Evaluation of performance characteristics of nano TiO₂ and TiO₂-ZnO composite for DSSC applications and electrochemical determination of potassium ferrocyanide using cyclic voltammetry

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Keywords: cyclic voltammetry, potassium ferrocyanide, photoanode, TiO₂-ZnO composite, dye-sensitized solar cells, j-V characteristics

Abstract
Nanoparticles of TiO₂ and TiO₂-ZnO composite (2:1 molar ratio) were synthesized utilizing the sol-gel and solution combustion approaches, respectively. Scanning electron microscopic, energy dispersive x-ray, x-ray diffraction, UV-visible spectroscopy, and Brunauer–Emmett–Teller analysis were employed to characterize the synthesized nanoporous TiO₂ and the composite of TiO₂-ZnO nanoparticles. Fabrication of dye-sensitized solar cells (DSSCs) was carried out by incorporating the synthesized nanoporous materials coating on the photoanodes using the doctor blade technique. Nano TiO₂ and the composite of TiO₂-ZnO were also analyzed using cyclic voltammetry test, and their performance was compared for the electrochemical detection of potassium ferrocyanide. The composite of TiO₂-ZnO exhibited better electrocatalytic activity in comparison with the pure TiO₂ nanoparticles. The fabricated DSSCs by employing nano TiO₂ particles and TiO₂-ZnO composite as the semiconductor photoanode materials were compared for photovoltaic performance. The DSSC fabricated with TiO₂ nanoparticles exhibited better photovoltaic performance with an efficiency of 2.22% and a short circuit current density of 0.014 mA cm⁻² than that fabricated with TiO₂-ZnO composite with an efficiency of 0.0022% and a short circuit current density of 0.014 mA cm⁻².

1. Introduction
The quality of life is significantly affected by the availability of energy. The intensified and devastating utilization of conventional energy resources has resulted in an environmental crisis. Due to the abundance of nature, an inexhaustible source like the energy from the Sun is contemplated as a feasible alternative energy source. Harvesting solar energy to solve drawbacks associated with global energy and the environment is a challenge that has guided the development of solar cells. A solar cell performs the function of converting photons with specific wavelengths to electricity. For the past fifteen years, the development of solar cells at low cost has been an area of intensive work for researchers [1–5]. Michael Gratzel [5] has developed a simple, low-cost dye-sensitized solar cell (DSSC) that emerged as a novel photoelectrochemical device. A DSSC comprises a photoanode, a redox electrolyte, and a counter electrode. In DSSC, the function of optical absorption and the separation of charge occurs at the photoanode in association with a sensitizer as a photon absorbing material and a wider bandgap semiconductor with a nanocrystalline morphology. Hence the vital stage in the formulation of DSSC is the selection of suitable semiconductors which can be employed as anode [5–8]. A schematic representation of DSSC is shown in figure 1. In its anatase phase, titanium dioxide (TiO₂) possesses a wide bandgap of 3.2 eV and has exhibited good results for DSSC applications. For the effective synthesis of nano anatase TiO₂, several methodologies have been utilized, of which the most simple and well-known techniques include sol-gel, solution combustion, and hydrothermal synthesis methods. Incorporating semiconductors as photoanodes in
DSSC applications necessitates them to be enormously porous with a high surface area to adsorb huge amounts of dye molecules that efficiently absorb the photons and release free electrons [9, 10]. Similarly, nano zinc oxide (ZnO) particles also possess a wide bandgap of 3.3 eV with better exciton electron mobility of 115 cm$^2$ V$^{-1}$ s$^{-1}$ [11]. ZnO particles exhibit greater conductivity and have a huge binding energy of $0.6 \times 10^2$ meV at ambient temperature. The specific chemical and structural properties of zinc oxide make it a multifunctional substance that could be utilized in electrochemical applications [12].

The current development in the nanoscience area has opened avenues for applying novel nanomaterials of desirable characteristics that can be utilized in electrochemical applications. Electrochemical techniques are employed to characterize the individual components of a cell. The kinetics of the electrochemical reactions occurring in the cell can be analyzed using these techniques. Cyclic voltammetry (CV) is one of the most widely used electrochemical methods. From the CV technique, the potentials of redox processes can be analyzed and the reversibility of the electron transfer process can be assessed. Verification of electrocatalytic properties of nano and micro materials can be done using cyclic voltammetry analysis, which is an efficient approach [13–17].

Chung et al reported the synthesis of TiO$_2$ nanoparticles of a specific surface area 47 m$^2$ g$^{-1}$ utilizing a solution combustion approach, which was used as photoanodes in the fabrication of DSSC [9]. Jongprateep et al employed solution combustion and sol-gel methods to synthesize titanium dioxide whose particle sizes were 44 and 48 nm, respectively [10]. Mohammed et al have described the fabrication of DSSC incorporating TiO$_2$ nanoparticles and a light-sensitive strawberry dye whose open-circuit voltage was estimated to be 0.14 V [18]. Giannouli et al reported the fabrication of DSSC with nanostructured TiO$_2$ as photoanode, which exhibited an open-circuit voltage of 0.51 V and an efficiency of 0.39% [19]. Wahyuningsih et al experimented with incorporating a composite of nano TiO$_2$–ZnO for the fabrication of DSSC [20]. Susanti et al have reported the formulation of DSSC from the anatase TiO$_2$ particles of size ranging from 0.2–0.4 μm [21]. Govindaraj et al have described the synthesis of nanorods of TiO$_2$ employing a hydrothermal approach that was utilized in the formulation of DSSC and resulted in an efficiency of 5.42% [22]. Rajamanickam et al have described the development of DSSC using TiO$_2$ nanorods/nanoparticles as the photoanodes and have utilized ruthenium dye as a sensitizer [23]. For harvesting solar energy, the improvement and advancement of DSSCs are essential and are of great interest to researchers.

The objective of the present study is to analyze the photovoltaic performance of the pure TiO$_2$ and the composite of TiO$_2$–ZnO, and evaluate the effect of integrating TiO$_2$ with nanoporous ZnO on the photovoltaic characteristics and the electrochemical reaction towards the detection of potassium ferrocyanide. The nanoparticles of TiO$_2$ and the composite of TiO$_2$–ZnO were synthesized using sol-gel and solution combustion techniques, respectively, and their crystallinity, morphology, and surface area were analyzed with a set of sophisticated material characterization techniques. Then, the synthesized nanomaterials were employed as photoanodes for the formulation of DSCCs and their photovoltaic properties, namely, open-circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), efficiency, and fill factor were estimated under a solar simulator (xenon arc lamp source) with radiation of 100 mW cm$^{-2}$. The nanoparticles and the composite were tested employing the cyclic voltammetry technique to evaluate the electrochemical characteristics and to study the effect of amalgamating TiO$_2$ with nano ZnO particles on the oxidation-reduction reaction of potassium ferrocyanide.
Consequently, the photovoltaic characteristics of nano TiO₂ particles and the composite of TiO₂-ZnO, and the electrochemical characteristics for detecting potassium ferrocyanide are assessed and reported.

2. Materials and methods

2.1. Chemicals utilized

The chemicals for the synthesis of nanomaterials and the fabrication of DSSC were procured and used directly without further purification. The chemicals procured for the study are titanium (IV) butoxide (>97% pure, Sigma Aldrich), zinc nitrate hexahydrate (>96% pure, Sigma Aldrich), glycine (99% pure, Fisher Scientific), methanol (99% pure, spectrum chemicals), ammonia (Spectrum chemicals), acetylacetone (98% pure, LOBA Chemie), triton X-100 (Fisher Scientific), tertiary butanol (RANKEK), acetonitrile (99.8% pure, Sigma Aldrich), N719 dye (Solaronix S A), Platisol T/SP (Solaronix S A), Iodolyte HI-30 (Solaronix SA).

2.2. Synthesis of nanoparticles of TiO₂ by sol-gel approach

The sol-gel approach was employed to synthesize TiO₂ nanoparticles; the procedure is adopted from Perumal et al. [24]. The precursors, titanium tetra butoxide, and methyl alcohol with a 1:4 molar ratio were taken in a beaker and placed on the magnetic stirrer. The contents in a beaker were kept at a temperature of 60 °C and subjected to constant stirring. To carry out the hydrolysis reaction, distilled water was added to this blend dropwise, and a ratio of 1:1 with methanol was maintained. Aqueous ammonia solution was added dropwise to maintain basic pH between 9 and 10. The contents were stirred constantly for 120 min and aged for 24 h after which a gel formation was observed. Methyl alcohol and distilled water were used to wash the gel to eliminate the impurities and unreacted components. The gel was placed in an oven at 80 °C for drying. The dried contents were calcined at a temperature of 450 °C for 120 min in a muffle furnace to obtain white-coloured TiO₂ nanoparticles.

2.3. Synthesis of TiO₂-ZnO composite by employing solution combustion approach

TiO₂-ZnO composite was synthesized using a solution combustion approach, as reported by Chung et al. [9]. The precursors, titanium tetra butoxide and zinc nitrate hexahydrate were used as precursors, and glycine was used as a fuel. The precursors were first hydrolysed and then subjected to nitration reaction. Titanium (IV) butoxide (6.8 ml) and ZnNO₃·6H₂O (2.35 g) were taken in a petri dish, and 3.6 ml of deionized water was added to it. Further, 1:1 nitric acid was added to the above mixture under constant stirring. The stoichiometric proportion of glycine was added to the petri dish, and the entire contents were kept in a muffle furnace at 400 °C and ignited. The formation of foam-type powder completes the reaction. Further, this foam-type powder was calcined at 450 °C for 120 min. A pinkish white coloured TiO₂-ZnO composite was produced, which was then ground in a mortar and pestle to obtain a fine powder of the composite.

2.4. Fabrication of DSSCs

The DSSCs were fabricated using a procedure reported by Govindaraj et al. [22] and Rajamanickam et al. [23]. Fluorine doped tin oxide (FTO) coated glass slides, TISXZ001 with 2.2 mm thickness, resistivity 7 Ω cm⁻², and transmittance greater than 85% were used as glass substrates for developing photoanode and counter electrodes. The FTO glass slides were rinsed with deionized water followed by ultrasonication in ethanol for 10 min and dried. 1.4 g of the synthesized nanoparticles/composite were blended with 0.2 ml of acetylacetone, and the contents were placed in mortar and pestle. To this, 5 ml of ethanol-water (1:1 vol/vol%) were added, and the contents were ground well. Triton X-100 of 0.4 ml was introduced dropwise to the above mixture to form a viscous paste. The paste thus prepared was deposited on the conductive side of the FTO glass slides using the doctor blade technique, which forms the photoanodes of DSSC. These photoanodes were dried at room temperature and sintered at 450 °C for half an hour. The photoanode films were soaked in a 5 mM N719 dye for about 24 h. Five millimolar N719 dye was prepared by dissolving a stoichiometric amount of dye in a 1:1 ratio of acetonitrile and tertiary butyl alcohol. After sensitising with dye, the films coated with nanomaterials were cleansed using ethyl alcohol and dried in the air. Viscous platisol was deposited over the conductive side of the other glass slide and employed as a counter electrode. The counter electrode was sintered at 400 °C for about 40 min and cooled down to room temperature. It was placed over the anodic film, and the duo electrodes were sandwiched using a folder clip. The Iodolyte electrolyte was introduced amid the two electrodes through capillary movement. The active functioning zone of the dye-sensitized solar cell was nearly 25 mm².

2.5. Cyclic voltammetry

To perform a cyclic voltammetry (CV), analytical equipment of Model CHI-660C potentiostat was employed. For electrochemical measurements, the conventional tri-electrode cell assemblage comprises a reference
electrode such as a saturated calomel electrode (SCE), a carbon paste electrode as a working electrode, and a counter electrode consisting of a platinum wire was utilized. For electrochemical measurements, either an unmodified or modified carbon paste working electrode containing pure TiO2 nanoparticles or TiO2-ZnO composite was used. The pH measurement was performed using MK VI digital pH meter, and the tests were conducted at room temperature [25].

2.5.1. Preparation of bare and modified electrodes utilizing carbon paste
To prepare a bare electrode, about 25% of silicon oil and 75% of graphite powder were melded in a mortar for 45 min to produce a homogenous blend of the carbon paste. It was then stuffed within the hollow fragment of a tiny tubular structure and compacted on a sheet of paper. The modified carbon paste electrode was prepared by adding 200 μg of the synthesized nanomaterials to the blended powder of graphite and silicon [26].

2.5.2. Electrolyte selection for CV analysis
A potassium chloride solution with a 0.1 M concentration was utilized as an electrolyte for CV analysis. For electrochemical detection measurement, 1 mM of potassium ferrocyanide in 0.1 M KCl solution was used as an electrolyte and CV was carried out at a scan rate of 50 mV s\(^{-1}\) at room temperature.

2.6. Characterization
Scanning electron microscopy (SEM, TESCAN, VEGA 3) was used to determine the morphology of the synthesized TiO2 nanoparticles and TiO2-ZnO composite. X-ray diffraction (XRD) with CuKα radiation with standard JCPDS (PAN Analytical powder Xpert-3) was employed to analyse the crystalline phase of the synthesized nanomaterials. The energy dispersive x-ray analysis (EDAX) was performed to verify the elemental composition of the prepared nanoparticles. The UV-visible absorption spectra of the TiO2 nanoparticles and TiO2-ZnO composites were analysed using UV-DRS spectrophotometer (Lamda 900, PerkinElmer) and the data was acquired with help of the UV WinLab. Brunauer–Emmett–Teller (BET) analysis was performed to determine the specific surface area of the nanomaterials using the Quantachrome NovaWin (version 11.05) instrument. The J-V (current density-voltage) characteristics of the fabricated DSSCs were analysed using a solar simulator with irradiation of 100 mW cm\(^{-2}\) and a Keithley 2400 source meter (computer-controlled). The photoelectrical conversion efficiency (η) of the fabricated DSSC was computed using the equation (1):

\[
\eta = \frac{I_{sc} V_{oc} FF}{P_{in}}
\]

where \(I_{sc}\), \(V_{oc}\), \(P_{in}\) and \(FF\) are the density of short circuit current (mA cm\(^{-2}\)), open-circuit voltage (V), the input solar power incident onto the DSSCs and fill factor, respectively.

3. Results and discussion

3.1. XRD-Analysis
Figures 2(a) and (b) demonstrate the XRD patterns of the TiO2 nanoparticles and TiO2-ZnO composite, respectively. From the XRD pattern (figure 2(a)) it is confirmed that the TiO2 nanoparticles are in 98.33%
anatase and 1.67% in rutile phase with the formation of highest diffraction peak at $2\theta = 25.41^\circ$ and other peaks at $2\theta = 37.84^\circ$, $47.96^\circ$, $53.94^\circ$, $54.81^\circ$, $62.54^\circ$, $69.18^\circ$, and $70.32^\circ$ correlating to standard diffraction planes $(101)$, $(004)$, $(200)$, $(105)$, $(211)$, $(118)$, $(116)$ and $(220)$ and these planes are in good agreement with ICDD #84–1286 [27].

The XRD graph presented in figure 2(b) emphasized the development of TiO$_2$-ZnO composite with anatase, rutile, and zinc phases with 66% crystallinity. The development of diffraction characteristic peaks corresponding to angle $2\theta = 25.36^\circ$, $47.97^\circ$, $53.61^\circ$ and $62.23^\circ$ correlated to the standard planes $(101)$, $(200)$, $(105)$ and $(118)$ of ICDD #84-1286 for anatase TiO$_2$ and for wurtzite ZnO, the formation of characteristic peaks of diffraction at an angle of $2\theta = 35.24^\circ$, $38.03^\circ$, $47.97^\circ$ and $56.73^\circ$ corresponding to the standard planes of $(002)$, $(101)$, $(102)$ and $(110)$ of ICDD #36-1451 [23] was observed. Crystallite size of the synthesized nano TiO$_2$ and the composite were computed using the Scherrer’s equation (2) [28–30]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where $D$ denotes the average crystallite size (nm), $\lambda$ gives the x-ray wavelength (nm), $\theta$ represents Bragg’s angle ($^\circ$), $\beta$ signifies the line broadening in radians, and the constant is denoted by $K$ (0.90). The crystallite size of particles of TiO$_2$ was enumerated as 11.65 nm, which is lower than the data reported by Perumal et al [24] of 14 nm. This may be due to the higher calcination temperature (550 $^\circ$C) utilized by Perumal et al [24], resulting in narrow XRD peaks. The TiO$_2$-ZnO composite particles were semi-crystalline, and the average crystallite size of
the composite was computed to be 30.35 nm which was greater than the values presented by Chung et al.[9], which was 22 nm. The work accomplished by Chung et al.[9] implicates the synthesis of pure TiO₂ nanoparticles using the solution combustion method, whereas the composite of TiO₂-ZnO has been synthesized in the present work using a similar method followed by Chung et al.[9]. A combination of titanium and zinc precursors solution might have resulted in a larger size of crystallites after subsequent hydrolysis, nitration, and combustion reaction. The synthesized material was slightly amorphous.

3.2. Energy-dispersive x-ray analysis
An EDAX analysis was performed to verify the synthesized nanomaterials' elemental composition, which is presented in figures 3(a) and (b), respectively. Since any element other than Ti and O is not detected in the EDAX spectrum of pure TiO₂ (figure 3(a)), the data confirm the absence of any impurity in the synthesized TiO₂ particles. In addition to this, the EDAX result verifies that the stoichiometry of TiO₂ with 58.40 and 41.60 wt% for Ti and O, respectively. Similarly, the EDAX analysis performed for the TiO₂-ZnO composite (figure 3(b)) shows that no other elements are present other than the expected Ti, O and Zn elements. The stoichiometry of synthesized TiO₂-ZnO composite was confirmed with the help of EDAX measurement with weight % of 37.52, 45.3, and 17.18 for Ti, O and Zn, respectively.

3.3. Scanning electron microscopy analysis
The SEM images of the nano TiO₂ (with magnification 67.7 kx) and the composite of TiO₂-ZnO (with magnification 66.0kx) are demonstrated in figures 4(a) and (b), respectively. From SEM analysis, the TiO₂ particles were observed to be nearly spherical, agglomerated with even particle distribution. Whereas the
particles of TiO₂-ZnO composite were observed to be slightly bigger and nearly spherical with even distribution of particles but more agglomerated compared to the pure TiO₂ particles.

3.4. UV analysis
The pure nano TiO₂ and the composite TiO₂-ZnO were evaluated using a UV-visible spectrophotometer and are represented in figure 5. From UV analysis, the bandgap energy for nano TiO₂ and TiO₂-ZnO composite were enumerated as 3.10 and 3.06 eV, respectively, which are lower than the bandwidth energy reported by Chung et al[9]. The work done by Chung [9] and his team include the synthesis of nano TiO₂ employing a gel combustion method using glycine as a fuel. The incorporation of ZnO nanoparticles with TiO₂ nanoparticles has resulted in a slight reduction in the bandgap. The redshift in cut-off wavelength and fall in bandgap might be owing to the higher calcination temperature utilized in the solution combustion approach. However, the impurities like carbon or sulphur were not found when the nanoparticles and the composite were synthesized.

3.5. BET surface area analysis
A BET test was performed to determine the surface area of the synthesized nanoparticles and the composite. The surface area of TiO₂ nanoparticles was found to be 51.23 m² g⁻¹ which was comparable with the results reported by Chung et al[9]; however, found to be lower than the area reported by Rajamanickam et al [23]. The surface area of the TiO₂-ZnO composite was determined to be 18.54 m² g⁻¹ which is lower in comparison with the data presented by Pugazhendhi et al [28]. Figures 6(a) and (b) demonstrate the N₂ adsorption-desorption isotherms of TiO₂ nanoparticles and TiO₂-ZnO composite, respectively. The specific surface area, pore diameter, and average pore volume of the synthesized nanomaterials are presented in table 1. The surface area of pure TiO₂.

Figure 6. Nitrogen adsorption-desorption plots of (a) TiO₂ nanoparticles and (b) TiO₂-ZnO composite.
nanoparticles was found to be greater than that of TiO$_2$-ZnO composite due to the higher temperatures involved during solution combustion synthesis. In contrast, the TiO$_2$ nanoparticles were synthesized using the sol-gel technique, which does not require higher temperatures to synthesise nanoparticles.

### 3.6. $j$-$V$ characterization

Figure 7 corresponds to the current-voltage characteristics of the DSSCs, which were fabricated utilizing photoanodes of nano TiO$_2$ and TiO$_2$-ZnO composite, respectively. From the $j$-$V$ characterization, we could observe that the DSSC fabricated utilizing the photoanode of nano TiO$_2$ has exhibited better photovoltaic performance than the DSSC fabricated employing the photoanode of TiO$_2$-ZnO composite. The open-circuit voltage of DSSCs formulated using nano TiO$_2$ and TiO$_2$-ZnO composite were enumerated to be 0.742 V and 0.534 V, respectively. The open-circuit voltage values of the present work are comparable to the $V_{OC}$ values reported by Chung et al [9]; but greater than those reported by Mohammed et al [18], Giannouli et al [19], Govindaraj et al [22] and Rajamanickam et al [23]. Chung et al have synthesized the TiO$_2$ nanoparticles employing solution combustion approach using distinct fuels such as glycine, urea, thiourea and have utilized it to fabricate DSSC [9]. Mohammed et al [18] and Giannouli et al [19] have incorporated TiO$_2$ nanoparticles as photoanodes but have utilized organic dye to develop DSSC. Govindaraj [22] and Rajamanickam [23] have synthesized TiO$_2$ nanorods employing a hydrothermal approach and have incorporated them as photoanodes in the development of DSSC. Synthesized TiO$_2$ nanoparticles were crystalline with a smaller size compared to TiO$_2$-ZnO composite, which was slightly amorphous.

The short circuit current density, $J_{SC}$ of the nano TiO$_2$ and TiO$_2$-ZnO composite based DSSCs were determined as 4.152 and 0.014 mA cm$^{-2}$, respectively. The density of short circuit current for the present work is lower compared to the data reported by Chung [9], Govindaraj [22], Rajamanickam [23]; but greater compared to the results presented by Wahyuningsih [20] and Susanti [21]. Wahyuningsih [20] and his team utilized

### Table 1. Specific surface area, pore diameter and pore volume of TiO$_2$ nanoparticles and TiO$_2$-ZnO composite.

| Nanomaterial   | Specific surface area (m$^2$ g$^{-1}$) | Pore diameter (nm) | Pore volume (cm$^3$ g$^{-1}$) |
|---------------|---------------------------------------|--------------------|-------------------------------|
| TiO$_2$       | 51.23                                 | 2.466              | 0.177                         |
| TiO$_2$-ZnO   | 18.54                                 | 3.46               | 0.067                         |

Figure 7. $j$-$V$ characteristics of the DSSCs formulated with pure TiO$_2$ and TiO$_2$-ZnO composite.
mechanochemical techniques for synthesizing TiO$_2$-ZnO nanorods, and the dye Ruthenium N3 was used for sensitization of DSSC. The TiO$_2$ powders of the anatase phase procured from Merck with the size of the particles ranging from 0.2–0.4 μm were utilized by Susanti et al [21] for DSSC applications, and the dye employed for sensitization was tamarillo extract which was an organic dye. The difference in voltage ($V_{OC}$) and current density ($J_{SC}$) values could have resulted owing to the size and morphology of the synthesized nanomaterials, various synthesis methods adopted, and the type of dye utilized for sensitization.

The efficiency of the fabricated DSSCs employing nano TiO$_2$ and the composite of TiO$_2$-ZnO were evaluated as 2.22 and 0.0022%, respectively. The efficiency exhibited by the cell formulated with TiO$_2$-ZnO composite is considerably low compared to the cell formulated with pure TiO$_2$, mainly due to the low fill factor, which may be owing to the electron recombination reactions. The efficiency values of the present work are lower compared to the results of Chung et al [9] and Rajamanickam et al [23]. However, the power conversion efficiency is greater than the figures presented by Susanti [21], which could be due to the incorporation of organic dye for DSSC applications by Susanti et al [21]. The present research work’s efficiency values are greater than the results presented by Giannouli et al [19] and Wahyuningsih et al [20] for the DSSC devised with nano TiO$_2$, but a reduction in efficiency was observed for the TiO$_2$-ZnO composite based DSSC. The variation in efficiency values could be owing to the specific surface area of the synthesized nanostructures, amorphous nature, and agglomeration of particles of TiO$_2$-ZnO, which might have led to poor loading of the dye and greater resistance for the electron mobility across the photoanode film [9] resulting in poor efficiency compared to the DSSC devised with pure crystalline TiO$_2$.

The $J$-$V$ parameters of the fabricated dye-sensitized solar cells are summarized in Table 2. We can observe that the DSSC formulated with TiO$_2$ nanoparticles has exhibited exceedingly high photovoltaic performance in comparison with the DSSC developed with the composite of TiO$_2$-ZnO. The DSSC formulated with modified TiO$_2$-ZnO composite has unveiled an open-circuit voltage of 0.534 V and an exceptionally lower efficiency of 0.0022%. The efficiency has drastically reduced due to the low fill-factor exhibited by the DSSC developed with TiO$_2$-ZnO composite as the photoanode.

Table 2. $J$-$V$ factors of the DSSCs formulated utilizing nano TiO$_2$ and TiO$_2$-ZnO composite.

| Photoanode      | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF (%) | Efficiency (%) |
|-----------------|--------------|-------------------------|--------|---------------|
| TiO$_2$         | 0.742        | 4.152                   | 71.97  | 2.220         |
| TiO$_2$-ZnO     | 0.534        | 0.014                   | 26.71  | 0.0022        |

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Figure 8 represents the $J$-$V$ characteristics of the DSSCs fabricated with pure TiO$_2$ and TiO$_2$-ZnO composite, under dark conditions. The DSSCs have shown the characteristics of a diode under dark conditions.
3.7. Cyclic voltammetry

Cyclic voltammetry tests of pure TiO$_2$ and the modified TiO$_2$-ZnO composite are demonstrated in figure 9. Cyclic voltammetry studies were carried out employing a carbon paste working electrode (CPE) for the electrochemical detection of potassium ferrocyanide. The cyclic voltammetry analysis of 1 mM potassium ferrocyanide at bare and nanomaterials (TiO$_2$ and TiO$_2$-ZnO composite) modified carbon paste working electrode was performed at the scan rate of 50 mV s$^{-1}$. From the cyclic voltammetry analysis, an increase in peak current at nano TiO$_2$ modified carbon paste electrode was not noticed for the electrochemical determination of potassium ferrocyanide, which indicates that the prepared nanoparticles of TiO$_2$ cannot act as an electrocatalyst for the standard probe. However, the modified composite material has exhibited superior properties when compared to the pure nano TiO$_2$. In figure 9, the continuous curve indicates the response of the bare electrode, and the discontinuous curves represent the response of the nano TiO$_2$ and TiO$_2$-ZnO modified electrodes to detect potassium ferrocyanide. It is evident from the cyclic voltammetry response that the TiO$_2$ modified carbon paste electrode has not demonstrated an increase in current with a diminished difference in peak potential [31].

A rise in peak current was noticed at the TiO$_2$-ZnO modified electrode, representing the electrochemical response for the detection of potassium ferrocyanide. The incorporated ZnO has played a crucial role in the electrocatalytic characteristics with nano TiO$_2$. In figure 9, the discontinuous curves specify an enhance in oxidation-reduction peak current. A pair of oxidation-reduction curves of potassium ferrocyanide was noted at the TiO$_2$-ZnO composite modified electrode. Owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of potassium ferrocyanide at the bare carbon paste electrode is a low current signal. However, the voltammetric response is improved at the modified carbon paste electrode, reflected by the enlargement of the peak currents and the decline of the potential difference. An increase in peak current was identified at the TiO$_2$-ZnO modified electrode, providing greater surface area, resulting in increased electrode contacting area of potassium ferrocyanide, thus facilitating its electrochemical detection [32–40]. Since the electrode modified with TiO$_2$-ZnO has exhibited better electrocatalytic property, it can be concluded that electron transfer via TiO$_2$-ZnO composite to the transparent conducting film is effective and the mobility of electrons could be increased by optimizing the properties of photoanode semiconductor material, that is, utilizing different molar concentrations of TiO$_2$ and ZnO for the synthesis of composite, enhancing the surface area of the composite, which may lead to improved efficiency [41].

Integration of nano TiO$_2$ particles with ZnO has resulted in the bandgap reduction from 3.10 to 3.06 eV. Also, the specific surface area of pure TiO$_2$ nanoparticles was higher than that of the composite modified with ZnO nanoparticles. Since DSSC necessitates a wider bandgap and higher specific surface area semiconductor photoanode, a decline in efficiency value was noticed for the DSSC formulated with TiO$_2$-ZnO compared to the DSSC’s efficiency with pure TiO$_2$. But the combination of nano TiO$_2$ and ZnO particles has enhanced the nanomaterials’ surface to volume ratio, which has facilitated enhancing the electrocatalytic properties. Hence the composite of TiO$_2$-ZnO has presented good electrochemical characteristics for the detection of potassium ferrocyanide in comparison with the pure TiO$_2$ nanoparticles.

**Figure 9.** Cyclic voltammetry for the detection of potassium ferrocyanide (a) with Bare CPE (b) with pure TiO$_2$ nanoparticles and (c) with TiO$_2$-ZnO composite.
4. Conclusion

The TiO$_2$ nanoparticles and the composite of TiO$_2$-ZnO were synthesized and utilized as anodes to formulate dye-sensitized solar cells (DSSCs). The photovoltaic characteristics of were analyzed under a xenon arc solar simulator of irradiation 100 mW cm$^{-2}$. The DSSC developed with pure TiO$_2$ exhibited a greater efficiency of 2.22% in comparison with the DSSC fabricated employing the composite of TiO$_2$-ZnO. Integration of ZnO with nano TiO$_2$ has resulted in reduced photovoltaic characteristics due to the electron recombination reactions, a decline in bandwidth, and specific surface area. However, a better electrocatalytic property of TiO$_2$-ZnO composite was verified by cyclic voltammetry analysis for the electrochemical determination of potassium ferrocyanide. The composite of TiO$_2$-ZnO can be utilized as a semiconductor photoanode material in the development of DSSC as it has exhibited better electrocatalytic characteristics which may facilitate effective transport of electrons across the semiconductor and transparent conducting oxide interfaces, which may lead to improvement in power conversion efficiency.

Acknowledgments

The authors are thankful to the ‘Centre for Advanced Materials Technology’, M S Ramaiah Institute of Technology, Bangalore for providing analytical facilities. We express our heartfelt gratitude to Mr Narendiran S and Dr Govindaraj R, SSN College of Engineering, Chennai, India for his helpful discussions.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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