

Functionally Engineered Egg Albumen Gel for Quasi-Solid Dye Sensitized Solar Cells

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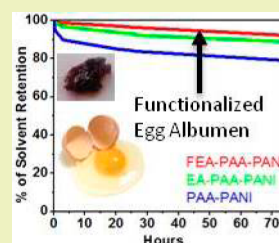
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S Supporting Information

ABSTRACT: In this report, we demonstrated an interesting application of a bioderived material for the dye sensitized solar cells (DSSCs). Egg white, the clear liquid in a hen's egg, which possesses a remarkable gelling/cross-linking ability, was applied in the form of a gel electrolyte in a DSSC architecture to enhance its durability. A hybrid gel composed of poly(acrylic acid), polyaniline and egg albumen was synthesized, and the cell efficiency, stability and durability of the corresponding DSSC device were studied in detail. The dye sensitized solar cell with the egg albumen based electrolyte demonstrated a conversion energy efficiency of 4.6%. Further, a chemically modified egg albumen with ethylenediaminetetraacetic dianhydride showed improved cross-linking, microstructural and conductivity properties of the gel, and yielded a remarkable 5.75% conversion efficiency. Electrochemical impedance spectroscopy data showed favorable characteristics for charge transport through the modified gel and supported the efficiency observations very well.

KEYWORDS: Egg albumen, gel electrolyte, dye sensitized solar cells



INTRODUCTION

The leakage and volatilization issues associated with the long-term operation of liquid electrolyte based dye sensitized solar cells (DSSCs), and the inconvenience of handling liquid electrolyte during the fabrication process, have made the commercialization of DSSCs rather difficult.¹ To circumvent this problem, efforts have been and are being undertaken to use solid organic/inorganic hole transporting materials,^{2,3} quasi-solid gel-type polymer electrolytes^{1,4} and room temperature ionic liquids^{5–7} to replace the liquid electrolyte. However, the energy conversion efficiencies of solid or quasi-solid DSSCs have remained relatively low as compared to those obtained with the liquid electrolytes. This is due to the poor pore-filling of TiO₂ coating and lower mobility of charged ions in the quasi-solid media as compared to that in the liquid media. The insufficient pore-filling allows less contact area of the electrolyte with the TiO₂/dye interface, affecting the dye regeneration process, and the lower mobility of charged ions in the quasi-solid media affects the photogenerated charge collection process. Due to these potential consequences, and their impact on the cell efficiency and stability, a nonliquid electrolyte system needs to be very carefully designed and engineered. The most crucial parameters that decide the performance of a quasi-solid electrolyte are ionic conductivity, solvent retention ability, stability-against-heat, microstructure and diffusivity of the redox species in the media.

With these considerations in mind, in the present work, we set out to utilize egg white albumen for the DSSC application, which is otherwise mostly been used in the food and cosmetic industries as a gelating or cross-linking material. Egg albumen (EA) is primarily composed of water (>90%) and proteins (~10%); constituting predominantly of albumins and a small fraction of mucoproteins and globulins.⁸ EA is a globular protein, containing various functional groups such as –COOH, –NH₂, –SH and –OH. It shows a variety of interesting characteristics such as high water solubility, excellent foaming and emulsifying ability, heat coagulability and, most remarkably, good ionic conductivity.^{9–12} The long chains of amino acids (with hydrophilic and hydrophobic functional groups) in the egg albumen proteins are all twisted and curled up, which make them spherical or globular in structure. When subjected to heat (above 80 °C), the amino acid chains undergo a nonreversible reaction and get unfolded or uncurled (termed as denaturation). Further, the linear chains interact with each other via different functional groups (as mentioned above) and form three-dimensional networks; for example, the thiol (–SH) functional groups of cysteine amino acids in adjacent chains form disulfide (S–S) bonds. The schematic in Figure 1 describes this denaturation process in egg albumen and

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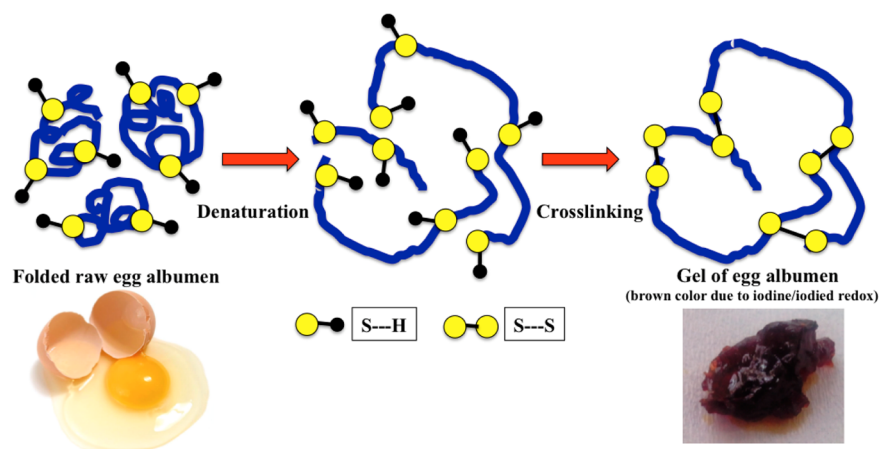


Figure 1. Schematic showing denaturation and cross-linking of egg albumen.

presents an image of a three-dimensionally cross-linked egg albumen based gel prepared in the present work.

There has been a great amount of research on the gelling and coagulating properties of EA and effects of various parameters such as temperature, pressure, chemical modifications and pH thereupon.^{9,10} However, some recent reports on the study of the conducting properties of EA¹¹ and, in general, of globular proteins,¹² have paved a way to many further electronic and electrochemical applications that can make use of such a highly functional gelator. Darvishi et al.¹¹ performed Ohmic heating of egg white and demonstrated that due to the good ionic conductivity (~ 0.4 S/m), egg white shows good Ohmic heating effects comparable to convectional heating. This conductivity was mainly due to the presence of over 90% of water, which facilitated the charge transport in it. In the dry or solid form, the conductivity is lower. Wen et al. used egg albumen in the form of a solid, dielectric layer and demonstrated a high performance field effect transistor.¹³ The low temperature cross-linking of egg albumen displayed formation of high quality films with impressive dielectric properties. In a more detailed study of electronic charge transport properties of globular proteins, Cohen and co-workers^{12,14} demonstrated considerable charge transport efficiencies in solid albumen monolayers. They observed a strong correlation between the charge transport efficiencies and presence/type of functional groups attached to the peptide chain of the proteins. This work emphasized that the electronic charge transport across such globular proteins cannot be interpreted by the usual coherent tunneling model (which is commonly used for junctions with an organic molecular monolayer), but a sequential inelastic transport model may be more suitable. This study established that proteins, with some functional engineering, can be used for building electronic devices. Taking into consideration these gelling and charge transport characteristics of egg albumen, we ventured into their application for the DSSC device for which both of these characteristics are very crucial for obtaining high performance and long-term stability.

A gel electrolyte used in DSSCs is typically composed of a polymer host, a solvent and an ionic conductor. The polymer matrix absorbs or traps the solvent (containing a redox couple) in and between the polymer chains. Hence the ionic charge transport can still take place in the trapped-liquid phase but the leakage and volatilization can be largely suppressed. Several types of gelling agents have been tried so far for DSSCs. Gelation of 3-methoxypropionitrile (MPN) based electrolyte

by poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has yielded thermally stable DSSCs with about 6% efficiency.^{15,16} Other gelling agents based on 2,4-di-*O*-dimethylbenzylidene-D-sorbitol (DMDBS)¹⁶ and amide-coupled polymers have also given good results.^{17–21} Gelation of ionic liquid based electrolytes by polyvinylpyridine that was cross-linked using a reaction with different alkyl dihalides, was investigated by Hayase and co-workers.²² They demonstrated that longer alkyl chains lead to better solar cell performance. Poly(ethylene oxide) (PEO) polymers have also been very popular as gelling polymers as they exist in several forms as electrolyte supports in solid state or quasi-solid state DSSCs. Pure as well as composite forms (with PVDF) of electrolytes have also been used utilizing silica, titania and many other inorganic additives.^{23–25} The size of the oligomer and the molecular weight have been shown to influence the conductivity of the electrolyte and, in turn, the DSSC performance.^{26,27} Similarly, composites of poly(ethylene oxide dimethyl ether) (PEODME) have shown very high performance with DSSC efficiencies of about 6.5%, caused by enhanced ionic conductivity.²⁸ Recent developments along these lines are geared toward more complex and multicomponent electrolyte systems, involving a polymer, an oligomer and a nanofiller, which provide overall better performance in terms of the efficiency and stability.^{29,30}

In the present work, we have synthesized a composite gel of EA with poly(acrylic acid) (PAA) and polyaniline (PANI). Although EA forms a stable, nonreversible gel, it does not have a good swelling ability. Therefore, PAA, a well-known superabsorbent polymer, has been used to absorb the solvent containing the redox ionic species I^-/I_3^- .^{27,28} Polyaniline is a conducting polymer and has been used earlier as a counter electrode as well as a hole transporter in dye sensitized solar cells,^{29,30} due to its electrocatalytic activity toward I^-/I_3^- redox reaction. In our work, PANI is used as well with the same purpose.

In an earlier work, we have studied EA and tried to engineer its properties via functionalization³¹ and morphology control.³² For example, we chemically modified EA lysyl residues ($-NH_2$) with ethylenediaminetetraacetic dianhydride (EDTAD) to attain carboxylic groups. As a result, the ionic conductivity and gel forming ability of EA was observed to be enhanced. In the present work, we have investigated both EA and the EDTAD-functionalized-EA (FEA) as the gelling agents for DSSC. The hybrid gel electrolytes of EA and FEA with PAA-

PANI (named as EA-PAA-PANI and FEA-PAA-PANI, respectively) have been characterized and discussed in detail in the following sections. The DSSC performance with the hybrid gels has been presented with impedance spectroscopic analysis and cell stability data.

EXPERIMENTAL DETAILS

Materials Used for the Synthesis of Hybrid Gels. Acrylic acid monomer (AC), *N,N*-methylene bis(acrylamide) (NMBA), ethylene diamine tetraacetic acid dianhydride (EDTAD) and lithium iodide were purchased from Sigma-Aldrich, St. Louis, USA. The organo-metallic sensitized dye N-719 [RuL2 (NCS) 2, L = 4,4-dicarboxylate-2,2-bipyridine] and ionic liquid 1-ethyl-3-methylimidazolium iodide (EMII) was obtained from Solaronix, SA (Switzerland). Aniline monomer and potassium peroxy disulfate (KPS) were brought from Thomas Baker Chemicals, Mumbai, India. Acetonitrile was obtained from Thermo Fischer Scientific, Mumbai, India. Potassium Iodide was purchased from Universal Laboratories, Mumbai, India. *N*-methyl-2-pyrrolidone (NMP), iodine and egg albumen ($M_w = 43\ 000$ Da) flakes were purchased from SD Fine Chemicals, Mumbai, India. The flakes were ground into a fine powder from which the water insoluble fraction was removed by centrifugation, whereas the soluble fraction was lyophilized to obtain a dry powder, which was used for all experiments.

Functional Modification of EA by EDTAD. Functionally modified egg albumen (FEA) was prepared according to the reported literature.³¹ A 10% (w/v) egg albumen solution was prepared in distilled water and the pH was adjusted to 10.5 by addition of 1 M NaOH. To this solution was added 0.5 g of ethylenediaminetetraacetic dianhydride (EDTAD) in a span of 1 h while stirring and maintaining the pH at 10.5. After the solution was stirred for 3–4 h at the same pH, the solution mixture was neutralized and dialyzed with deionized water using an activated dialysis bag of molecular weight cutoff 12 kDa to remove salts. After 48 h of dialysis, the functionally modified egg albumen solution was lyophilized to obtain dry powder.

Synthesis of Hybrid Gels of EA and FEA with Poly(acrylic acid) (PAA) and Poly(aniline) (PANI). Preparation of EA-PAA and FEA-PAA. EA-PAA and FEA-PAA superabsorbent polymers were synthesized according to the procedure given by Tang et al.³³ 1.0 g of EA or FEA and 10 g of acrylic acid monomer were dissolved in 15 mL of distilled water. Subsequently, an initiator, potassium peroxydisulfate (KPS), was added at a weight ratio of 0.08 (initiator: acrylic acid), followed by cross-linker *N,N*-methylene bis(acrylamide) (NMBA) at the weight ratio of 0.005 (cross-linker: acrylic acid) and polymerized in inert atmosphere at 80 °C under vigorous stirring. After the solution became viscous, the solution was cooled to room temperature and the resultant product was filtered, washed with excess of distilled water to remove any impurities and finally vacuum-dried for more than 12 h.

Preparation of EA-PAA-PANI and FEA-PAA-PANI. EA-PAA-PANI and FEA-PAA-PANI hybrid gels were prepared according to the following procedure: 0.2 g of EA-PAA or FEA-PAA composite was immersed in a predetermined amount of aniline (ANI) monomer and hydrochloric acid (HCl) solution (1 mL ANI in 300 mL of water of pH 2.5). It was kept at ambient conditions for 48 h, which resulted in the absorption of ANI monomer into the protein–PAA network and lead to the formation of a swollen gel. After swelling, the swollen sample was allowed to soak in 20 mL of 0.0365 M KPS solution and allowed to polymerize at 4 °C for 48 h in dark. After polymerization, the product was filtrated, washed and dried.

Gel-electrolyte was prepared by soaking 0.2 g of the respective dried EA-PAA-PANI and FEA-PAA-PANI hybrid in liquid electrolyte for more than 96 h to reach absorption saturation. The liquid electrolyte was composed of 0.1 M EMI, 0.06 M I₂, 0.1 M KI and 0.1 M LiI in a mixed organic solvent of *N*-methyl-2-pyrrolidone (NMP) and acetonitrile (AC) at a 1:4 (v/v) ratio. The soaked gels were used as such for further studies.

The details about characterization of hybrid gels and fabrication and characterization of DSSCs have been provided in the Supporting Information (ESI-1 to ESI-V).

RESULTS AND DISCUSSION

Figure 2 shows the reaction scheme for chemical modification of EA with EDTAD. Based on the reaction conditions, EDTAD

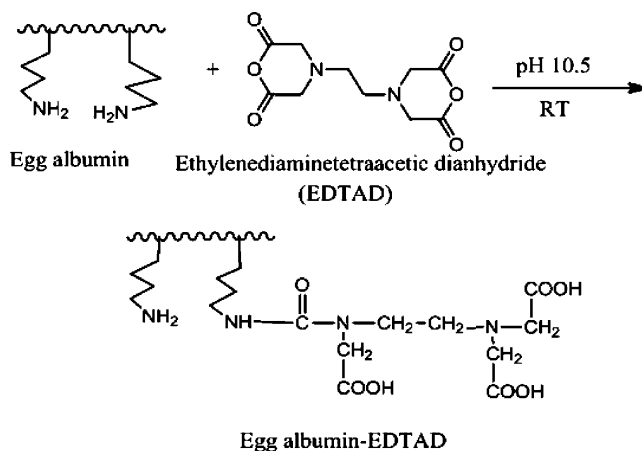


Figure 2. Reaction scheme for the functionalization of egg Albumen with EDTAD.

introduced three carboxylic groups for each lysyl residue. The procedure for the estimation of functionally modified lysyl residues has been presented in the Supporting Information (ESI-1). According to this, 30% of lysyl residues were modified with EDTAD.

Being a natural and biodegradable protein, it is important to determine the heat stability of egg albumen. This is also important because the temperature of a DSSC device can reach as high as 70–80 °C during operation under 1 sun illumination. Figure 3 presents the differential scanning calorimetry (DSC)

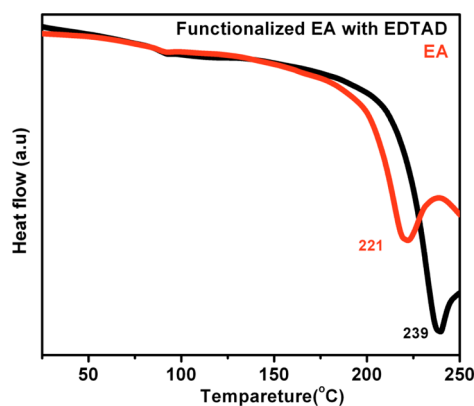


Figure 3. Differential scanning calorimetry data for EA and FEA.

data of EA and FEA. EA starts its degradation from 200 °C and shows the maximum degradation peak at 221 °C. This indicates that EA based gels can be structurally and chemically stable during the operational temperatures of the solar cells. Interestingly, FEA starts its degradation at a slightly higher temperature, i.e., from 215 °C and shows degradation peak at 239 °C. This suggests that FEA is more stable than EA. This could be explained as follows. During the functionalization process, EA was exposed to higher pH (10.5–11), which could give a head start to the protein denaturation process. Therefore, during the process of gelation upon heating, more sulfhydryl (–SH) groups were exposed to form disulfide cross-links. Thus,

the number of cross-links formed in FEA was more as compared to EA, as EA was not denatured before heating.

The infrared (IR) spectra of EA, FEA and EDTAD are presented in the Supporting Information (ESI-V). Figure 4

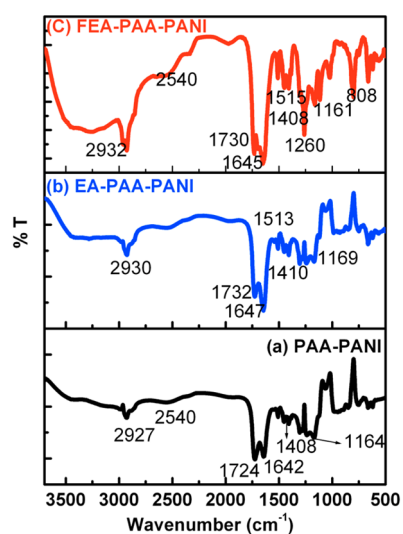


Figure 4. Fourier transform infrared spectroscopy (FTIR) spectra of the three hybrid gels: (a) PAA-PANI, (b) EA-PAA-PANI and (c) FEA-PAA-PANI.

presents the IR spectra of hybrid gels of EA-PAA-PANI and FEA-PAA-PANI (the enlarged version of this plot in the region 1100 to 1750 cm^{-1} is presented in the Supporting Information as Figure S1). For comparison, the spectra for gel without albumen, i.e., of only PAA-PANI, has also been presented. According to the reported literature, the protonated PANI shows a strong absorption band at 1154 cm^{-1} due to the high degree of electron delocalization.³⁴ However, in Figure 4a, this peak has shifted to higher frequency, i.e., at 1164 cm^{-1} , suggesting less protonation of PANI. This also indicates that the PAA-PANI hybrid has less interaction between carboxylic acid groups of PAA and the nitrogen atoms of PANI. In the case of EA-PAA-PANI (Figure 4 b), this peak shifts further to 1169 cm^{-1} . However, with the modification of EA by EDTAD, the peak shifts back to a lower frequency, at 1161 cm^{-1} (Figure 4c), signifying increase in the protonation of PANI in the case of FEA. This attribute shows a strong correlation with the conductivities of these hybrid gels, as demonstrated later in Table 1. The IR of PAA-PANI (Figure 4a) shows a characteristic peak corresponding to the carboxylic group at 1724 cm^{-1} , indicating the presence of PAA, and a peak at 1642 cm^{-1} due to $-\text{C}=\text{N}-$, indicating the presence of PANI. In EA-

Table 1. Solvent Absorption Ability and Conductivity Data of the Hybrid Gels

sample	initial weight (W_1) (g)	weight after swelling (W_2) (g)	liquid absorbency (g/g)	conductivity ($\mu\text{S}/\text{cm}$)
PAA	0.23	4.67	18.52	
EA-PAA	0.20	1.91	8.15	43
FEA-PAA	0.25	2.55	9.19	86
PAA-PANI	0.25	4.61	16.90	88
EA-PAA-PANI	0.18	1.96	9.76	62
FEA-PAA-PANI	0.21	2.68	11.68	102

PAA-PANI and FEA-PAA-PANI, the amides I and II of EA and FEA are merged with these bands and hence slight changes in intensity and peak-positions are observed. In all the IR spectra of hybrid gels, a shoulder peak at 2540 cm^{-1} is observed due to the protonated imine nitrogen ions NH^+ , which implies that the gels are conductive. In earlier studies, similar observations also have been reported for PAA-PANI.³⁴

Figure 5 presents the field emission scanning electron microscopy (FESEM) images of the hybrid gels, PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI. These images have been captured on the gel samples upon freeze-drying, and breaking them, so as to have a cross-sectional view. Figure 5a,c,e demonstrates the low magnification images, which clearly show the axis around which the gels were sliced. Figure 5b,d,f shows higher magnification views (the gels start charging and, to some extent, degrading beyond 6000 \times magnification). Having a favorable microstructure of the gel is very important, so as to have maximum solvent absorption and retention ability. The important aspects of the microstructure in this context are porosity, pore size distribution and surface roughness of the gels. As seen in Figure 5, the microstructure of the gel constituted with PAA-PANI (a, b) is more smooth as compared to that of the EA (c, d) and FEA (e, f) constituted gels. The rough and porous features in the EA and FEA based gels can be attributed to the cross-linking behavior of EA. The effect of such a porous microstructure was reflected well on the solvent absorption and retention ability of EA and FEA based hybrid gels, as discussed later. Moreover, as the PANI molecule has a high percentage of $-\text{NH}$ groups, the $-\text{COOH}$ functional groups in the EA and FEA (30% more due to functionalization) can interact through hydrogen bonding and enable more uniform blending of PANI in the case of the EA- and FEA-PAA-PANI gels.

Table 1 shows the solvent absorption capacity and conductivity data for the hybrid gels of PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI. For comparison, PAA and first stage blends of EA-PAA and FEA-PAA have also been analyzed. The procedure used for the solvent absorption analysis is provided in the Supporting Information (ESI-II c).

PAA is a hydrophilic superabsorbent polymer containing carboxylic functional groups at every repeat unit. However, it is not conducting and needs incorporation of a cross-linker in order to help it retain the absorbed solvent. Because the most commonly used solvents for dissolving lithium iodide/iodine redox species for DSSCs are organic, such as acetonitrile or *n*-methoxypropionitrile (NMP), PAA can be engineered to have amphiphilic groups via gelatin, poly(ethylene glycol) or glycerin, etc.^{25,27,28} We observed that the solvent absorbency of PAA in acetonitrile is around 18.52; however, with the compositions of EA and FEA, it decreased to 8.15 and 9.19, respectively. This is due to the higher density of cross-linking in these gels. A similar trend is observed in case of PANI containing gels, showing absorbencies of 16.9 with PAA-PANI, 9.76 with EA-PAA-PANI and 11.8 with FEA-PAA-PANI. Interestingly, in both the cases, the absorption ability of the gel containing FEA is higher than the gel containing EA, in spite of FEA being more cross-linked. This may be due to the advanced denaturation of FEA during the functionalization process and incorporation of carboxylic groups that can enable this gel to allow more solvent to be absorbed. The ionic conductivity data in Table 1 show that the conductivity of FEA containing gels is almost double compared to those containing EA. This can again be due to the functional engineering of FEA

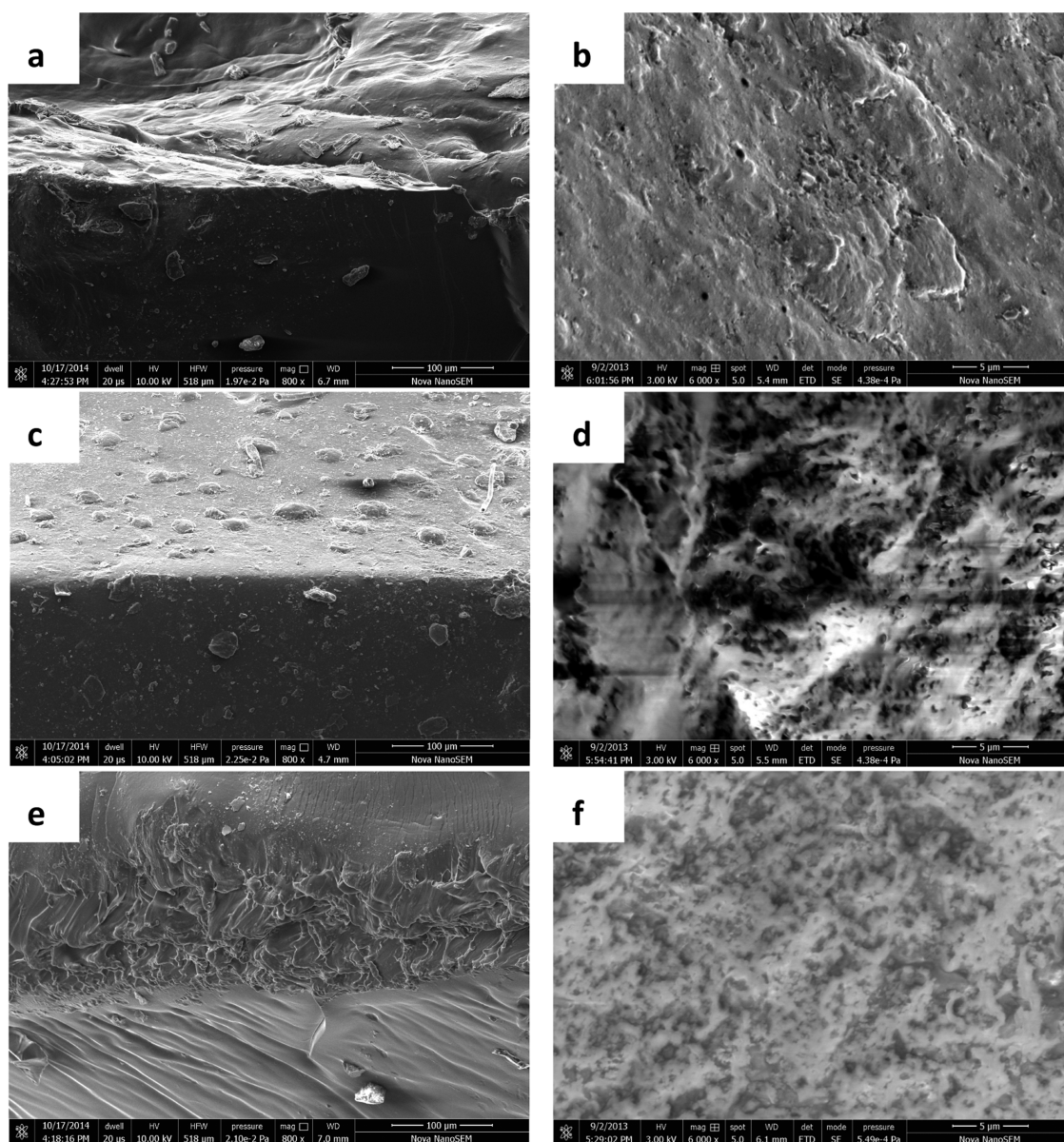


Figure 5. FESEM images of hybrid gels of PAA-PANI (a, b), EA-PAA-PANI (c, d) and FEA-PAA-PANI (e, f) (magnification: a, c, e, 800 \times ; b, d, f, 6000 \times).

to have higher % of $-\text{COOH}$ groups, and its increased-and-uniform uptake of PANI, which contributes to higher conductivity.

Another most important property associated with the solvent absorbency of gel electrolytes is solvent retention ability (measurement protocol is described in the Supporting Information section ESI-II-f). The solvent retention ability depends on the density of cross-links formed in the gel, which act like cages and prevent rapid evaporation of the solvent. Figure 6 presents the gravimetric (% of solvent lost over time) analysis of the PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI hybrid gels, and compares their solvent retention ability. Most interestingly, although the PAA-PANI hybrid gel shows the highest solvent absorbency (as seen in Table 1), its solvent retention ability is poorer than EA- or FEA based hybrid gels. This is clearly due to the cross-linking ability of egg albumen that creates more efficient traps for the solvent. The higher solvent retention ability of FEA containing gel also correlates

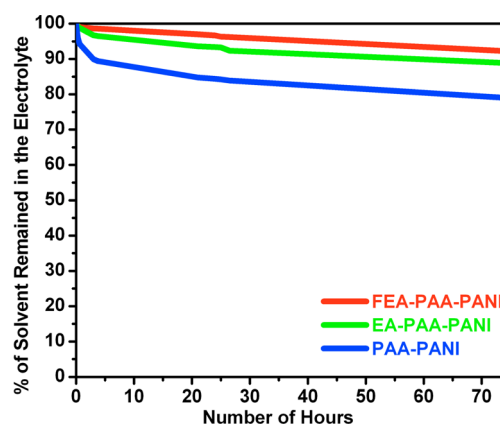


Figure 6. Solvent retention ability of PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI gels.

well with the DSC data (Figure 3) that showed extended degradation temperature of FEA due to the stronger cross-linking in this gel.

As the present work demonstrates an optoelectronic application of the egg albumen based hybrid gels, we also measured their optical absorption spectra in the UV–visible region as a matter of curiosity. The same has been presented in the Supporting Information as Figure S3. The UV–visible spectra show that with higher degree of cross-linking in the gel from PAA-PANI to EA-PAA-PANI to FEA-PAA-PANI, the gels become more opaque in the visible light. It is important to note that the DSSC cell is illuminated from the backside of the TiO₂/dye/light harvesting layer coating, and the gel is placed on the other side of this architecture. Therefore, there is no direct interference of the optical absorption of any hybrid gel with that of TiO₂ and dye. Most of the incident light gets absorbed in the path length of TiO₂/dye coating itself.

Figure 7 presents the photocurrent–voltage characteristics of DSSCs fabricated with the hybrid gel electrolytes, namely PAA-

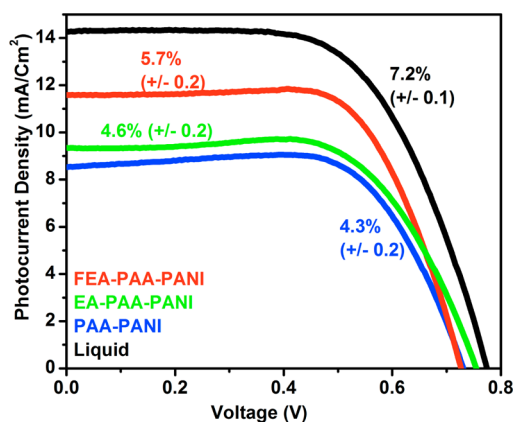


Figure 7. *I*–*V* data of PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI hybrid gel based DSSCs compared with liquid electrolyte based DSSC.

PANI, EA-PAA-PANI and FEA-PAA-PANI. Table 2 presents the corresponding DSSC parameters; open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF). A total of four sets of samples were tested under identical conditions and the % variations in the data have been mentioned, respectively. We optimized the thickness of TiO₂ layer for gel based devices, which was around 10 to 13 μm . The *I*–*V* data presented in this paper is only for the devices with optimized TiO₂ layer thicknesses.

Figure 7 shows representative case *I*–*V* plots among the four sets of samples. The DSSC efficiency obtained by only PAA-PANI based gel electrolyte is 4.3%, whereas that with the PAA-EA-PANI gel is 4.6% and that with the FEA-PAA-PANI gel it is 5.75%. Taking into account the % variation in all the DSSC parameters shown in Table 2, the main differentiating parameter for the three cases is J_{sc} . The V_{oc} values for all the

three cases were in the range of 0.72 to 0.75 V, whereas the fill factors were around 0.65 to 0.70. However, the J_{sc} of the FEA containing gel was always 1 to 1.5 mA/cm² higher as compared to that of the EA or gels without EA. This can clearly be associated with the higher conductivity of the FEA based gel electrolyte, which allowed faster charge transport toward the counter electrode. The higher conductivity of FEA based gels has already been discussed to be due to the extra –COOH functional groups. For comparison, the DSSC performance of liquid electrolyte based DSSC is also been presented in Figure 7 and the parameters are given in Table 2. The corresponding data on incident photon to current efficiency (IPCE) measurements are presented in the Supporting Information as Figure S4. The IPCE data are consistent with the trends exhibited by the *I*–*V* data. It can be observed that the main difference in the performance of liquid- vs gel electrolyte based DSSCs comes from the short circuit photocurrent, which can be expected from the difference in the diffusion of ionic species in liquid and gel electrolytes. Also it is important to note here that the optimum thickness of the TiO₂ layer for the liquid electrolyte based DSSCs was higher than that for gel based DSSCs, around 15–17 μm . We postulate that at higher thicknesses of TiO₂ layers, the seepage of solvent via the gel is less, which translates to poorer device performance. A similar effect was observed with respect to the increase in the EA or FEA concentration in the hybrid gel. Beyond a certain concentration the solvent absorption/retention ability of the gel gets hampered as it becomes more solid-like, and this strongly affects the DSSC performance. Therefore, the data presented here is with the optimum ratio of EA (or FEA) to PAA/PANI.

The stability of the DSSC devices was also tested over a longer duration. For this study, some additional cells were fabricated with acetonitrile based liquid electrolyte, and all the cells were sealed using an identical sealing protocol (described in the Supporting Information section ESI-IV-c). The stability data are presented in Figure 8, which shows that the DSSCs with EA and FEA containing gels show a longer stability as compared to the devices with liquid electrolyte and PAA-PANI based gels. The FEA hybrid gel based DSSC shows the longest stability among all. These data show a very good correlation with the solvent retention ability data of the hybrid gels, shown in Figure 6. The decrease in the solar cell performance over time can be mainly associated with the evaporation of the solvent, as the sealing protocol was not entirely perfect as compared to the commercial DSSC cells. However, for having a comparative analysis of the stability performance of liquid and gel based DSSCs, the present sealing method and data were considered as sufficient.

To further understand the effect of the functional engineering of EA on the DSSC performance, especially on the mobility or diffusivity of the iodine/iodide redox species through the gel, we performed electrochemical impedance spectroscopy (EIS) analysis. Figure 9 shows the EIS data of the DSSCs fabricated

Table 2. Typical DSSC Parameters with the Hybrid Gels (with % Variation in Four Sets of Samples)

sample	J_{sc} (mA/cm ²)	V_{oc} (V)	fill factor	efficiency (%)
PAA-PANI	8.52 (\pm 0.5)	0.73 (\pm 0.01)	0.70 (\pm 0.01)	4.36 (\pm 0.2)
EA-PAA-PANI	9.31 (\pm 0.3)	0.75 (\pm 0.01)	0.66 (\pm 0.03)	4.63 (\pm 0.2)
FEA-PAA-PANI	11.60 (\pm 0.5)	0.73 (\pm 0.02)	0.67 (\pm 0.03)	5.75 (\pm 0.2)
liquid electrolyte	14.50 (\pm 0.3)	0.77 (\pm 0.02)	0.65 (\pm 0.02)	7.20 (\pm 0.1)

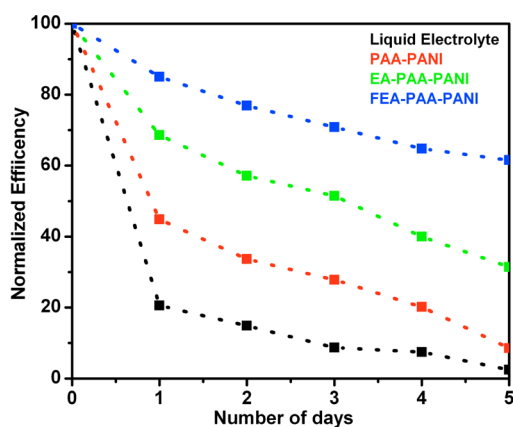


Figure 8. Stability data of the DSSC devices fabricated with liquid electrolyte and hybrid gel electrolytes of PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI.

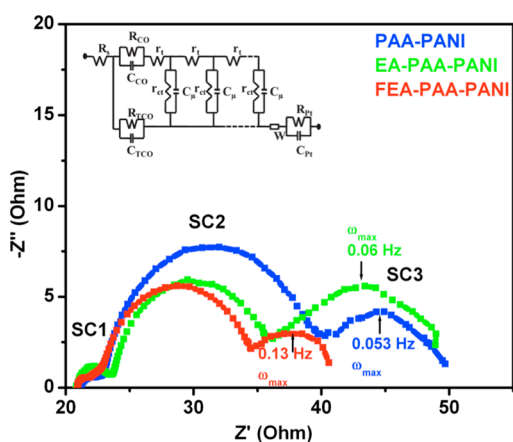


Figure 9. Electrochemical impedance spectroscopy data of DSSC fabricated with PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI gels.

with PAA-PANI, EA-PAA-PANI and FEA-PAA-PANI gel electrolytes. The experimental details of the EIS set up have been provided in the Supporting Information (ESI-IV b). The Nyquist plot representation of the EIS data is manifested as a series of semicircles corresponding to the series of interfaces present in a DSSC; for example, the high frequency semicircle (SC1, first semicircle on the left-hand side) corresponds to the Pt counter electrode/electrolyte interface, the medium frequency (SC2, mid range frequency) semicircle corresponds to the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface and the low frequency (SC3, last semicircle on the right-hand side) semicircle corresponds to the diffusion of redox species I^-/I_3^- through the electrolyte. The EIS data can be mathematically fitted into the transmission line model, shown as an inset in Figure 9. The resistance, capacitance and characteristic frequency parameters extracted through this data fitting are presented in Table 3. R_s

Table 3. Parameters Extracted by Fitting the EIS Data of DSSCs with the Transmission Line Model

sample	R_s (Ω)	R_{ct} (Ω)	C_{ct} (mF)	R_{diff} (Ω)	C_{diff} (μF)	ω_{max} (Hz) of SC3
PAA-PANI	21.1	22.8	1.05	38.2	166.9	0.06
EA-PAA-PANI	20.5	23.7	1.41	35.3	169.3	0.05
FEA-PAA-PANI	20	17	1.47	31.1	80.3	0.13

represents the series resistance of the DSSC, which considers the sheet resistance of FTO coated glass and adhesion of TiO_2 coating with FTO. This resistance is around the same for the three cases of DSSCs with the gel electrolytes. R_{ct} is the charge transfer resistance of the TiO_2/dye electrolyte interface and C_{ct} is the chemical capacitance associated with R_{ct} . In the context of the present work, this can be associated with the pore-filling and microstructure of the gel electrolyte that will allow an intimate contact with the dye-coated TiO_2 nanoparticles, and to the conductivity of the gel that will allow fast regeneration of the excited dye. R_{ct} of FEA containing DSSC is the lowest among all, suggesting that the higher conductivity and the microstructure of this gel are favorable for the charge transfer at the interface of dye and electrolyte. The observation of highest J_{sc} obtained with FEA based DSSCs fits well with this analysis. The trend obtained with the C_{ct} values also fits well with this scenario.

The analysis of the semicircle SC3 is the most important for the gel based DSSCs, because it is possible to determine the diffusion coefficient of the lithium iodide ions through the gel electrolyte from the characteristic frequency (ω_{max}) of this semicircle. This can be obtained as follows

$$D_{\text{I}_3^-} = \frac{1}{2.5} \delta^2 \omega_{\text{max}} \quad (1)$$

where δ is the overall thickness of the cell (decided by the thickness of the separator), which is $\sim 60 \mu\text{m}$, and ω_{max} is the characteristic frequency of the third semicircle. Thus, the diffusion coefficients obtained are as follows: $8.64 \times 10^{-7} \text{ cm}^2/\text{s}$ in PAA-PANI gel, $7.63 \times 10^{-7} \text{ cm}^2/\text{s}$ in EA-PAA-PANI and $1.87 \times 10^{-6} \text{ cm}^2/\text{s}$ in FEA-PAA-PANI. The highest diffusion coefficient in FEA based gel confirms that the chemical modification of EA has been translated remarkably well with respect to the charge transport properties of EA.

CONCLUSION

In this work, we have demonstrated a new scientific application of egg protein through appropriate molecular engineering. The cross-linking property of egg albumen was utilized in the quasi-solid state dye sensitized solar cells. Further, we chemically modified the egg albumen with EDTAD and demonstrated that the functionalized egg albumen has a better cross-linking ability and higher conductivity. This was supported by the better DSSC performance (in terms of efficiency as well as stability) of the devices fabricated with functionalized egg albumen gels. The egg albumen gel based DSSC showed 4.6% efficiency, and the functionalized egg albumen based gel showed a considerably higher 5.75% efficiency.

ASSOCIATED CONTENT

Supporting Information

(a) All characterization details of the hybrid gels, (b) fabrication/sealing method of DSSCs, (c) FTIR, UV/visible spectra of hybrid gels and (d) IPCE data of DSSCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The experimental work was designed by Sarika Kelkar and performed by Sarika Kelkar, Komal Pandey, Shruti Agarkar, Nidhi Saikhedkar and Mukta Tathawdekar; the work was inspired by the previous work on egg albumen by Dr. Rathna V. N. Gundloori. The paper was jointly written by Sarika Kelkar, Rathna V. N. Gundloori and Satishchandra Ogale. All authors have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

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