

# Effect of optical property of surfactant-treated TiO<sub>2</sub> nanostructure on the performance of TiO<sub>2</sub> photo-electrochemical cell

M. Y. A. Rahman · A. A. Umar · L. Roza · M. M. Salleh

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**Abstract** TiO<sub>2</sub> nanostructures have been treated using different kind of surfactant to modify its optical absorption and morphology. TiO<sub>2</sub> nanostructures were prepared via simple method on indium tin oxide (ITO) surface, namely, liquid-phase deposition technique (LPD) at 50°C. The TiO<sub>2</sub> nanostructures film with a thickness of about 236 nm was annealed at 400°C for 1 h in the air to enhance the interconnectivity of the particles. The dense and compact TiO<sub>2</sub> nanoparticle with different shape, particle size and surface morphology was used as a photovoltaic material in a photo-electrochemical cell of ITO/TiO<sub>2</sub>/electrolyte/platinum. TiO<sub>2</sub> nanostructure films were treated with three different kinds of surfactants: cetyltrimethylammonium bromide (CTAB), hexamethylenetetramine (HMT) and polyvinylpyrrolidone (PVP). It was found that the film treated with HMT performed best, with a  $J_{sc}$  of 57.5  $\mu\text{A}/\text{cm}^2$ . In conclusion, optical absorption, band gap and grain size of TiO<sub>2</sub> nanostructure influenced the performance of the cell.

**Keywords** Liquid phase deposition · Photo-electrochemical cell · Surfactant · TiO<sub>2</sub> nanostructure

## Introduction

The growth of nanostructure materials with controllable shape and particles size has been intensively studied in order to obtain novel and excellent properties. Many studies reported that the use of TiO<sub>2</sub> nanostructure in photoelectrochemical cells improved its performance, due to their large surface area which provides a direct pathway for electrons to transfer. Particle size and shape are two parameters that affect the performance of dye-sensitized solar cell [1]. TiO<sub>2</sub> nanostructures with high photo-activity and good optical property depend on their particle size and shape. TiO<sub>2</sub> nanostructures' photoelectrochemical cells with high efficiency can be fabricated by simple method [2]. The mesoporous titania film with dense and compact structure is an important component of the cell in order to obtain high conversion efficiency [1]. To achieve a highly crystalline TiO<sub>2</sub> nanostructure with modified morphology and shape, several techniques can be used: sol-gel, chemical vapour deposition, hydrothermal process and screen printing [3]. These techniques can produce a TiO<sub>2</sub> nanostructure with different structures such as sphere, cube [4], nanotube [5], nanorod-like crystal [7], nanowire, nanodisk and fiber. However, these techniques are costly and complicated for preparing TiO<sub>2</sub> nanostructures. Also, these techniques are unable to scale up to larger area devices. For these reasons, an easy and simple technique for TiO<sub>2</sub> nanostructure growth is required.

Liquid-phase deposition (LPD) is a simple technique to prepare TiO<sub>2</sub> film via hydrolysis of metal-fluoro complex in the presence of boric acid at an ambient temperature [7–10]. LPD can be used to synthesize TiO<sub>2</sub> nanoparticles on indium tin oxide (ITO) substrate by dipping the substrate into a solution containing 0.1 M (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> and 0.2 M H<sub>3</sub>BO<sub>3</sub>. LPD-prepared thin film nanostructures can be used to

M. Y. A. Rahman (✉) · L. Roza  
College of Engineering, Universiti Tenaga Nasional,  
Kajang,  
Selangor 43009, Malaysia  
e-mail: yusri@uniten.edu.my

A. A. Umar (✉) · M. M. Salleh  
Institute of Microengineering and Nanoelectronic (IMEN),  
Universiti Kebangsaan Malaysia (UKM),  
Bangi,  
Selangor 43600, Malaysia  
e-mail: akrajas@ukm.my

improve the performance of photo-electrochemical cells. Mesoporous  $\text{TiO}_2$  thin films can also be treated with organic dopant such as DNA and methylene blue to  $\text{TiO}_2$  film [11, 12]. LPD was augmented with the addition surfactant into solution as described in several reports [13–15]. The particle size and shape of  $\text{TiO}_2$  nanostructures can be controlled during the growth of  $\text{TiO}_2$  nanostructures by LPD treated with surfactant technique.

We have synthesized  $\text{TiO}_2$  nanoparticles with different optical absorption and morphology. We prepared a  $\text{TiO}_2$  nanostructure on ITO substrate using the LPD technique. The surfactants were used to control these properties of  $\text{TiO}_2$  nanostructures [15, 16]. Three kinds of  $\text{TiO}_2$  nanostructure with surfactants—cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP) and hexamethylenetetramine (HMT)—were prepared at the same preparation conditions. All  $\text{TiO}_2$  samples were utilized in a photoelectrochemical cell of ITO/ $\text{TiO}_2$ /liquid electrolyte/platinum. The objective of the work was to study the effect of surfactants on the optical absorption and morphology of  $\text{TiO}_2$  nanostructures and correlate them with the cell performance in terms of  $J_{sc}$  and  $V_{oc}$ .

## Experimental

### Materials

Materials that were used for preparing  $\text{TiO}_2$  nanostructure are ammonium hexafluorotitanate  $(\text{NH}_4)_2\text{TiF}_6$  purchased from Sigma-Aldrich, boric acid purchased from Wako Chemical. CTAB was purchased from Amresco ISC Bioexpress, and HMT and PVP were purchased from Acros Organics. These materials were used without further purification. ITO-coated glass with a sheet resistance of 9–22  $\Omega$ /sq was purchased from VinKarola instrument USA.

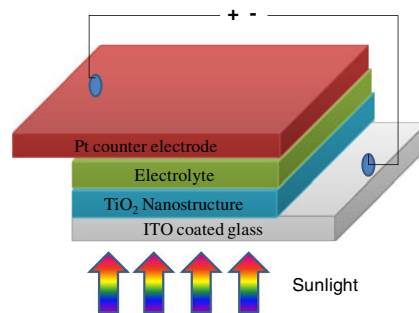
### Preparation of $\text{TiO}_2$ nanoparticle

ITO substrate was cleaned by wet cleaning of acetone, followed by 2-propanol in ultrasonic bath and dried under nitrogen flow. The substrate was immersed into a 10-ml solution containing 0.1 M  $(\text{NH}_4)_2\text{TiF}_6$ , 0.2 M  $\text{H}_3\text{BO}_3$  in deionized water. The precursor solutions were mixed with different surfactants (CTAB, HMT and PVP, respectively). The cleaned substrates were suspended vertically in the solution at 50°C for 4 h. Then, the substrates were taken out and cleaned by deionized water. The samples were removed and washed with acetone to remove residual solution on a glass side. The coated substrates were dried under nitrogen flow at room temperature. Finally, the samples were annealed at 400°C for 1 h to remove an organic binder and to enhance the interconnectivity of the particles. Field

emission-scanning electron microscopy (FE-SEM) Zeiss Supra 55VP FE SEM model was used to study the microstructure in terms of shape and particle size of the samples. Optical spectrophotometer UV–Vis lambda 900 Perkin Elmer was used to study the optical absorption of the samples. Preparation of  $\text{TiO}_2$  nanostructure treated with surfactant will change morphology and particles size with high density. The average grain sizes of the samples were estimated by taking the size of three particles of  $\text{TiO}_2$ . It is expected that this will improve the performance of the cell. By treating  $\text{TiO}_2$  with a surfactant, it is possible to enhance the optical absorption of  $\text{TiO}_2$  nanostructure in the visible region (~400 nm). The band gap,  $E_g$ , of the samples can be estimated from the absorption spectra.

### Fabrication and performance study of photo-electrochemical cell

The preparation of  $\text{TiO}_2$  nanostructure as photovoltaic material has been described in the “Experimental” section. Platinum films as counterelectrode were prepared by sputtering platinum pellet on ITO substrate. An electrolyte containing 0.5 M LiI/0.05 M  $\text{I}_2$ /0.5 M *tert*-butylpyridine (TBP) in acetonitrile was used as the redox couple. The electrolyte was sandwiched between the  $\text{TiO}_2$  nanoparticle film and the counterelectrode and shown in Fig. 1. The cell was clamped in order to optimise the interfacial contact between the layers making up the cell, the liquid electrolyte–platinum electrode and  $\text{TiO}_2$ –electrolyte. The performance study of the cell was carried out using an AM 1.5 simulated light with intensity of 100  $\text{mW cm}^{-2}$ . The illuminated area of the cell is 0.8  $\text{cm}^2$ . The current–voltage curve of the cell under illumination was recorded by a Keithley high voltage source model 237 interfaced with personal computer. Each photovoltaic measurement was carried out five times using five  $\text{TiO}_2$  samples treated with three different surfactants to confirm the accuracy the result.  $J$ – $V$  curves are presented in the “Result and discussion” section.



**Fig. 1** Structure of the photo-electrochemical cell

## Results and discussion

### Characterizations of TiO<sub>2</sub> nanostructure

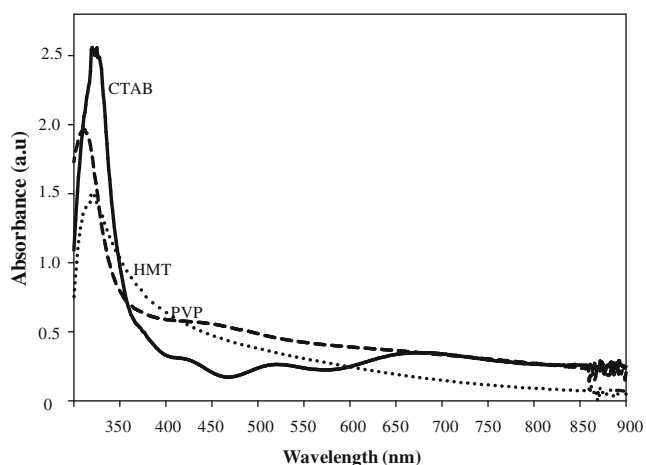
Figure 2 shows the UV–Vis absorption spectra of TiO<sub>2</sub> nanostructure treated with three different types of surfactants. It was observed that TiO<sub>2</sub> treated with HMT had the highest optical absorption in the ultraviolet region at the wavelength of 400 nm compared with the other two samples. It is believed that the photo-electrochemical cell operates at this wavelength approaching the visible region. Therefore, the numbers of electron–hole pairs generated in this cell are larger than the other two cells. Thus, the performance of the cell in terms of current will improve [17].

Figure 3 shows the plot of  $(\alpha h\nu)^{1/2}$  as a function of photon energy,  $h\nu$  for TiO<sub>2</sub> treated with three different types of surfactants. We performed a simple model for calculating the band gap of all three TiO<sub>2</sub> samples. Using the UV–Vis optical absorption spectra shown in Fig. 2, Fig. 3 is presented in order to estimate the indirect band gap for each sample using the equation:

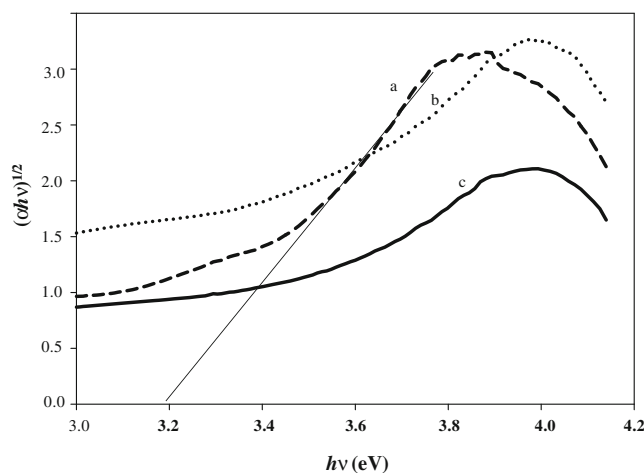
$$(\alpha h\nu)^{1/2} = B(h\nu - E_g)$$

where  $E_g$ ,  $\nu$ ,  $h$  and  $B$  are the band gap, absorbance, light frequency, Planck’s constant ( $6.63 \times 10^{-34}$  J s) and the corresponding absorption constant, respectively [18].

Table 1 shows the estimated band gap of each sample. As shown in the table, the TiO<sub>2</sub> nanostructure treated with HMT has the lowest band gap compared with the other two samples. The result is consistent with the optical absorption for all three samples. With the lowest  $E_g$  of 3.05 eV, it is expected that the TiO<sub>2</sub> nanostructure treated with HMT will generate the highest number of electron–hole pairs when illuminated with light. With the lower band gap, it is easier for electrons to be excited from valence band to



**Fig. 2** Typical UV–Vis absorption spectra of TiO<sub>2</sub> nanostructure treated with surfactants



**Fig. 3** Plot of  $(\alpha h\nu)^{1/2}$  versus photon energy ( $h\nu$ ) for calculating band gap of TiO<sub>2</sub> nanostructure treated with a CTAB, b HMT and c PVP

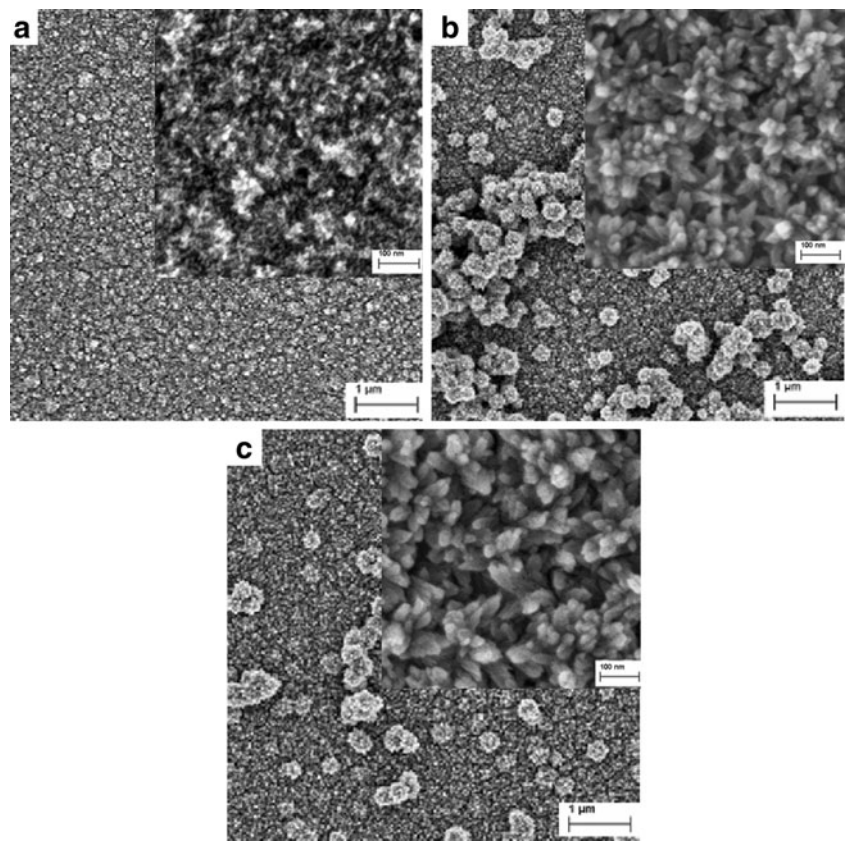
conduction band of TiO<sub>2</sub> [4]. The band gap is determined by drawing a straight line at the linear part of the plot as shown in Fig. 3. The observed indirect band gap energy of TiO<sub>2</sub> was calculated to be 3.2 eV, corresponding well with values reported in the literature (3.0–3.2 eV) [19]. This observation also eliminates the existence of a secondary phase of anatase and rutile in TiO<sub>2</sub> nanostructure, whose indirect band gap of TiO<sub>2</sub> was reported in the range of 3.0 and 3.2 eV, respectively.

Figure 4 shows the surface morphology of TiO<sub>2</sub> nanostructures treated with three different types of surfactants. The TiO<sub>2</sub> nanostructures exhibit high density and compact surface area without forming any cracks. It can clearly be seen that treating TiO<sub>2</sub> nanostructure with surfactant changes the morphology in terms of particle size of TiO<sub>2</sub> nanostructure. Actually, the actual mechanism for the variation of morphology upon surfactant treatment is not yet well understood. However, the following fact could be considered: when TiO<sub>2</sub> was treated with CTAB, a relatively thinner grass-like structure was produced. This result is in contradiction with those treated with HMT and PVP, which produce relatively rougher morphology. This can be directly related to the unique functional group of the surfactant. CTAB with positively charge amine group [CTA<sup>+</sup>] [20], exhibiting a strong binding to the TiO<sub>2</sub> crystalline plane. This will lead to the production of smoother morphology in terms of smaller grain size. Meanwhile, HMT with a

**Table 1** Band gap, grain size and thickness of TiO<sub>2</sub> nanostructures treated with different type of surfactants

TiO <sub>2</sub> sample	$E_g$ (eV)	Grain size (nm)	Thickness (nm)
HMT	3.05	25	237
CTAB	3.20	10	236
PVP	3.21	30	196

**Fig. 4** FESEM images of TiO<sub>2</sub> nanostructure treated with various surfactants: a CTAB, b HMT, c PVP



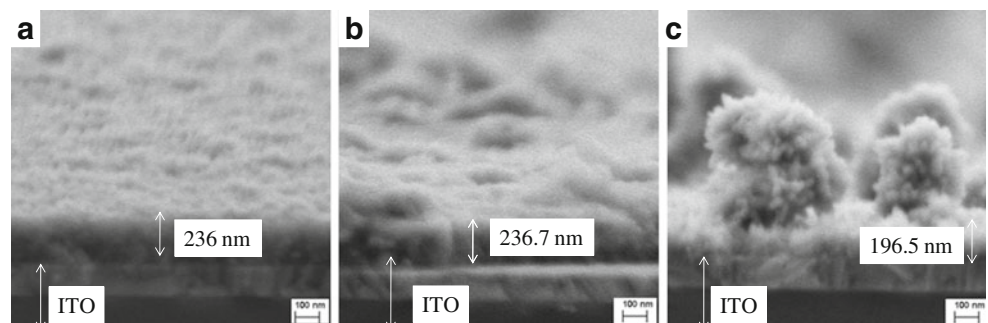
relatively weak amine group [21] and PVP with a relatively weak phosphine group were attached onto the TiO<sub>2</sub> crystalline plane with high flexibility. In other words, this shows a dynamic attachment that allows the growth of a particular plane to expand. Therefore, relatively bigger grain sizes were obtained.

TiO<sub>2</sub> nanostructure with high density and compact surface area was used as a photovoltaic material which acts as a blocking layer in the cell [6]. High-density TiO<sub>2</sub> nanostructure synchronized with compact structure without any cracks and cavities will enhance the contact surface area between TiO<sub>2</sub> nanostructure and ITO to provide more electron pathways for photo-regeneration electrons and improve the performance of the cell. This prevents the charge carrier

recombination between the ITO layer and liquid electrolytes to take place.

Figure 4 shows the cross-sectional FESEM images of the TiO<sub>2</sub> nanostructure treated with three different kinds of surfactants. The thickness of each sample was obtained from the SEM micrograph and presented in Table 1. The TiO<sub>2</sub> nanostructure treated with HMT has the highest thickness while the one treated with PVP has the lowest thickness. It is expected that the thickness of the TiO<sub>2</sub> layer influences the performance of the photo-electrochemical solar. It is worth mentioning that the thicker TiO<sub>2</sub> nanostructure treated with surfactant acts as a blocking layer to prevent the charge recombination between electrons and holes [5, 6]. Thicker TiO<sub>2</sub> provides a larger number of electron–hole pairs and

**Fig. 5** Cross-sectional FESEM images of TiO<sub>2</sub> nanostructure treated with various surfactants: a CTAB, b HMT, c PVP



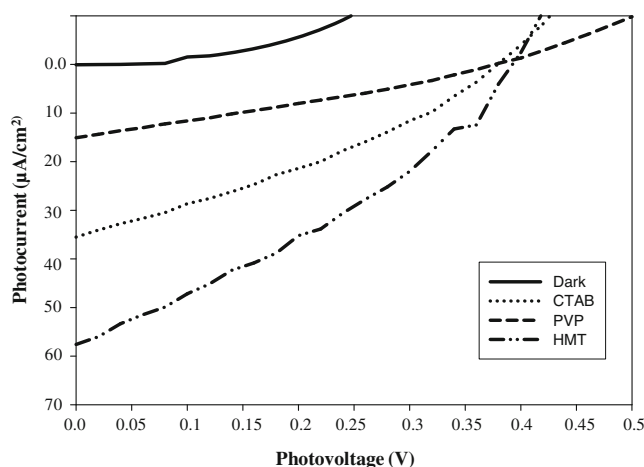


then improves the performance of the cell. A previous work reported that TiO<sub>2</sub> nanostructure was prepared with two layers, first layer with thickness 90 nm acted as blocking layer [5]. Comparing with the thickness of the cell reported by Park et al. [5], the TiO<sub>2</sub> layers for the cells developed in this work are thicker for photoelectrons to diffuse into the ITO layer.

Performance of the photo-electrochemical cell of ITO/TiO<sub>2</sub>/electrolyte/platinum

Figure 5 shows the current density–voltage ( $J$ – $V$ ) curves under illumination for the photo-electrochemical cell with TiO<sub>2</sub> nanostructure treated with three different surfactants. The cell with TiO<sub>2</sub> nanostructure treated with HMT had the highest  $J$ – $V$  curve compared with the cell with TiO<sub>2</sub> treated with CTAB and PVP. These  $J$ – $V$  curves are bigger than those reported by Chou et al. [19]. However, the shapes of the curves are about the same. The result is supported by the UV–Vis optical absorption, the estimated band gap of TiO<sub>2</sub> nanostructure treated with HMT is the lowest (3.05 eV). Furthermore, this TiO<sub>2</sub> sample possesses the highest optical absorption in the region approaching visible region (~400 nm). Therefore, the numbers of electron–hole pairs generated in this cell are bigger than the other two cells. Thus, the performance of the cell in terms of current will be improved. It is also found that the photo-current generated in this work is higher than that reported by Taslim et al. [22] and Rahman et al. [23] since the cell utilized liquid electrolyte. The photo-electrochemical cell reported by Taslim et al. [22] utilized a solid electrolyte of PAN-PC-LiClO<sub>4</sub>. As is well known, the conductivity of liquid electrolyte is much higher than that of the solid electrolyte. Higher conductivity and lower interfacial resistance lead to a higher amount of generated photo-current in the device.

The photovoltaic parameters are analyzed from the current density–voltage curve shown in Fig. 6 and illustrated in Table 2. These results indicate that optical properties, morphology and thickness of TiO<sub>2</sub> nanostructure had an effect on the performance. The cell with the TiO<sub>2</sub> nanostructure treated with HMT shows the highest  $J_{sc}$ . The result can be linked with the optical absorption and the estimated band gap of the TiO<sub>2</sub> sample. From the result shown in Table 1, it is clearly seen that there is no correlation between the performance of the cell and the grain size of the TiO<sub>2</sub> nanostructure. The performance of the cell does not increase with the decreasing grain size of TiO<sub>2</sub>. It is expected that smaller grain size of TiO<sub>2</sub> will lead to better performance of the cell, as reported in one study [17]. The TiO<sub>2</sub> film with the smallest grain size will provide the best interfacial contact at the interface of TiO<sub>2</sub>–electrolyte, causing more holes to be captured by iodide ion in the electrolyte. This will lead to



**Fig. 6**  $J$ – $V$  characteristics of TiO<sub>2</sub> photo-electrochemical cell TiO<sub>2</sub> nanostructure treated with various types of surfactant under illumination of 100 mW cm<sup>-2</sup> light

a faster rate of recombination and excitation of electron–hole pairs in TiO<sub>2</sub> [18]. Thus, better performance of the cell is expected [22]. However, the performance of the cell can be linked with the optical absorption of the TiO<sub>2</sub> nanostructure. Higher optical absorption and lower band gap will cause more electron–hole pairs to be excited from valence band to conduction band of TiO<sub>2</sub> to produce current when illuminated with light. With the lower band gap, it is easier for electrons to be excited from valence band to conduction band without requiring more energy [23]. Thus, the performance of the cell in terms of current is improved.

## Conclusions

TiO<sub>2</sub> nanostructures treated with surfactants, HMT, CTAB and PVP, have successfully been prepared on ITO substrate using the LPD technique. The TiO<sub>2</sub> nanoparticle samples with different optical absorption and morphology were used as photovoltaic material in a photo-electrochemical cell of ITO/TiO<sub>2</sub>/electrolyte/platinum. The cell utilizing the TiO<sub>2</sub> film treated with HMT had the best performance in terms of  $J_{sc}$ , which was 57.5 μA/cm<sup>2</sup>. The higher optical absorption and lower band gap of TiO<sub>2</sub> resulted in the highest performance of the cell.

**Table 2** Photovoltaic parameter of photo-electrochemical cell TiO<sub>2</sub> nanostructure treated with various surfactants

Surfactant	$J_{sc}$ (μA/cm <sup>2</sup> )	$V_{oc}$ (V)	Fill factor, FF
CTAB	33.5	0.36	0.344
HMT	57.5	0.38	0.340
PVP	16.1	0.28	0.255

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