) gel-coated TiO_2/dye film, each obtained at a depth of $5\,\mu m$ from the top surface of the film.
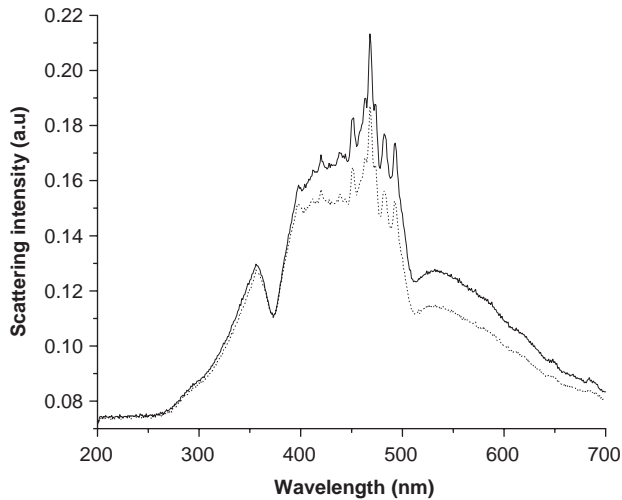

Fig. 3. Light scatterings of a gel-coated TiO_2/dye film (solid line) and a TiO_2/dye film (dotted line). Scattering intensities were measured at $10°$ from the light source.
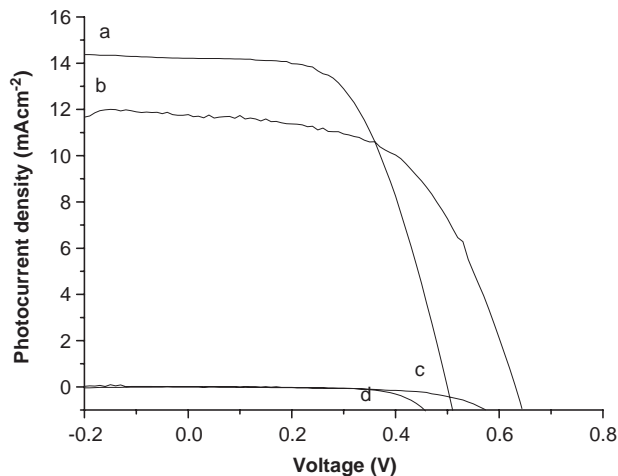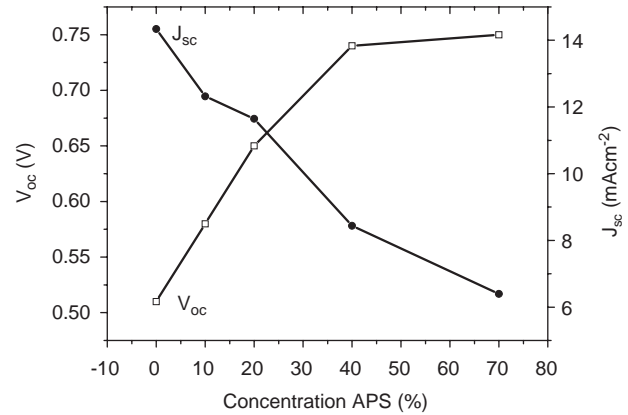

Fig. 5. Dependences of V_{oc} and J_{sc} on the composition of APS in the hybrid gel.

Table 1
Photovoltaic parameters of the quasi-solid state DSSCs with different compositions of APS[a] in the respective hybrid gels

Vol% of APS[a]	V_{oc}(V)	J_{sc} (mA cm^{-2})	FF	η(%)	pH[b]
0	0.51	14.34	0.55	4.1	4.2
10%	0.58	12.32	0.50	3.6	5.9
20%	0.65	11.65	0.60	4.5	6.2
40%	0.74	8.44	0.57	3.5	7.5
70%	0.75	6.40	0.60	2.9	8.6

[a]3-Aminopropyltrimethoxysilane .
[b]pH values of the hybrid gels.

Fig. 4. J–V curves of DSSCs using the hybrid gels: (a) without APS and (b) with 20% APS at the light intensity of $100\,m\,Wcm^{-2}$. The curves (c) and (d) depict respective dark J–V characteristics of (a) and (b).
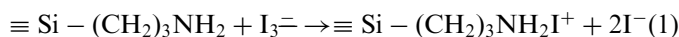
comparable to that obtainable for a DSSC with liquid electrolyte under our experimental conditions, indicating the good porosity and ion permeability of the hybrid gel for enabling the diffusion of I^- and I_3^- ions.

It is known that oxygen atoms in the ethylene glycol moieties shift the flat band potential of TiO_2 to negative values due to their Lewis base nature, contributing to a V_{oc} increase [23]. APS being a base is also expected to shift negatively the flat band potential of TiO_2. A comparison of the V_{oc} values with the pH values of the corresponding hybrid gels in the cases of different compositions of APS (Table 1) reveals that there is a steady increase of V_{oc} with the increase of APS content. It is understood that the flat band potential of TiO_2 shifts negatively with the increase of the basicity of the electrolyte, which in turn increases the

exceeds the 4.1% efficiency of the reference cell. With increase of the APS content, the V_{oc} shows an increase, while the J_{sc} shows a steady decrease, with reference to the V_{oc} and J_{sc} of the reference cell. The J_{sc} values are

V_{oc}, because V_{oc} is the difference of this flat band potential of TiO_2 and standard reduction potential of the redox couple I^-/I_3^-.

The dependence of the J_{sc} on the composition of APS in the hybrid gel can also be explained on the basis of the shift of the flat band potential of TiO_2. The negative shift of flat band potential with the increase of pH enables a negative shift of the conduction band edge of TiO_2, which may result in a less favorable mutual alignment of conduction band of TiO_2 with low lying excited states of the sensitizing dye. This is evidenced by the IPCE measurements. The IPCE curves in Fig. 6 show that with the increase in the composition of APS, i.e., with the increase of pH, the IPCE values decrease; this decrease in IPCE values is consistent with the decrease of respective photocurrents as can be seen in Table 1. Similar reduction of IPCE values with *tert*-butylpyridine was observed by Boschloo et al. [24]. Furthermore, the reduction in photocurrents with higher contents of APS (above 20%) in the hybrid gels may be due to the complex formation between I_3^- and primary amine groups of the Lewis base, NH_2 from APS, as shown below in Eq. (1) [25,26].

$$\equiv Si - (CH_2)_3NH_2 + I_3^- \rightarrow \equiv Si - (CH_2)_3NH_2I^+ + 2I^- \quad (1)$$

This complex formation reduces the effective I_3^- concentration in the electrolyte, thereby decreasing the flow of
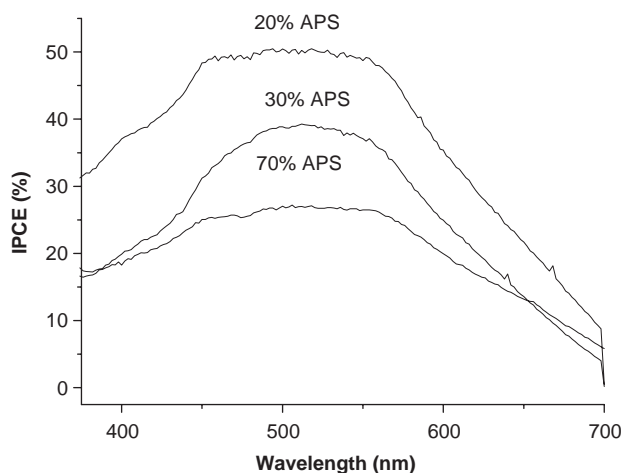

Fig. 6. IPCE spectra of quasi-solid state DSSCs fabricated with different compositions of APS in the hybrid gels.

current in the circuit. The complex formation was verified by UV absorption spectra (not shown). Peaks of the spectra of ethanolic solution of $2 \times 10^{-4} M$ I_2 were observed to be at 288.9 and 358.2 nm. Same solution additionally containing 20% APS has showed a red shift of these peaks by about 1.4 nm. This red shift is attributed to the formation of the complex as above.

To find the effects of substituents of the amino group in APS on the performance of DSSCs, we prepared two similar hybrid gels using 3-(triethoxysilyl)-propylaniline (AnilinePS) and 3-benzophenoanilinopropyl triethoxysilane (BPS) instead of APS. This study is related to the report by Kang et al. on the role of terminal groups of oligomers in determining performances of DSSCs [25]. While AnilinePS was obtained commercially from Aldich, BPS was prepared as per the procedure given by Spange et al. [27]. We intended to replace the amino functional group of APS with the functional groups of aniline and benzophenoaniline of AnilinePS and BPS, respectively. Corresponding hybrid gels, represented also in Scheme 1, were prepared by the same procedure as that of APS-containing hybrid gel. The photovoltaic properties of the DSSCs using AnilinePS and BPS were measured and the results are shown in Table 2. We fixed the compositions of these bases to be 20%, at which we have obtained the best performance of the cell with APS (Table 1). The rate of the hybrid gel formation with AnilinePS or BPS is expected to be slower than that with APS, owing to the fact that APS is associated with primary amine unlike the cases with AnilinePS or BPS. This leads to the lesser yields of the hybrid gels with AnilinePS or BPS relative to the yield of hybrid gel with APS. As a result, the hybrid gels with AnilinePS and BPS were found to be more acidic (Table 2), owing to their more residual acetic acid.

Table 2 reveals that the DSSCs with AnilinePS and BPS show lower conversion efficiencies than that of DSSC with 20% APS; this is essentially due to low V_{oc} in the case of AnilinePS and low J_{sc} in the case of BPS. It is possible that the bulkier aniline and benzophenoaniline groups of AnilinePS and BPS, respectively, do not interact with the TiO_2 particles of the electrode as efficiently as the amino group of APS. This lesser interaction of AnilinePS or BPS with TiO_2 particles would result in lesser negative shift of flat band potential of TiO_2, and thereby in a lesser V_{oc}, relative to the V_{oc} in the case of APS. The quite low J_{sc}

Table 2
Photovoltaic parameters of quasi-solid state DSSCs with hybrid gels containing APS and its derivatives

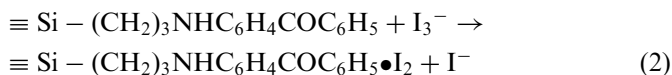| Composition of base (vol%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)	pH[d]
20% APS[a]	0.65	11.65	0.60	4.5	6.2
20% AnilinePS[b]	0.56	12.40	0.52	3.7	4.4
20% BPS[c]	0.64	8.39	0.58	3.3	4.6

[a] 3-Aminopropyltrimethoxysilane.
[b] 3-(triethoxysilyl)-propylaniline.
[c] 3-Benzophenoanilinopropyl triethoxysilane.
[d] pH values of the hybrid gels.

obtained with the hybrid gel prepared with BPS may be due to the formation of a charge transfer complex between I_3^- and the phenyl groups, as follows [28]

$$\equiv Si - (CH_2)_3NHC_6H_4COC_6H_5 + I_3^- \rightarrow$$
$$\equiv Si - (CH_2)_3NHC_6H_4COC_6H_5 \bullet I_2 + I^- \qquad (2)$$

which reduces the effective I_3^- concentration in the electrolyte, thereby decreasing the flow of current in the circuit and thus the J_{sc}.

Having investigated the effects of change of pH of the hybrid gels by means of an essentially inorganic base, APS, we intend to study the effects of pure organic bases in the gel, belonging to heteroaromatic/aromatic amines, on the performance of a DSSC.

4. Conclusions

A quasi-solid state DSSC was constructed by using a hybrid gel consisting of TEOS, PEG and APS. The composition of the hybrid gel was confirmed by FT-IR spectra and FE-SEM analyses. FE-SEM images of the gel-coated TiO_2 film showed a uniform continuous distribution of the gel within the film and increased size of TiO_2 particles. Increased light scattering by gel-coated TiO_2 film also supported the observation of increased effective size of TiO_2 particles. The V_{oc} increased while the J_{sc} showed a steady decrease with increase of the APS content, and a maximum conversion efficiency of 4.5% was obtained for a DSSC by using 20% of APS in its hybrid gel. The V_{oc} increase is explained on the basis of negative shift of the flat band potential of TiO_2 due to respective increase in pH of the hybrid gel. The decrease of J_{sc} is attributed to mutual unfavorable alignment of the conduction band edge of TiO_2 with the low lying excited states of the N3 dye. Reduction in photocurrent owing to higher contents of APS in the hybrid gel may also be due to a complex formation between I_3^- and NH_2 of APS. When the amino group of APS was replaced by bulkier aniline and benzophenoaniline groups, conversion efficiencies of the corresponding DSSCs were reduced due to the less effective shift of band edge of TiO_2, and possibly due to a charge transfer complex formation between I_3^- and the phenyl groups.

Acknowledgment

References

[1] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269.
[2] B. O' Regan, M. Grätzel, Nature 353 (1991) 737.
[3] M.K. Nazeeruddin, A. Kay, I. Rodicio, B.R. Humphrey, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[4] P. Wang, C. Klein, R. Humphry-Baker, S.M. Zakeruddin, M. Grätzel, Appl. Phys. Lett. 86 (2005) 123508(1).
[5] M. Grätzel, J. Photochem. Photobiol. A: Chem. 164 (2004) 3.
[6] Y. Saito, N. Fukuri, R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, Electrochem. Commun. 6 (2004) 71.
[7] T. Kitamura, M. Maitani, Y. Wada, S. Yanagida, Chem. Lett. 10 (2001) 1054.
[8] Q.-B. Meng, K. Takahashi, X.-T. Zhang, I. Sutanto, T.N. Rao, O. Sato, A. Fujishima, H. Watanabe, T. Nakamori, M. Uragami, Langmuir 19 (2003) 3572.
[9] B. O' Regan, F. Lenzmann, R. Muis, J. Wenke, Chem. Mater. 14 (2002) 5023.
[10] M. Matsumoto, Y. Wada, T. Kitamura, K. Shigaki, T. Inoue, M. Ikeda, S. Yanagida, Bull. Chem. Soc. Jpn. 74 (2001) 387.
[11] T. Stergiopoulos, I.M. Arabatzis, G. Katsaros, P. Falaras, Nano Lett. 2 (2002) 1259.
[12] W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada, S. Yanagida, Chem. Commun. 4 (2002) 374.
[13] A.F. Nogueira, M.A. De Paoli, Sol. Energy Mater. Sol. Cells 61 (2000) 135.
[14] A.F. Nogueira, J.R. Durrant, M.A. De Paoli, Adv. Mater. 13 (2001) 826.
[15] A.F. Nogueira, M.A.S. Spinacé, W.A. Gazotti, E.M. Girotto, M.-A. de Paoli, Solid State Ionics 140 (2001) 327.
[16] S.H. Kal, J. Joseph, J. Lee, K.-J. Kim, J. Electrochem. Soc. 152 (2005) A1378.
[17] M. Biancardo, K. West, F.C. Krebs, Sol. Energy Mater. Sol. Cells 90 (2006) 2575.
[18] S. Lu, R. Koeppe, S. Günes, N.S. Sariciftci, Sol. Energy Mater. Sol. Cells 91 (2007) 1081.
[19] M. Biancardo, K. West, F.C. Krebs, J. Photochem. Photobiol. A: Chem. 187 (2007) 395.
[20] E. Stathatos, P. Lianos, C. Krontiras, J. Phys. Chem. B 105 (2001) 3486.
[21] J. Joseph, K.-M. Son, R. Vittal, J. Lee, K.-J. Kim, Semicond. Sci. Technol. 21 (2006) 697.
[22] B. Orel, U.O. Krasovec, U.L. Stangar, J. Sol–Gel Sci. Tech. 11 (1998) 87.
[23] R. Komiya, L. Han, R. Yamanaka, A. Islam, T. Mitate, J. Photochem. Photobiol. A: Chem. 164 (2004) 123.
[24] G. Boschloo, H. Lindstrom, E. Magnusson, A. Holmberg, A. Hagfeldt, J. Photochem. Photobiol. A: Chem. 148 (2002) 11.
[25] M.S. Kang, Y.J. Kim, J. Won, Y.S. Kang, Chem. Commun. 21 (2005) 2686.
[26] N.A. Al-Hashimi, Spectrochim. Acta Part A 60 (2004) 2181.
[27] S. Spange, A. Seifert, H. Müller, S. Hesse, C. Jäger, Angew. Chem. Int. Ed. 41 (2002) 1729.
[28] F.C. Grozema, R.W.J. Zijlstra, M. Swart, P.T. Van Duijnen, Int. J. Quantum Chem. 75 (1999) 709.