Article

Enhancement of Charge Transport of a Dye-Sensitized Solar Cell Utilizing TiO₂ Quantum Dot Photoelectrode Film

Siti Nur Azella Zaine ^{1,2,*} , Norani Muti Mohamed ², Mehboob Khatani ³ and Muhammad Umair Shahid ^{4,5}

¹ Chemical Engineering Department, University of Technology PETRONAS, Seri Iskandar 32610, Malaysia

² Centre of Innovative Nanostructures and Nanodevices (COINN), University of Technology PETRONAS, Seri Iskandar 32610, Malaysia; noranimuti_mohamed@utp.edu.my

³ Electrical and Electronic Department, University of Technology PETRONAS, Seri Iskandar 32610, Malaysia; mkhatani3@gmail.com

⁴ Fundamental and Applied Science Department, University of Technology PETRONAS, Seri Iskandar 32610, Malaysia; engr.umairshahid@live.com

⁵ Department of Physics, Faculty of Science, University of Sialkot, Sialkot 51310, Pakistan

* Correspondence: azella.zaine@gmail.com

Abstract: A dye-sensitized solar cell (DSC) is the third generation of solar technology, utilizing TiO₂ nanoparticles with sizes of 20–30 nm as the photoelectrode material. The integration of smaller nanoparticles has the advantage of providing a larger surface area, yet the presence of grain boundaries is inevitable, resulting in a higher probability of electron trapping. This study reports on the improvement of charge transport through the integration of quantum dot (QD) TiO₂ with a size of less than 10 nm as the dye absorption photoelectrode layer. The QD TiO₂ samples were synthesized through sol–gel and reflux methods in a controlled pH solution without surfactants. The synthesized samples were analyzed using microscopic, diffraction, absorption, as well as spectroscopic analyses. A current–voltage and impedance analysis was used to evaluate the performance of a DSC integrated with synthesized TiO₂ as the photoelectrode material. The sample with smaller crystallite structures led to a large surface area and exhibited a higher dye absorption capability. Interestingly, a DSC integrated with QD TiO₂ showed a higher steady-state electron density and a lower electron recombination rate. The shallow distribution of the trap state led to an improvement of the electron trapping/de-trapping process between the Fermi level and the conduction band of oxide photoelectrode material, hence improving the lifetime of generated electrons and the overall performance of the DSC.

Keywords: surfactant-free synthesis; quantum dots TiO₂; dye absorbing layer; electron recombination; dye-sensitized solar cell

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1. Introduction

A dye-sensitized solar cell (DSC) is the third generation of photovoltaic cells that has a similar mechanism to photosynthesis in nature, with efficient performance under low-light conditions [1,2]. Unlike Si PV, the effective charge separation of a DSC allows for better performance in diffused sunlight, allowing for easy integration in the facade of buildings and indoor applications such as glass walls, sunblinds, awnings, roofing, self-powered Internet of Things (IoT) devices, and wireless sensor networks [3,4]. The structure of a DSC consists of three parts, namely, a dye-sensitized photoanode, a redox couple electrolyte, and a catalytic conductive substrate [5]. In the presence of sunlight, photons strike the dyes with enough energy, producing dye-excited states, resulting in the injection of electrons into the conduction band of the photoelectrode TiO₂. The original dye state was restored subsequently by electron donation of the redox electrolyte [6–10]. In actual conditions, the generated electrons could travel in the reverse direction and recombine with the oxidized dyes before the regeneration process occurs (Figure 1). The dynamic

competition between the generation and recombination of the electrons is the bottleneck restricting the development of a DSC with a higher performance efficiency [11–13].

Figure 1. Schematic energy diagram and working mechanism of a DSC.

The porous nanostructure photoelectrode material, typically TiO₂, is the heart of a DSC. The photoelectrode is responsible for providing a large surface area for dye sensitizers, acting as an electron acceptor and an electronic conductor [14]. An extensive simulation study by Usami (1997) concluded that the optimal configuration of a photoelectrode consists of three parts, namely, a thin rutile blocking and passivation layer, a dye absorption layer, and a top scattering layer [15]. The rutile layer deposited on the conductive substrate acts as a blocking layer by avoiding direct contact of the conductive substrate with the redox electrolyte and, at the same time, improving the adhesion of the photoelectrode film to the conductive substrate. The dye absorption layer is the middle layer in between the thin rutile layer and the scattering layer. It provides sufficient surface area to anchor the dye sensitizer molecules for the absorption of light [16]. Meanwhile, the top scattering layer helps to improve the optical path length of incident light within the photoelectrode film. The layer is made up of either micron-sized particles [17], a dual function micro–nano structure such as aggregates [18,19], multiscattering structures [20,21], one-dimensional (1D) nanostructures such as nanowires [22] or nanotubes [16], and so forth. The proposed structure allows for light confinement, thus improving light absorption through multiple scattering and the total reflection of the incident light [23].

The nanostructure TiO₂ was synthesized through various routes, namely, sol–gel [24–27], hydrothermal [28–31], solvothermal [32–35], co-precipitation [36,37], polyol synthesis [38,39], and so forth. Amongst the reported methods, sol–gel has been the most explored and preferred method due to low-temperature processing procedures, ease of controlling the reaction parameters, and high homogeneity [40]. The sol–gel method produced polydispersed amorphous nanoparticles, which require further calcination to improve crystallinity. Moreover, it is very challenging to control the shape and size of the nanoparticles due to the high rate of the hydrolysis reaction, hence resulting in agglomeration [41]. Usually, a surfactant is added to control the hydrolysis rate, the shape, and the size of the nanoparticle [41–43]. The surfactant prevents agglomeration by reducing the solid–liquid interface energy, thus reducing collision and contact between nucleates [43]. Nevertheless, the presence of a surfactant leads to tedious washing procedures that reduce the active site of the nanomaterials [44,45].

In most conventional DSCs, the dye absorption layer consists of TiO₂ nanoparticles with sizes of about 20 nm [8,16–19,22]. Theoretically, further reducing the size of nanoparti-

cles gives an added advantage of a large surface area and contact points, allowing for a higher dye absorption [46]. However, a study conducted by Chou et al. (2007) has shown that the amount of absorbed dye reduces as the size of nanoparticles reduces from about 23 nm to 10 nm [47]. It is anticipated that the capability of nanoparticles to absorb dye molecules is influenced by the facets and the surface energy of the particles [47]. Moreover, smaller nanoparticles result in higher grain boundaries, increasing the probability of electron trapping, hence affecting the performance of a DSC [5,46–48]. On the other hand, a study reported by Tang et al. (2009) has shown that, despite having low dye-absorption, a low-crystalline film exhibits a comparable performance with a high-crystalline film, provided the presence of a well mesoporous inner structure [49].

Here, we report on the improvement of charge transport through the integration of QD TiO₂ with a size of less than 10 nm as the dye absorption photoelectrode layer. The QD TiO₂ was successfully synthesized in a controlled pH solution at high water to the precursor molar ratio without surfactants. Most of the previously reported studies related to QD TiO₂ were related to the implementation of it as a thin passivation layer [50] or the composite of TiO₂ nanoparticles with QD materials such as graphene [51–53] and cadmium selenide [54,55]. However, in this study, the QD TiO₂ was utilized as the photoelectrode dye absorbing layer. To the best of the authors' knowledge, there is a limited number of reports focusing on the utilization of QD TiO₂ as the photoelectrode dye absorbing layer. The higher grain boundaries of QD TiO₂ increase the transport resistance of generated electrons [5,46–48]. Interestingly, the synthesized QD TiO₂ reported in this study exhibits a higher dye absorption and a slower rate of electron recombination, thus improving the overall performance efficiency of the DSC despite the presence of smaller nanoparticles of less than 10 nm compared with the commercially available TiO₂ nanoparticles.

2. Materials and Methods

2.1. Synthesis of Crystalline QD TiO₂

A TiO₂ nanoparticles sample was synthesized through the sol–gel reflux method using titanium isopropoxide (CAS No. 546-68-9, MERCK, Selangor, Malaysia) as a precursor. In a typical procedure, a pH 2 water solution was first prepared using deionized water and glacial acetic acid (CH₃COOH, CAS No. 64-19-7, MERCK, Selangor, Malaysia). Then, 0.2 M titanium isopropoxide in an absolute ethanol solution was added dropwise under vigorous stirring. The molar ratio of the acidic water to the titanium isopropoxide was fixed at 110:1. The solution refluxed at 90 °C for 4 h. The precipitate was collected by evaporating the solution using a rotary evaporator at 80 °C with a speed of 50 rpm. Then, the sample was dried in a convection oven at 90 °C overnight.

2.2. Characterization of Crystalline QD TiO₂

A high-resolution transmission electron microscope (HRTEM, TECNAI F20 X-Twin, Hillsboro, Oregon, United States) was used to evaluate the particle size and morphology of the synthesized TiO₂. Surface area and porosity analyzers (TriStar II 3020, Micromeritics, Norcross, Georgia, USA) were used to evaluate the surface area, pore size, and pore volume degassed at 300 °C for 3 h. The phase of the prepared photoelectrode film was evaluated using an X-ray diffraction analysis (XRD, Empyrean, PANalytical, Malvern, UK) operated at 45 kV using a Ni-filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) with a step scan size of 0.01° and an omega of 2 in the range of 2 θ of 10° to 80°. An ultraviolet-visible spectroscopy (UV-Vis, Cary 100, Agilent, Santa Clara, CA, USA) was used to evaluate the dye absorption capability of the printed photoelectrode films in the wavelength range of 200 nm to 800 nm.

2.3. Fabrication and Performance Analysis of DSC

The pastes were prepared based on a previously reported study [56,57]. An amount of 6 g of the synthesized QD TiO₂ sample was converted into a paste by mixing it with 20 mL of ethanol as the solvent, 1 mL of acetic acid and 5 mL of deionized water as the dispersion agent, 3 g of ethyl cellulose in 30 g of ethanol as the binder, and 20 g

of terpineol as the rheology agent. A control sample was prepared using commercially available TiO_2 nanoparticles (CAS No. 1317-70-0, MERCK, Selangor, Malaysia). The paste was then printed on a fluorine tin oxide (FTO)-coated glass substrate and heat-treated in a six-zone belt furnace with the temperatures of 300 °C, 510 °C, 505 °C, 350 °C, 270 °C, and 180 °C for the consecutive zones with a conveyor speed of 140 mm/min. The photoelectrode films were soaked overnight in 0.254 mM of di-tetrabutylammonium cis-bis(isothiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II) (N719) dye at room temperature. The dye coated photoelectrode films were assembled in a sandwich layer with a platinum (Pt) counter electrode and sealed with a hot-melt thermoplastic gasket. An iodide/triiodide (high-stability electrolyte, EL-HSE) as redox electrolyte was then injected through a pre-drilled hole on the counter electrode side. The redox electrolyte was composed of a mixture of 1-propyl-3-methyl-imidazolium iodide, 4-tert-butyl pyridine, lithium iodide, guanidinium thiocyanate, and iodine in acetonitrile as a solvent. The hole was sealed using aluminium backed bynel. The N719 dye, platinum paste, electrolyte and aluminium backed bynel were sourced from Greatcell Solar, Queanbeyan, Australia.

The performance of the fabricated DSCs was verified using a universal photovoltaic test system (UPTS, Greatcell Solar, Queanbeyan, Australia) at 100 mW/cm² of simulated light of air mass at a 1.5 (AM-1.5) radiation angle under variable load. The system was integrated with a solar simulator (Greatcell Solar, Queanbeyan, Australia), a Keithley 2420 source meter (Tektronix, Beaverton, OR, USA), and a current-voltage (I-V) testing software (I-V Software, Version 9, 2015, Michael Kelzenberg, Pasadena, CA, USA). The results were taken based on the average value of at least five samples per batch and repeated for three batches. The external quantum efficiencies (EQEs) of the DSCs were obtained using an incident-photon-to-electron conversion efficiency measurement system (IPCE, Greatcell Solar, Queanbeyan, Australia) with a 300 W xenon lamp. The analyzed active areas were about 0.25 cm². An electrochemical impedance spectroscopy (EIS) analysis was carried out in the dark at various forward bias voltages in the 300 kHz to 0.1 Hz of frequency range and an alternating current (AC) modulation signal of 10 mV using PCI4-300 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA). Echem Analyst (Version 7.8.2, Gamry Instruments, Warminster, Pennsylvania, USA) software was used to fit the frequency-dependent impedance and the performance compared with commercial TiO_2 -based DSCs.

3. Results

The morphology of the synthesized QD TiO_2 and commercial TiO_2 nanoparticles was analyzed using HRTEM, and the images are shown in Figure 2. The HRTEM analysis shows that the synthesized QD TiO_2 (Figure 2a,b) is in the form of irregular shapes with a size of about 5 nm. Meanwhile, the commercial sample (Figure 2c,d) was in the form of nanoparticles with a size of about 30 nm. At higher magnifications, the samples clearly show the interlayer spacing of approximately 0.358 nm and 0.383 nm for the synthesized QD TiO_2 and commercial TiO_2 , respectively, corresponding to a lattice plane of the TiO_2 anatase phase. Figure 2a,b prove that the synthesized QD TiO_2 sample is free of submicron-size aggregates. The presence of a large molar ratio of water to the precursor in a controlled pH solution controlled the hydrolysis rate, leading to the separation of the nucleation and the growth stage, thus ensuring a complete hydrolysis process and preventing the formation of submicron-size aggregates.

Figure 2. HRTEM images of the synthesized QD TiO₂ at (a) 88 KX and (b) 530 KX, and commercial TiO₂ nanoparticles at (c) 88 KX and (d) 360 KX.

An analysis using a surface area and pore size analyser shows that both the synthesized QD TiO₂ and the commercial TiO₂ nanoparticles exhibit type IV adsorption–desorption isotherms (Figure 3a). The inflection of the volume of nitrogen adsorbed at high relative pressure, P/P^0 , corresponds to the presence of the mesoporous structure. Based on the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda (BET–BJH) analysis, the synthesized QD TiO₂ exhibits a surface area of 152.41 m²/g, a pore size of about 6 nm, and a pore volume of 0.23 cm³/g. Meanwhile, the commercial TiO₂ nanoparticles sample exhibits a surface area of 53.36 m²/g, a pore size of 20.24 nm, and a pore volume of 0.27 cm³/g. Based on the plot of pore diameter (Figure 3b), the synthesized sample exhibits a narrow pore volume distribution that indicates a well-dispersed QD TiO₂. The successful synthesis of dispersed QD TiO₂ without utilizing surfactant was contributed by the presence of a large molar ratio of water to the precursor in a controlled pH environment, leading to the separation of the nucleation and growth stages, thus ensuring a complete hydrolysis process. On the other hand, the commercial TiO₂ nanoparticle sample exhibits a region with larger pores of more than 50 nm due to the submicron size agglomerations. The large size of the pore diameters corresponds to the agglomerated particles emphasized in the red circle of Figure 2c while the pore distribution below 25 nm represents the porous structure of the nanoparticle.

Figure 3. The (a) absorption–desorption isotherm and (b) pore size distribution of the synthesized QD TiO₂ and commercial TiO₂ nanoparticles.

The prepared photoelectrode films were tested using an XRD analysis to evaluate the crystallinity and the phase presence. Figure 4 shows the XRD of the samples deposited on the FTO substrate. A bare FTO was also tested as a comparison. An XRD analysis confirms that both TiO₂ samples were in the form of an anatase phase with peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.0°, 61.7°, 62.7°, 68.8°, 70.3°, and 75.1° corresponding to Miller indices of (101), (004), (200), (105), (211), (213), (204), (116), (220), and (215), respectively. The peaks at about 26.5°, 33.7°, 37.8°, 51.5°, 61.6°, and 65.6° correspond to the tin oxide phase (PDF 00-046-1088); peaks at 31.2°, 51.5°, 61.6°, 65.6°, 70.9°, and 78.5° correspond to tin fluoride (PDF 01-085-2126); while peaks at about 26.5°, 42.4°, and 54.6° correspond to the silicon dioxide phase (PDF 01-089-8937). The presence of these phases is well matched with the compositions of the glass substrate coated with a thin layer of FTO. The crystallite size calculated using Scherer's formula gave average crystal sizes of about 8.6 nm and 25 nm

for the synthesized QD TiO₂ and the commercial TiO₂ nanoparticles, respectively. The results obtained were in good agreement with the size estimated from HRTEM analysis.

Figure 4. The XRD of the QD TiO₂ and commercial TiO₂ samples printed on FTO substrates.

A UV-Vis analysis of the desorbed dye solution of the dyed photoelectrode film was tested to evaluate the capability of photoelectrode film to anchor dye molecules. Figure 5 shows the absorbance spectrum of the N719 solution desorbed using diluted ammonium hydroxide for the synthesized and commercial TiO₂ nanoparticles. Based on a UV-Vis analysis, both samples exhibit typical absorbance spectra of N719 dye solutions with three absorbance peaks at about 310 nm, 370 nm, and 510 nm, attributed to the ligand-centered charge transfer (LCCT) transitions and the metal-to-ligand charge transfer (MTLC) transitions of the N719 dye molecules [58,59]. The analysis confirmed that the synthesized TiO₂ nanoparticle sample shows higher absorbance for the entire wavelength region of 200–600 nm corresponding to the higher dye concentration in the diluted ammonium hydroxide. The higher amount of dye molecules increased the number of injected electrons into the conduction band of the photoelectrode network, thus increasing the value of the short-circuit current.

The prepared photoelectrode film was then integrated into the DSC with a Pt counter electrode and iodide electrolyte. The fabricated DSC based on the synthesized nanoparticle sample was tested for I–V characteristic and the result was compared with the DSC based on the commercial TiO₂ nanoparticle sample as the photoelectrode film. Figure 6 shows the I–V curve of the synthesized and commercial TiO₂ nanoparticles tested under a 100 mW/cm² intensity of an illuminated xenon lamp at an AM-1.5 radiation angle. Table 1 shows the photovoltaic properties, namely, short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and performance efficiency (η) of the fabricated DSC using the synthesized and commercial TiO₂ nanoparticles.

Figure 5. Absorbance spectra of the desorbed dye solution of the QD TiO₂ and commercial TiO₂ nanoparticles.

Figure 6. J–V curve of the QD TiO₂ and commercial TiO₂ nanoparticle-based DSCs.

Table 1. Photovoltaic properties of the QD TiO₂ and commercial TiO₂ nanoparticle-based DSCs.

Sample	Particle Size (nm)	Active Area (cm ²)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	Reference
QD TiO ₂	5–7	1.00	10.34 ± 0.4	0.761 ± 0.01	0.565 ± 0.01	4.44 ± 0.09	*
Commercial TiO ₂	25–30	1.00	8.94 ± 0.2	0.792 ± 0.01	0.618 ± 0.02	4.37 ± 0.03	*
TiO ₂ nanoporous	20	0.25	10.100	0.678	0.630	4.100	[60]
TiO ₂ nanoparticles	12	0.16	11.743	0.583	0.670	4.594	[61]
Screen printed TiO ₂ nanoparticles	20	0.25	10.030	0.760	0.720	5.480	[1]

* Value obtained from this study.

The I–V analysis shows that the QD TiO₂-based DSC exhibits higher J_{sc} , hence leading to a better performance efficiency of $4.44 \pm 0.09\%$. The improvement of J_{sc} was related to the smaller size of nanoparticles, resulting in the availability of a large surface area for anchoring dye molecules. Increasing the number of anchored dye molecules increased the chances of harvesting the photon radiance, increasing the number of generated electrons and thus increasing the current density. The higher amount of dye molecules has increased the number of the injected electrons into the conduction band of the photoelectrode network, thus increasing the value of J_{sc} .

Table 1 compares the reported photovoltaic properties of typical DSCs composed of a TiO₂ photoelectrode film, a N719 dye, and an iodide and tri-iodide redox electrolyte. Based on the tabulated data, the previous studies reported performance efficiencies in the range of 4.1% to 5.48%. However, the photovoltaic properties except for V_{oc} of the fabricated DSC based on the synthesized QD TiO₂ as the photoelectrode film are lower compared with those reported by Subalakshmi and Senthilselvan in 2018. This is due to the larger active area used to fabricate the DSC in this study. Increasing the active area prevents a smooth transport of electrons within the photoelectrode film due to the deepened trap state distribution, thus increasing the rate of electron recombination in the higher voltage region and reducing the charge collection efficiency [62].

Figure 7 shows the EQE of DSCs integrated with QD TiO₂ and commercial TiO₂ photoelectrode films. The photocurrent action spectra exhibit two peaks at wavelengths of about 335 nm and 530 nm. The small distribution of photocurrent peaks at the lower wavelength (~335 nm) corresponds to direct light harvesting by the TiO₂ semiconductor with an energy of approximately 3.2 eV. A broader spectrum in the visible region with a maximum peak at about 530 nm was attributed to the absorption of N719 dye molecules. The result is in good agreement with the J–V analysis, where the QD TiO₂ exhibits higher photocurrent efficiency, suggesting the enhancement of quantum efficiency compared with the commercial TiO₂ based DSC. Moreover, the commercial TiO₂ nanoparticles exhibit a broad spectrum in the wavelength range of 380 nm to 450 nm. The broad spectrum corresponds to the large, agglomerated particles, as evident in the FESEM analysis [12,63].

The QD TiO₂ exhibits a lower value of V_{oc} and FF compared with the commercial TiO₂ nanoparticles. The variation in the V_{oc} and FF values was related to the electron transport properties and the internal resistance of the cells. An EIS analysis was used to evaluate the electrochemical properties of the DSCs. Figure 8 shows the Nyquist, Bode, and phase plots of fabricated DSCs based on synthesized and commercial TiO₂ nanoparticles. The data were fitted based on the equivalent circuit, as shown in the inset of Figure 8. The R_s of the equivalent circuit signifies the sheet resistance of the substrate, and the contact resistance between the substrate and photoelectrode film. The value was measured from the gap between the y-axis and the small semicircle of the Nyquist plot. The R_1 and CPE_1 signify the resistance and constant phase element of the charge transfer resistance at the counter electrode, represented by the small semicircle of the Nyquist plot at the high-frequency range. The large semicircle of the Nyquist plot represents the electron transport properties of the photoelectrode and electrolyte interface. A Bisquert open model was used to fit the data [64]. Their measured and calculated electrochemical properties, namely, transport resistance (R_t), recombination resistance (R_{br}), chemical capacitance (C_{μ}), electron lifetime (τ_n), reaction rate constant for recombination (k), electrons diffusion coefficient (D_n), effective diffusion length (L_n), and steady-state electron density in the conduction band (n_s) are tabulated in Table 2.

Figure 7. IPCE analyses of the QD TiO₂ and commercial TiO₂ nanoparticle-based DSCs.

Figure 8. Cont.

Figure 8. (a) Nyquist plot, and (b) Bode and phase plot of the QD TiO₂ and commercial TiO₂ nanoparticle-based DSCs.

Table 2. Electrochemical properties of the QD TiO₂ and commercial TiO₂ nanoparticle-based DSCs.

Sample	R_t (Ω)	R_{br} (Ω)	C_μ (μF)	τ_n (s)	k (s ^{−1})	D_n (cm ² s ^{−1})	L_n (μm)	n_s (cm ^{−3})
QD TiO ₂	3.99	51.16	3.41×10^{-3}	0.175	5.7304	0.74×10^{-6}	3.583	4.56×10^{17}
Commercial TiO ₂	2.11	117.5	9.18×10^{-4}	0.107	9.3304	5.17×10^{-6}	7.442	1.23×10^{17}

The EIS analysis reveals that the DSC fabricated with the synthesized QD TiO₂ as the photoelectrode film exhibited higher transport resistance and lower electron recombination resistance compared with the commercial TiO₂ nanoparticle sample. This was due to the presence of a smaller size of nanoparticles resulting in the presence of larger grain boundaries and structural defects, preventing the smooth transportation of electrons, and reducing the value of electron diffusion and electron diffusion length as tabulated in Table 2. This condition promotes the recombination of the injected electrons in the conduction band of TiO₂ with the oxidized species of electrolyte and dyes instead of the injected electrons travelling to the external circuit. Even though the R_{br} value of the QD TiO₂ is smaller, the cell exhibits a slower k compared with the commercial TiO₂-based DSC, thus leading to higher τ_n . Moreover, the fabricated cell based on the synthesized QD TiO₂ sample also shows a higher value of steady-state electron density in the conduction band of TiO₂ compared with the commercial TiO₂-based DSC. The outcome can be explained by the larger surface area of the QD TiO₂, which allows for a larger amount of dye to be anchored, thus increasing the number of generated electrons, which improves the number of injected electrons from the LUMO to the conduction band of TiO₂.

The high n_s value reflects the high C_μ value of the synthesized QD TiO₂ compared with the commercial TiO₂ nanoparticle sample. The C_μ resembles the change in the electron density over a small variation of chemical potential and expressed as in Equation (1):

$$C_\mu = q_e^2 \frac{\partial}{\partial E_F} \int_{E_2}^{E_1} F(E - E_{Fn}) g_n(E) dE \approx q_e^2 g_n(E_F) \quad (1)$$

where $F(E - E_{Fn})$ is the occupation factor of the Fermi–Dirac distribution function while $g_n(E)$ is the density of state, which is expressed as in Equation (2):

$$g_n(E) = \frac{N_L}{k_B T_o} \exp[(E - E_c)/k_B T_o] \quad (2)$$

where k_B is the Boltzmann constant; N_L is the density of localized states; and T_o is a parameter with a temperature unit that determines the depth of the distribution below the lower edge of the conduction band, E_c . Based on these two equations (Equations (1) and (2)), an exponential distribution of chemical capacitance was derived and expressed as Equation (3) [65–68]:

$$C_\mu = C_o \exp\left(\frac{\alpha q_e}{k_B T} V\right) = C_o \exp\left(\frac{q_e}{k_B T_o} V\right) \quad (3)$$

where α is the measure of the depth of trap energy distribution, which equals T/T_o . The trap state distribution of the fabricated DSC was analyzed by conducting EIS analyses at different bias potentials (from 0.8–0.35 V). Figure 9 shows the measured chemical capacitance based on the EIS analyses of the cells integrated with synthesized QD TiO₂ and commercial TiO₂ nanoparticle samples.

Figure 9. The chemical capacitance of the QD TiO₂ and commercial TiO₂ nanoparticle-based DSCs obtained from the EIS analyses in the dark.

The plotted graph shows that the QD TiO₂ exhibits an exponential trend with a steeper slope compared with the commercial TiO₂ nanoparticle-based DSC. Based on the analysis, the α values of the QD TiO₂ and the commercial TiO₂ nanoparticle-based DSC were calculated to be about 0.253 and 0.217, respectively. A bigger α indicates a narrower distribution of the electronic state's density, which helps with the electron trapping and de-trapping phenomena [65,67,69]. A shallow distribution of the trap state helps the trapped electrons at the Fermi level to be de-trapped back to the conduction band of the oxide photoelectrode material. This finding supports the results of a lower rate of electron recombination and higher steady-state electron density, thus leading to a longer lifetime of electrons and a higher value of produced current density.

4. Conclusions

The QD TiO₂ was successfully synthesized through the sol–gel reflux method in a controlled pH of the water–acetic acid solution without surfactants. The large surface area brought about by the small QD structure results in an increase in the capability of the photoelectrode material to anchor large amounts of dye, leading to a higher steady-state electron density and improving the generation of electrons. Moreover, the fabricated cell also exhibits a slower electron recombination rate due to the shallow distribution of the trap state of the synthesized QD TiO₂-based DSC. This characteristic helps the trapped electrons at the Fermi level be released back to the conduction band of oxide photoelectrode materials, thus improving the lifetime of generated electrons. However, the successful development of QD TiO₂ potentially applied as the thin blocking layer of the photoelectrode configuration in which the titanium chloride treatment is replaced still faces the challenge of substrate corrosion.

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