Dye-sensitized solar cells based on TiO₂ particulate gels: Impact of gel formation mechanism on photovoltaic performance

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Abstract

In this work the influence of different particulate gels on morphology and photoelectric performance of TiO₂ dye-sensitized solar cells (DSCs) is studied. Two coagulant and flocculant agents are used to convert a TiO₂ particulate sol into the gels using double layer compression and charge neutralization mechanisms. One more TiO₂ particulate gel is also prepared by changing the pH of the sol using acid: alkoxide molar ratio higher than the critical ratio to obtain an unstable sol. Based on X-ray diffraction (XRD) analysis, the films contain primary nanoparticles with average crystallite size of 13-15 nm. Field emission scanning electron microscopy (FE-SEM) images show uniform, nanostructured and porous microstructure of the films. For acid- coagulated condition the deposited films show large spherical particles (140-260 nm) containing small nanoparticles, while for base-coagulated condition the films contain 20-40 nm nanoparticles. Photovoltaic measurements reveal that DSCs made of basic particulate gel show higher cell efficiency (i.e., 7.68 %) than those prepared by acidic particulate gel (i.e., 6.02 % and 7.08 %). Such enhancement of efficiency is attributed to the small particle size of the

films leading to large surface area for high dye adsorption and good interconnectivity of the nanoparticles for electron transport improvement.

Keywords: Dye-sensitized solar cells; particulate gels; double layer compression; charge neutralization; unstable sol by pH control.

1. Introduction

Direct conversion of solar radiation into electrical power by the application of photovoltaic devices is desirable from the aspect of user-friendly applications. Nanocrystalline dye-sensitized solar cells (DSCs) presented by Oregan and Gratzel in 1991 with photoelectric energy conversion rate of 7.1 %, are considered to be one of the most promising alternative for silicon based solar cells due to their low cost fabrication [1]. Among oxide semiconductor materials are generally used for DSCs, TiO_2 shows good chemical stability under visible irradiation in various solutions and is nontoxic and inexpensive. In addition, it can be prepared by simple processes such as the sol-gel methodology [2]. Many factors such as microstructure, morphology, thickness of the TiO_2 film, the porosity of the film, type of dye and electrolyte, and the resistivity of the electrodes influence on the performance of DSCs. Basically, high efficiency DSCs show porous structure of deposited film with good adherence to the substrate as well as good interconnectivity between TiO_2 nanoparticles [3,4]. An enhancement in power conversion efficiency is obtained for the TiO_2 photoanode electrode composed of uniform particles and aggregates with regular shape due to improvement of light scattering and dye loading [5]. Agglomeration of TiO_2 nanoparticles may be suppressed by surface charging mechanism by adding an acid into the TiO_2 sol due to electrical double layer repulsion [6]. The sum of repulsive electrostatic force (interaction of electrical double layer surrounding each nanoparticle) and the attractive van der Waals force identifies the agglomeration of nanoparticles according to

DLVO theory (after Derjaguin, Landau, Verwey and Overbeek) [7,8]. Destabilization in a colloidal system requires a reduction in the electrical potential (i.e., zeta potential) between the fixed layer of counterions and the bulk of the liquid [9]. Coagulation and flocculation can occur by four different mechanisms including double layer compression, charge neutralization, colloid entrapment and bridging [10]. Double layer compression involves the addition of an indifferent electrolyte which increases the ionic strength of the solution and the charge density of diffuse layer but surface charge of particles remains constant. Therefore, compression of diffuse layer leads to reduction of the double layer thickness and particle agglomeration occurs at high concentration of the electrolyte [11]. Charge neutralization involves adsorption of a charged coagulant on the surface of the colloid which carries a charge opposite to that of the colloid. Therefore, the zeta potential of the system is reduced resulting in a near zero net charge. However, under base-coagulated condition the entire charged surface is not neutralized and the flocculation occurs due to an increase in ion concentration. Consequently, even with a small amount of the base, the flocculation occurs and the viscosity of colloidal systems increases [12]. In the present work we employ two different mechanisms, such as double layer compression and charge neutralization, to prepare TiO_2 particulate gels from a stable sol. For this purpose, hydrochloric acid and ammonia solution are used as the coagulant and flocculant agents. In addition, one more particulate gel is made by changing the pH of the sol using acid: alkoxide molar ratio higher than the critical ratio to obtain an unstable sol. The prepared gels have a porous and three-dimensional microstructure. For preparation of the photoanode electrodes, the gels are converted into the viscous pastes using a binder. A systematic study of the TiO_2 particulate gel formulation is presented and the impact of gel preparation method under acid-coagulated and base-coagulated conditions on morphology and consequently on the performance of DSCs is reported.

2. Experimental

2.1. Preparation of the stable TiO₂ sol

The transparent and stabilized TiO₂ sol was prepared by a particulate sol-gel process based on the optimised methodology previously reported [13]. Titanium tetraisopropoxide (TTIP) with a purity of 97 % (Aldrich, UK) was used as a precursor. Deionized water and hydrochloric acid (HCl) 37 % (Merck, Germany) were used as dispersing media and catalyst for peptization, respectively. The water–acid mixture with molar ratio of HCl:H₂O = 0.5:351.3 was stabilized at 70°C, and this temperature was kept constant throughout the experiment, together with continuous stirring. 1 mol of TTIP was added, forming a white thick precipitate, which gradually peptized for 2 h to form a clear sol. The mean hydrodynamic size and zeta potential of TiO₂ particles in the sol are 18 nm and 47 mV, respectively (Fig. S1).

2.2. Synthesis of TiO₂ nanoparticles

TiO₂ nanoparticles were prepared by a modified process analogous to the procedure previously reported [14] which is a combination of sol-gel and hydrothermal methods. The synthesized TiO₂ nanoparticles present the anatase structure with an average crystallite size of 5±1 nm (Fig. S2). Titanium tetraisopropoxide (TTIP) with a purity of 97 % (Aldrich, UK), used as titanium precursor, was dissolved in 1-octanol with a purity of 99 % (Merck, Germany) as a solvent in order to form a 0.55 M transparent precursor solution. TiO₂ sol was formed by adding deionized water dropwise with a molar ratio of [H₂O]/[Ti] = 3.3:1 into the solution during stirring. The sol was stirred for 30 minutes to complete hydrolysis and condensation reactions. The obtained sol was transferred into a Teflon-lined stainless steel autoclave at a filling ratio of 70 %, heated at 180 °C for 4 h and normally cooled to room temperature. Finally the obtained precipitates were washed with dilute ethanol and deionized water several times and dried at 25 °C.

2.3. Preparation of TiO₂ particulate gels and pastes

Two different TiO₂ particulate gels were prepared under acid-coagulated and base-coagulated conditions aided by double layer compression and charge neutralization mechanisms, respectively. For this purpose, hydrochloric acid and ammonia solution with various contents were added to the prepared stable TiO₂ sol to obtain acidic particulate gel (APG) and basic particulate gel (BPG). An alternative to prepare a particulate gel is changing the pH to slightly reduce the stability of the sol. For the sol prepared by a particulate sol-gel route, the mole of acid per mole of alkoxide used in the peptization step has a significant influence on the gelation of the sol. There is a critical acid concentration at which the volume of the gel is a minimum. Deviation from the critical acid concentration, to higher or lower values, causes a sharp increase in the volume of the gel (i.e., unstable sol). Therefore, one more TiO₂ particulate gel (i.e., PG) was also prepared by changing the pH of the sol using various concentrations of HCl higher than the critical acid concentration during the preparation of the sol. Preparation conditions of all TiO₂ particulate gels are presented in Table 1. TiO₂ pastes were finally prepared by mixing the prepared gels, TiO₂ nanoparticles and a binder.

2.4. Fabrication of DSCs

TiO₂ pastes were coated onto fluorine doped tin oxide (FTO) substrates with a sheet resistance of 7 Ω /sq by controlling the spin coater parameters to obtain the desired thickness. In order to identify the optimal thickness, the effect of film thickness was investigated on photovoltaic characteristics of the cells, being 17 ± 1 μ m the optimal thickness. This thickness was kept almost constant for all three categories to determine the optimum concentration of acid and base. Before deposition, the substrates were cleaned with acetone and ethanol and followed by ultrasound treatment. After each cycle of coating, the films were dried at 60 °C and finally annealed at 400 °C for 2 h in air atmosphere. A post-treatment with TiCl₄ solution was applied to

the freshly sintered TiO₂ electrodes and then annealed again at 450 °C for 30 min. The resulting electrodes were soaked in 0.3 mM ruthenium (II) dye (Ruthenium 535-bisTBA dye, N719, solaronix) solution (using ethanol as solvent) for 18 h. Immediately after washing and drying the electrodes with ethanol, they were used for photovoltaic measurements. The counter platinum electrode was prepared by coating a FTO substrate with a drop of H₂PtCl₆ solution followed by annealing at 450 °C for 30 min. The counter electrode was placed over the dye adsorbed photoanode electrode and sealed with a small square of sealing sheet (SX 1170-60, solaronix). Finally the redox electrolyte composed of 0.6 M dimethylpropylimidazolium iodide, 0.1 M LiI, 0.05 M I₂ and 0.5 M 4-tertbutylpyridine in acetonitrile was injected into the cell.

Table 1. Processing parameters of prepared three different TiO₂ particulate gels by acid-coagulated condition, base-coagulated condition and changing the pH of the sol.

Gel	Processing parameter			
APG	n_{HCl} / n_{TiO_2}			
	2.3	4.5	10.3	13.0
BPG	n_{NH_3} / n_{TiO_2}			
	0.42	0.83	1.26	1.68
PG	n_{HCl} / n_{TTIP}			
	0.8	1.2	2.0	2.5

2.5. Measurements and characterization

The crystal structure, morphology and absorption spectra of the electrodes were characterized by X-ray diffraction (XRD) using an X'Pert Pro MPD, Cu-K α -diffractometer, by field emission scanning electron microscope (FE-SEM) using a Mira 3-XMU and by Ultraviolet-Visible (UV-Vis) spectroscopy using a 6705 JENWAY spectrometer, respectively. TiO₂ film thickness was measured by a Tensor Alpha-step Profilometer. The specific surface area and pore volume of the samples were measured by nitrogen adsorption from Brunauer-Emmet-Teller (BET) and Barret-

Joyner-Halenda (BJH) equation at 77.35 K using a Micromeritics Tristar 3000 analyzer. Photovoltaic characteristics of fabricated cells were measured using Zahner Cimps pcs solar simulator (Zahner, Kronach, Germany) under 1 Sun AM 1.5G simulated sunlight and irradiance of 100 mW/cm².

3. Results and discussion

3.1. Microstructure

Fig. 1 shows FE-SEM micrographs of the photoanode electrodes deposited by TiO₂ pastes using acidic particulate gels (APG) with various contents of HCl. The film prepared by low HCl content (i.e., $n_{HCl}/n_{TiO_2} = 2.3$) showed a mixture of large agglomerations (~ 2.6 μm) and outspread small particles with average grain size of 20-60 nm (Fig. 1-a). By increasing HCl concentration up to $n_{HCl}/n_{TiO_2} = 4.5$, the electrical double layer forces increased for formation of small agglomerations (Fig. 1-b). Further increase of HCl resulted in an increase in ionic strength of the sol and, therefore, double layer compression and coagulation of particles. Consequently, a broad size distribution of the particles can be observed for the gels containing $n_{HCl}/n_{TiO_2} = 10.3$. This may result in an increase in the porosity and surface area of TiO₂ films and, therefore, improvement of dye adsorption (Fig. 1-c). As can be seen in Fig. 1-d, the porosity of deposited film using $n_{HCl}/n_{TiO_2} = 13$ was decreased due to its broad size distribution of the particles; in which the small particles were located between the porosity of the big particles.

Fig. 1. FE-SEM images of the surface morphology of deposited electrodes using acidic particulate gel (APG) with various n_{HCl}/n_{TiO_2} molar ratios: (a) 2.27, (b) 4.5, (c) 10.3 and (d) 13.

FE-SEM images of the photoanode electrodes deposited by TiO₂ pastes using basic particulate gels (BPG) with various contents of NH₃ are illustrated in Fig. 2. Due to positive charge of

particles in prepared stable TiO_2 sol, addition of the basic aqueous solution of ammonia resulted in neutralization of the particles near the point of zero charge (PZC). Since neutralization and consequent agglomeration and flocculation take place gradually, small particles and uniform microstructure were obtained, resulting in an increase in surface area and, therefore, improvement of dye adsorption. As it can be observed, the surface morphology of all deposited films, except that prepared by BPG with $n_{\text{NH}_3}/n_{\text{TiO}_2} = 1.68$, were almost similar containing a dense film with some surface cracks after annealing at 450 °C. The formation of the surface cracks can be explained by the fact that under capillary forces rearranging ability decreases due to enhancement of agglomeration degree. Therefore, the imposed tensile stresses by substrate can be less relaxed [15]. The film prepared using BPG with the highest ammonia content presented big particles and cracks due to neutralization of entire particles. Such big cracks may act as electron traps and influence on the diffusion coefficient [16].

Fig. 2. FE-SEM images of the surface morphology of deposited electrodes using basic particulate gel

(BPG) with various $n_{\text{NH}_3}/n_{\text{TiO}_2}$ molar ratios: (a) 0.42, (b) 0.83, (c) 1.26 and (d) 1.68.

Fig. 3 shows FE-SEM images of the photoanode electrodes deposited by TiO_2 pastes using particulate gel (PG) prepared by changing the pH to slightly reduce the stability of the sol. This was carried out using HCl as a strong acid to control the hydrolysis reaction by deviation from the critical acid: alkoxide ratio, resulted in coagulation and flocculation. It was found that the viscosity of the paste and the roughness of deposited films depend on HCl concentration and both were increased with increasing acid: alkoxide ratio due to high coagulation and flocculation of the particles. Moreover, in this case an inter-particle connection of hydrogen-bounded network of TiO_2 nanoparticles which are covered by hydroxyl groups, is formed [17]. The hydroxyl groups on the surface of TiO_2 increase by HCl treatment, enhancing hydrogen bonding

[18]. During the drying process, as the temperature rises the hydroxyl groups on the surface make strong chemical bonds which leads to aggregation [19]. Therefore, by increasing HCl:TTIP ratio agglomeration of nanoparticles occurs as a result of decreasing zeta potential, leading to improvement of inter-particle connectivity.

Fig. 3. FE-SEM images of the surface morphology of deposited electrodes using particulate gel (PG) aided by changing the pH of the sol with various n_{HCl}/n_{TTIP} molar ratios: (a) 0.8, (b) 1.2, (c) 2.0 and (d) 2.5.

The thickness of the film can be controlled by spin coating parameters. The parameters were tailored to obtain the desired thickness. Therefore, cross-sectional view of deposited photoanode electrode using basic particulate gel (BPG) with $n_{NH_3}/n_{TiO_2} = 0.83$ is demonstrated in Fig. 4. The desired thickness of 17 ± 1 μm was determined based on photovoltaic characteristics of fabricated DSCs which showed the highest performance.

Fig. 4. FE-SEM image of cross-sectional view of deposited photoanode electrode using basic particulate gel (BPG) with $n_{NH_3}/n_{TiO_2} = 0.83$.

3.2. Crystal structure

The crystal structures of TiO_2 electrodes prepared by three different methods (i.e., APG, BPG and PG) are shown in Fig. 5. It can be observed that BPG film had crystalline anatase (1 0 1) structure, whereas APG and PG films showed a mixture of anatase and rutile phases. The anatase structure was detected by its 2θ peaks at 25.50° , 25.65° and 25.67° and the rutile phase was determined by its peaks at $2\theta = 44.53^\circ$ and 44.74° . A slight shift in both anatase and rutile peaks was observed in comparison with the reference patterns, being anatase (1 0 1) at $2\theta =$

25.30° and rutile (2 1 0) at $2\theta = 44.59^\circ$. High concentration of acid causes the appearance of some defects which affects changing the lattice parameter of the crystal [20]. This might result in a strain gradient, inducing a slight shift to a lower angle for compressive stress and a higher angle for tensile stress. The average crystallite size of the samples (see Table 2) was estimated using Scherrer equation [21]:

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (\text{Eq. 1})$$

where λ is the wavelength of Cu (k_{α_1}) which is 1.5406 Å, k a constant with a value of 0.9, β is the full width at half maximum of the peak (FWHM) and θ is the diffraction angle at maximum intensity. It is evident that the average crystallite size of all electrodes is almost the same, being in the range 13.5-14.6 nm.

Fig. 5. XRD patterns of TiO₂ electrodes prepared by APG ($n_{\text{HCl}}/n_{\text{TiO}_2} = 10.3$), BPG ($n_{\text{NH}_3}/n_{\text{TiO}_2} = 0.83$) and PG ($n_{\text{HCl}}/n_{\text{TTIP}} = 2$) methods.

3.3. Photovoltaic performance of DSCs

3.3.1. Effect of thickness of photoanode electrode

The effect of film's thickness on photovoltaic characteristics of DSCs fabricated by APG method with $n_{\text{HCl}}/n_{\text{TiO}_2} = 10.3$ was studied in order to determine the optimum thickness. Photovoltaic parameters such as short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) of the electrodes, with different thicknesses prepared in a constant acid concentration as determined by J-V measurement are summarized in Table 3. In addition, the photocurrent density-voltage (J-V) curves of the electrodes are illustrated in Fig. 6. Light absorption can be increased drastically by increasing thickness of the cells made of dye-adsorbed nanoporous TiO₂. This increase is predominantly related to an

increase in surface area which leads to an increase in injection current from excited dyes to the conduction band of TiO₂. The J_{SC} and PCE of DSCs were first increased and then decreased with increasing film's thickness. Therefore, photovoltaic characteristics changed with thickness of the film, reaching a maximum at specific value of $17 \pm 1 \mu\text{m}$. Consequently, APG17 cell showed the highest efficiency of 6.02% and J_{SC} of 13.0 mA/cm² among all cells. For the film thicker than $17 \pm 1 \mu\text{m}$, J_{SC} decreased as a result of back electron transfer to I₃⁻ ions that through it loss conduction band electrons in TiO₂ increased.

Table 2. The average crystallite size of TiO₂ electrodes prepared by various particulate gels (i.e., APG, BPG and PG).

Sample	Peak	Diffraction angle (°)	Coagulant agent ratio	d (nm)
APG	Anatase (1 0 1)	25.50	10.3	14.6
	Rutile (2 1 0)	44.53		
BPG	Anatase (1 0 1)	25.65	0.83	14.5
PG	Anatase (1 0 1)	25.67	2.0	13.5
	Rutile (2 1 0)	44.74		

Table 3. The influence of film's thickness on photoelectric parameters of DSCs fabricated by APG method with $n_{\text{HCl}}/n_{\text{TiO}_2} = 10.3$.

DSC	Thickness (μm)	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	PCE (%)
APG7	7	7.82	0.73	72.0	4.11
APG12	12	9.85	0.72	69.6	4.95
APG17	17	13.0	0.71	65.2	6.02
APG22	22	9.93	0.70	64.9	4.51

Fig. 6. Photocurrent density-voltage curves of DSCs fabricated by APG method with $n_{\text{HCl}}/n_{\text{TiO}_2} = 10.3$ and various thicknesses.

It is evident that the open circuit voltage of all fabricated DSCs was almost the same, being in the range 0.70-0.73 V. This can be related to the difference between the Fermi level of TiO_2 and the redox potential of the electrolyte, which is the same for all cells. However, the back electron transfer is facilitated due to an increase in the number of trapping surface states, resulted in a small decrease in V_{OC} . Furthermore, fill factor of the cells decreased with increasing film's thickness and this was attributed to an increase of cell's resistance [22]. Therefore, an optimum film thickness as a result of balance between recombination centers and dye loading results in improvement of photovoltaic performance.

3.3.2. Effect of preparation method of the particulate gels

Since the highest cell efficiency was achieved for the photoelectrode with thickness of 17 ± 1 μm , all fabricated DSCs with different particulate gels (i.e., APG, BPG and PG) were prepared with the same thickness. The photocurrent density-voltage (J-V) characteristics of these DSCs are illustrated in Fig. 7. Moreover, their corresponding photovoltaic parameters are summarized in Table 4. It is evident that for DSCs made of APG, the J_{SC} was increased up to 13 mA/cm^2 with increasing acid: TiO_2 molar ratio from 2.3 to 10.3. Further increase in acid content resulted in a decrease in J_{SC} . This observation refers to this fact that there is an optimum porosity content at a specific molar ratio of hydrochloric acid. Pores can act as electron traps and have a negative effect on electron transport but, on the other hand, they may enhance dye loading as a result of increasing the surface area. Therefore, the optimum acid: TiO_2 molar ratio of 10.3 resulted in the highest PCE of 6.0%. As mentioned earlier, the uniform particles size distribution was observed for the APG103 electrode, leading to an enhancement of dye adsorption. The amount of adsorbed dye was determined by UV-Vis spectrometer using of 0.1 molar NaOH solution. The adsorption of N719 dye for APG103 cell was found to be the highest at the dye spectral maximum (i.e., 308 nm) among all cells in this category, as shown in Fig. 7-a. Some defect

centers which may capture electrons on the excited state of sensitized-dye of molecules are created on the surface state of TiO₂ porous film by acid treatment. These defects lead to lower electron transportation efficiency in high HCl concentration. O⁻ on the surface of TiO₂ may relates to the process of electron injection from excited state of dye molecules to the conduction band of TiO₂ and also the combination between dye molecules and TiO₂ film that both of them are close to J_{SC}. The addition of H⁺ which may adsorb both to the surface of TiO₂ and form a bond with O⁻, decreases the O⁻ and results in a decrease in J_{SC} with further content of the acid [20]. Furthermore, HCl as a strong acid increases the surface hydroxyl groups so that the interparticle bonding of the electrode improves, leading to improvement of connectivity between the nanoparticles and enhancement of the fill factor. As the internal resistance of the cells is the most effective parameter on the FF, further increase of acid:TiO₂ molar ratio may increase the surface resistance of FTO substrate, resulting in reduction of FF.

Figs. 7-b and 7-c show the photocurrent density-voltage (J-V) characteristics of DSCs prepared by BPG and PG, respectively. The maximum cell efficiency of 7.68% and 7.08% were achieved for BPG83 and PG20, respectively. As confirmed by FE-SEM images, the deposited films using basic particulate gels had better interconnectivity and smaller particle size than those prepared by APG and PG, leading to higher surface area and, therefore, higher dye adsorption, as shown in Fig. 8. BPG83 had a remarkable amount of dye adsorption as a result of a balance between size of the particles and pores. Keeping in mind the two-sided effect of pores and configuration of particles size distribution, an optimal $n_{\text{NH}_3}/n_{\text{TiO}_2}$ and $n_{\text{HCl}}/n_{\text{TTIP}}$ ratios terminates the highest J_{SC} and PCE of the cells. It has been reported that when a strong acid is used, positive shift of conduction band edge of TiO₂ occurs and the surface of TiO₂ is protonated, leading to reduction of open circuit voltage [23]. Furthermore, NH₃ treatment creates wider adsorption windows. Excitation of electrons from the occupied state toward the conduction state at a newer region results in new adsorption windows [24]. Consequently, the most likely reason for enhancement

of PCE, V_{oc} and J_{sc} of DSCs made of BPG can be assigned to contribution of the optical adsorption capability of NH_3 and their good microstructure.

Fig. 7. Photocurrent density-voltage curves of fabricated DSCs made of different particulate gels: (a) APG, (b) BPG and (c) PG.

Table 4. Photoelectric parameters of DSCs made of different particulate gels molar ratio of coagulant agent in three different methods.

Cell	Gel type	Parameter	Molar ratio	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
APG23	Acidic-coagulated	n_{HCl}/n_{TiO_2}	2.3	7.76	0.71	76.1	4.19
APG45			4.5	10.50	0.71	69.0	5.14
APG103			10.3	13.0	0.71	65.2	6.02
APG130			13.0	8.59	0.72	74.0	4.57
BPG42	Basic-coagulated	n_{NH_3}/n_{TiO_2}	0.42	13.41	0.72	64.0	6.18
BPG83			0.83	15.61	0.72	68.3	7.68
BPG126			1.26	13.10	0.72	62.3	5.90
BPG168			1.68	9.29	0.70	66.6	4.33
PG8	Unstable sol by pH control	n_{HCl}/n_{TTIP}	0.8	9.21	0.70	72.5	4.67
PG12			1.2	12.05	0.70	69.2	5.84
PG20			2.0	14.81	0.69	69.0	7.08
PG25			2.5	12.0	0.72	69.7	6.02

Fig. 8. Dye adsorption of DSCs made of different particulate gels: (a) APG, (b) BPG and (c) PG.

3.4. BET analysis

The nitrogen adsorption-desorption isotherm of the samples had the highest cell efficiency for each category (i.e., APG103, BPG8 and PG20) are represented in Fig. 9. Moreover, the insets illustrate the corresponding pore size distribution curves of the samples. Based on IUPAC assortments, the isotherms corresponding to all aforementioned samples indicate a combination of types II and IV related to mesoporous materials with an upper size restriction since the adsorption and desorption branches are closed in the region of saturation pressure. These samples are not purely mesoporous since there is no plateau at higher relative pressure as in a

typical type IV isotherm as a result of the completion of mesopore filling. The presence of macropores leads to the absence of the plateau at high P/P^0 relative pressures, as seen in type IV [25]. Furthermore, the similarity between the hysteresis isotherm shapes with type H2, according to IUPAC, shows complex pore networks include disordered mesopore network. The pore size distribution of the samples was calculated by BJH method. The inset of Fig. 9-a shows pore size distribution of APG103 with a sharp peak diameter of about 4.6 nm, whereas a sharp peak around 5.3 nm is observed for BPG8 and PG20 (Figs. 9-b and 9-c). Table 5 summarizes N_2 adsorption characteristics of the samples. The specific surface area of APG103, BPG8 and PG20 was measured 55, 65 and 50 m^2/g , respectively. These results were consistent with FE-SEM images as BPG film had the smallest particles size among all samples, resulted in the highest surface area.

Fig. 9. Nitrogen adsorption-desorption isotherms and pore size distribution curves of prepared particulate gels: (a) APG103, (b) BPG8 and (c) PG20.

Table 5. Effect of the preparation method of the particulate gels on N_2 adsorption-desorption characteristics.

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	P_{BET} (nm)
APG103	55	12.6	10.4
BPG8	65	14.9	16.2
PG20	50	11.5	11.7

4. Conclusions

To summarize, we presented a fabrication method of porous TiO_2 particulate films for solar cell applications via different particulate gel processes aided by double layer compression mechanism, charge neutralization mechanism, and unstable sol by pH control. For the double layer compression and charge neutralization mechanisms the processing parameters of

n_{HCl}/n_{TiO_2} and n_{NH_3}/n_{TiO_2} were tailored, while n_{HCl}/n_{TTIP} ratio was modified higher than the critical ratio for obtaining an unstable sol. XRD analysis manifested that the deposited films using APG and PG had a mixture of anatase and rutile phases with mainly anatase structure, whereas that of made of BPG composed of pure anatase phase. The average crystallite size of all films was calculated in the range 13-15 nm. Based on FE-SEM images, it was found that the deposited films had porous structure, containing large particles of 2.6 and 1.4 μm for those made of APG and PG, respectively and 20-60 nm nanoparticles in case of BPG. In addition, agglomeration of particles and formation of cracks were observed by increasing HCl and NH_3 contents as the coagulant and flocculant agents, respectively. The photovoltaic measurements showed that the highest cell efficiency of 7.68% was achieved for DSC made of BPG83 due to good interconnectivity of the particles and dye loading improvement. Such enhancement of dye adsorption was assigned to small particle size and high surface area of deposited film. Furthermore, DSCs fabricated by APG103 and PG8 had the highest PCE of 6.02% and 7.08% among the prepared cells in their corresponding group. The presented strategy of particulate gel process opens up new insights into the fabrication of TiO_2 DSCs and improvement of their cell efficiency.

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Table 1. Processing parameters of prepared three different TiO₂ particulate gels by acid-coagulated condition, base-coagulated condition and changing the pH of the sol.

Gel	Processing parameter			
APG	n_{HCl}/n_{TiO_2}			
	2.3	4.5	10.3	13.0
BPG	n_{NH_3}/n_{TiO_2}			
	0.42	0.83	1.26	1.68
PG	n_{HCl}/n_{TTIP}			
	0.8	1.2	2.0	2.5

Table 2. The average crystallite size of TiO₂ electrodes prepared by various particulate gels (i.e., APG, BPG and PG).

Sample	Peak	Diffraction angle (°)	Coagulant agent ratio	d (nm)
APG	Anatase (1 0 1)	25.50	10.3	14.6
	Rutile (2 1 0)	44.53		
BPG	Anatase (1 0 1)	25.65	0.83	14.5
PG	Anatase (1 0 1)	25.67	2.0	13.5
	Rutile (2 1 0)	44.74		

Table 3. The influence of film's thickness on photoelectric parameters of DSCs fabricated by APG method with $n_{HCl}/n_{TiO_2} = 10.3$.

DSC	Thickness (μm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
APG7	7	7.82	0.73	72.0	4.11
APG12	12	9.85	0.72	69.6	4.95
APG17	17	13.0	0.71	65.2	6.02
APG22	22	9.93	0.70	64.9	4.51

Table 4. Photoelectric parameters of DSCs made of different particulate gels molar ratio of coagulant agent in three different methods.

Cell	Gel type	Parameter	Molar ratio	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
APG23	Acidic-coagulated	n_{HCl}/n_{TiO_2}	2.3	7.76	0.71	76.1	4.19
APG45			4.5	10.50	0.71	69.0	5.14
APG103			10.3	13.0	0.71	65.2	6.02
APG130			13.0	8.59	0.72	74.0	4.57
BPG42	Basic-coagulated	n_{NH_3}/n_{TiO_2}	0.42	13.41	0.72	64.0	6.18
BPG83			0.83	15.61	0.72	68.3	7.68
BPG126			1.26	13.10	0.72	62.3	5.90
BPG168			1.68	9.29	0.70	66.6	4.33
PG8	Unstable sol by pH control	n_{HCl}/n_{TTIP}	0.8	9.21	0.70	72.5	4.67
PG12			1.2	12.05	0.70	69.2	5.84
PG20			2.0	14.81	0.69	69.0	7.08
PG25			2.5	12.0	0.72	69.7	6.02

Table 5. Effect of preparation method of the particulate gels on N₂ adsorption-desorption characteristics.

Sample	S _{BET} (m ² /g)	V _{tot} (cm ³ /g)	P _{BET} (nm)
APG103	55	12.6	10.4
BPG8	65	14.9	16.2
PG20	50	11.5	11.7

Fig. 1. FE-SEM images of the surface morphology of deposited electrodes using acidic particulate gel (APG) with various n_{HCl}/n_{TiO_2} molar ratios: (a) 2.27, (b) 4.5, (c) 10.3 and (d) 13.

Fig. 2. FE-SEM images of the surface morphology of deposited electrodes using basic particulate gel (BPG) with various n_{NH_3}/n_{TiO_2} molar ratios: (a) 0.42, (b) 0.83, (c) 1.26 and (d) 1.68.

Fig. 3. FE-SEM images of the surface morphology of deposited electrodes using particulate gel (PG) aided by changing the pH of the sol with various n_{HCl}/n_{TTIP} molar ratios: (a) 0.8, (b) 1.2, (c) 2.0 and (d) 2.5.

Fig. 4. FE-SEM image of cross-sectional view of deposited photoanode electrode using basic particulate gel (BPG) with $n_{NH_3}/n_{TiO_2} = 0.83$.

Fig. 5. XRD patterns of TiO_2 electrodes prepared by APG ($n_{HCl}/n_{TiO_2} = 10.3$), BPG ($n_{NH_3}/n_{TiO_2} = 0.83$) and PG ($n_{HCl}/n_{TTIP} = 2$) methods.

Fig. 6. Photocurrent density-voltage curves of DSCs fabricated by APG method with $n_{HCl}/n_{TiO_2} = 10.3$ and various thicknesses.

Fig. 7. Photocurrent density-voltage curves of fabricated DSCs made of different particulate gels: (a) APG, (b) BPG and (c) PG.

Fig. 8. Dye adsorption of DSCs made of different particulate gels: (a) APG, (b) BPG and (c) PG.

Fig. 9. Nitrogen adsorption-desorption isotherms and pore size distribution curves of prepared particulate gels: (a) APG103, (b) BPG8 and (c) PG20.

(a)

(b)

(c)

(d)

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(APG) with various n_{HCl}/n_{TiO_2} molar ratios: (a) 2.27, (b) 4.5, (c) 10.3 and (d) 13.

(a)

(b)

(c)

(d)

Fig. 2. FE-SEM images of the surface morphology of deposited electrodes using basic particulate gel

(BPG) with various $n_{\text{NH}_3}/n_{\text{TiO}_2}$ molar ratios: (a) 0.42, (b) 0.83, (c) 1.26 and (d) 1.68.

(a)

(b)

(c)

(d)

Fig. 3. FE-SEM images of the surface morphology of deposited electrodes using particulate gel (PG) aided by changing the pH of the sol with various n_{HCl}/n_{TTIP} molar ratios: (a) 0.8, (b) 1.2, (c) 2.0 and (d) 2.5.

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(a)

(b)

(c)

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