

## Research Article

# Tuning Anatase-Rutile Phase Transition Temperature: $\text{TiO}_2/\text{SiO}_2$ Nanoparticles Applied in Dye-Sensitized Solar Cells

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$\text{TiO}_2/\text{SiO}_2$  nanoparticles with 3, 5, and 10 molar percent of silica, were synthesized by hydrothermal method and characterized by SEM, TEM,  $\text{N}_2$  adsorption-desorption isotherms, X-ray diffraction, and Raman and UV-Vis spectroscopy. While pristine  $\text{TiO}_2$  thermally treated at 500°C presents a surface area of  $36 \text{ m}^2 \text{ g}^{-1}$  ( $\pm 10 \text{ m}^2 \text{ g}^{-1}$ ),  $\text{TiO}_2/\text{SiO}_2$  containing 3, 5, and 10 molar percent of silica present surface areas of 93, 124, and  $150 \text{ m}^2 \text{ g}^{-1}$  ( $\pm 10 \text{ m}^2 \text{ g}^{-1}$ ), respectively.  $\text{SiO}_2$  is found to form very small amorphous domains well dispersed in the  $\text{TiO}_2$  matrix. X-ray diffraction and Raman spectroscopy data show that anatase-to-rutile phase transition temperature is delayed by the presence of  $\text{SiO}_2$ , enabling single-anatase phase photoanodes for DSSCs. According to the  $I \times V$  measurements, photoanodes with 3% of  $\text{SiO}_2$  result in improved efficiency, which is mainly related to increased surface area and dye loading. In addition, the results suggest a gain in photocurrent related to the passivation of defects by  $\text{SiO}_2$ .

## 1. Introduction

Since the seminal work published by Regan and Graetzel in 1991, DSSCs have been widely studied and have become a broad research field involving semiconductors, organic dyes, inorganic complexes, and electrolytes [1–4]. One of the main components of a DSSC is the nanocrystalline mesoporous photoanode [5]. So far, the most efficient devices are assembled with  $\text{TiO}_2$  photoanodes in anatase phase, allowing the fastest charge transfer rates [6, 7].  $\text{TiO}_2$  presents adequate energy gap, high surface area, adequate pore size, high pore volume, nanometric particle size, crystal size, and tunable doping level [8]. Aiming to improve these properties, the development of synthetic approaches to obtain single-anatase phase and shape-controlled  $\text{TiO}_2$

nanoparticles is warranted to provide a significant contribution to the field.

The anatase-to-rutile solid-solid phase transition is found to happen in a very wide range of temperatures and is not only dependent on the size of the particles but also on the preparation method, shape of the nanostructure, and presence of dopants and structural defects [9–16]. Indeed, the control over phase formation during the synthesis and the phase transition during thermal treatment are main concerns due to the undesirable formation of the rutile phase at higher temperatures. Aiming to obtain photoanodes assembled with single-anatase phase  $\text{TiO}_2$ , many works have been developed on the effect of dopants, structural defects, sample preparation, and thermal treatment on  $\text{TiO}_2$  [17]. Within this context,  $\text{SiO}_2$  is frequently used to control textural, structural,

and morphological properties of  $\text{TiO}_2$ , improving the efficiency of DSSCs.  $\text{SiO}_2$  is mainly applied in the form of particles to increase porosity and to enhance light scattering in  $\text{TiO}_2$  photoanodes. Recently, the literature reported the preparation of  $\text{TiO}_2/\text{SiO}_2$  mixed oxides using the sol-gel method and ball milling to decrease the  $\text{TiO}_2$  particle size [6, 9]. In these studies, silica moieties were found to be well dispersed and contributed to maintain the anatase phase even after thermal treatment at  $500^\circ\text{C}$  [18–21].

The hydrothermal method is the most used approach to synthesize nanostructured  $\text{TiO}_2$  for DSSC. It is a simple and efficient route to obtain a nanosize and shape-controlled  $\text{TiO}_2$  nanoparticles and has also been explored to prepare  $\text{TiO}_2/\text{SiO}_2$  for different applications [10, 22]. In this paper, the main goal is to evaluate the effect of different contents of  $\text{SiO}_2$  in a  $\text{TiO}_2$  matrix in terms of morphology, surface area, phase transition temperature, and application in DSSC.

## 2. Materials and Methods

**2.1. Materials.** Titanium(IV) isopropoxide 97% (TIPOT) (Sigma-Aldrich), tetraethyl orthosilicate 98% (TEOS) (Sigma-Aldrich), absolute ethanol 99% (Synth), isopropyl alcohol 99.5% (Sigma-Aldrich), hydrofluoric acid 40% (HF) (Merck), nitric acid 68% (Sigma-Aldrich), Ruthenizer 535-bisTBA (Solaronix), chloroplatinic acid hexahydrate  $\geq 37.50\%$  (Sigma-Aldrich), and Meltonix were obtained from Solaronix.

**2.2. Synthesis of  $\text{TiO}_2/\text{SiO}_2$  Nanopowders.** The nanoparticles were synthesized following a previously reported hydrothermal method with modification [19, 23]. In a 0.50 L flask, 0.027 L (0.35 mol) of isopropyl alcohol, 0.030 L (0.1 mol) of TIPOT, and either no TEOS or different amounts of TEOS were added to obtain pristine  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SiO}_2$  with 3, 5, and 10 molar percent of  $\text{SiO}_2$ . The mixture was maintained at  $60^\circ\text{C}$  under constant stirring. 0.160 L of distilled water was added rapidly under vigorous stirring affording a hydrolysis molar ratio  $h = (\text{H}_2\text{O})/(\text{Ti})$  of 90. After 15 min, 0.0013 L of  $\text{HNO}_3$  and 0.0011 L of HF were added as catalysts. The system was maintained under reflux overnight. The samples were washed with absolute ethanol, centrifuged, and dried by evaporation at  $60^\circ\text{C}$  for 24 h. The nanoparticles were labelled as S0 (pristine  $\text{TiO}_2$ ), S3 (3% of  $\text{SiO}_2$ ), S5 (5% of  $\text{SiO}_2$ ), and S10 (10% of  $\text{SiO}_2$ ).

**2.3. Thermal Treatments.** The samples, S0, S3, S5, and S10, were thermally treated at 300, 400, 500, 600, 700, 800, 900, and  $1000^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  for two hours.

**2.4. Microscopy Analysis.** The morphology was obtained by transmission electron microscopy (TEM) using MET JEM 1200. A small amount of sample was dispersed in isopropyl alcohol using a 450 W ultrasound horn, followed by deposition onto a carbon-coated copper grid.

**2.5. UV-Visible Spectroscopy.** Diffuse reflectance was performed using a Shimadzu UV-2450PC spectrophotometer with an integrating sphere ISR-2200, at room temperature.

**2.6.  $\text{N}_2$  Adsorption-Desorption Isotherms.**  $\text{N}_2$  adsorption-desorption isotherms were determined at the liquid nitrogen boiling point, using a Tristar II 3020 Kr Micromeritics equipment. The samples were previously degassed at  $120^\circ\text{C}$  under vacuum, for 12 h. The specific surface areas were determined by the BET (Brunauer, Emmett and Teller) multipoint technique, and the pore size distributions were obtained by using the BJH (Barrett, Joyner, and Halenda) and DFT (Density Functional Theory) methods.

**2.7. X-Ray Powder Diffraction (XRD).** X-ray powder diffraction (XRD) patterns were obtained using the Siemens D500 diffractometer with  $\text{Cu-K}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) in a  $2\theta$  range from  $10$  to  $90^\circ$  with a step size of  $0.05^\circ$  and time of 0.4 s per step.

**2.8. Dye-Sensitized Solar Cell Assembly.**  $\text{TiO}_2/\text{SiO}_2$  pastes were screen printed on the transparent conductive substrate (fluorine-doped tin oxide (FTO)) previously soaked in 40 mM  $\text{TiCl}_4$  aqueous solution at  $90^\circ\text{C}$  for 30 minutes. The procedure to obtain the  $\text{TiO}_2/\text{SiO}_2$  paste can be found elsewhere [24]. The substrate was heated on a hot plate at  $125^\circ\text{C}$  for 20 min and at  $500^\circ\text{C}$  for 30 min in a tubular oven. The mesoporous  $\text{TiO}_2$ - (S0) or  $\text{TiO}_2/\text{SiO}_2$ - (S3, S5, and S10) based electrodes were immersed in 0.5 mM cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)-N-719 solution of acetonitrile/tertbutyl alcohol (1 : 1 v/v) and kept at room temperature 24 h. The counter electrodes were prepared by coating the FTO surface with a  $30 \mu\text{L}$  of 1 mM hexachloroplatinic acid and heated to  $400^\circ\text{C}$ . The mediator, responsible for the regeneration of the dye, was placed in between the dye-sensitized photoanode and the counter electrode. The device was sealed using a polymeric film of low melting temperature (Meltonix). The electrolyte was a 0.6 M BMII, 0.03 M  $\text{I}_2$ , 0.10 M guanidinium thiocyanate, and 0.5 M 4-tertbutyl pyridine in a mixture of acetonitrile and valeronitrile (85 : 15).

**2.9. Characterization of the DSSCs.** The performance of the DSSCs was evaluated by current versus potential measurements, carried out using the 300 W Xenon arc lamp and the AM1.5 filter. The power of the simulated light was calibrated to  $100 \text{ mW}/\text{cm}^2$  and recorded by the Keithley picoammeter, model 2400.

## 3. Results and Discussion

Figure 1 shows the TEM images of the as-synthesized samples and after thermal treatment at  $500^\circ\text{C}$ . Before thermal treatment, one can observe dispersed and irregularly shaped nanoparticles with average size smaller than 10 nm (Figures 1(a)–1(d)). After thermal treatment, one can observe the formation of agglomerates. The TEM of S0 (pristine  $\text{TiO}_2$ ) shows the formation nanoparticles with average size larger than 30 nm (Figure 1(e)); meanwhile, the presence of  $\text{SiO}_2$  (samples S3, S5, and S10) clearly inhibited nanoparticle growth, resulting in smaller particles with an average size of 10 nm. In the mesoporous photoanodes obtained from these samples (Figure S1), the effect of  $\text{SiO}_2$  is also found to result in the formation of smaller agglomerates. EDS

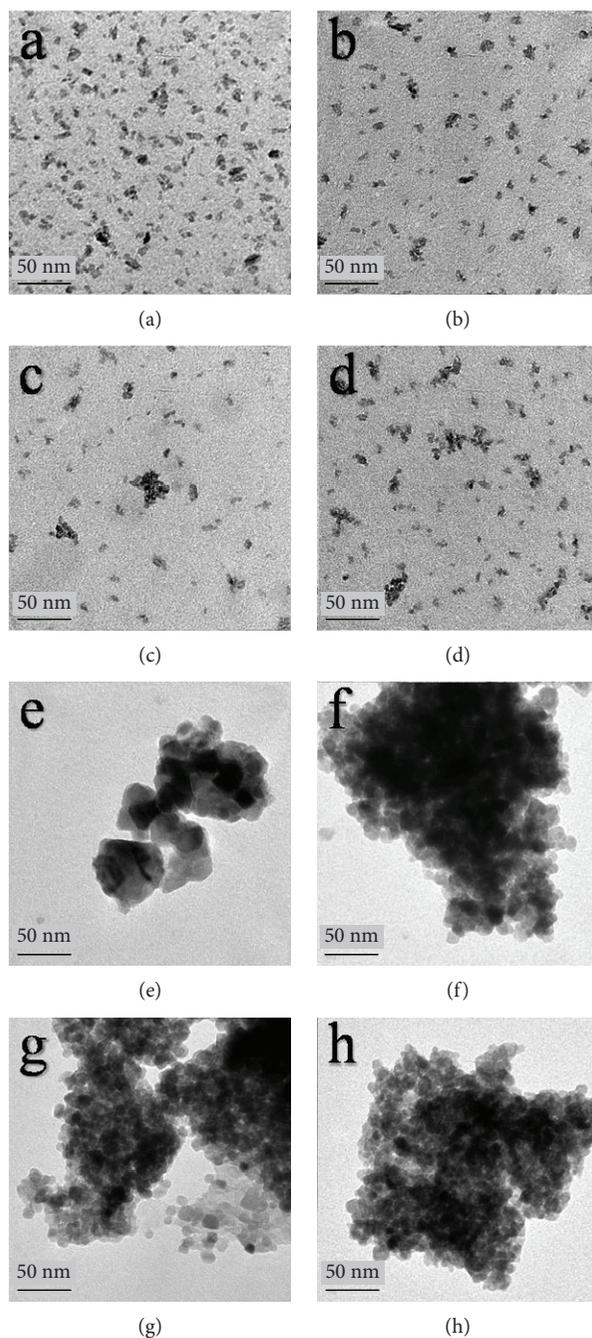


FIGURE 1: TEM images of S0, S3, S5, and S10 before (a–d) and after (e–h) thermal treatment.

analysis (Table S1) confirms the increase of silica content along with the increasing amount of silica precursor.

$N_2$  adsorption-desorption isotherms and BJH pore size distribution of the samples thermally treated at  $500^\circ\text{C}$  (the same temperature used to prepare the photoanodes for DSSC) are shown in Figures 2(a) and 2(b), respectively. The thermally treated samples were labelled as S0C, S3C, S5C, and S10C. All isotherms are type IV, typical of mesoporous materials with hysteresis in high relative pressures [25]. The hysteresis curves undergo a shift to low pressure with the increase of  $\text{SiO}_2$  content changing the mesopore-size

distribution profile. While S0C presents large pore-size distribution profile between 10 and 22 nm in diameter, the presence of  $\text{SiO}_2$  results in mesopores with sharper distribution and smaller diameters (Figure 2(b)). In very low relative pressures ( $P/P_0 < 0.05$ ), which is related to the micropore region, an increase in amount of adsorbed nitrogen is observed from S0C to S10C. DFT micropore distribution curves, shown in the inset of Figure 2(b), confirm the increase in microporosity produced by the silica moiety.

The surface area and pore volume of the samples are presented in Table 1. As one can observe, pristine  $\text{TiO}_2$  (S0C)

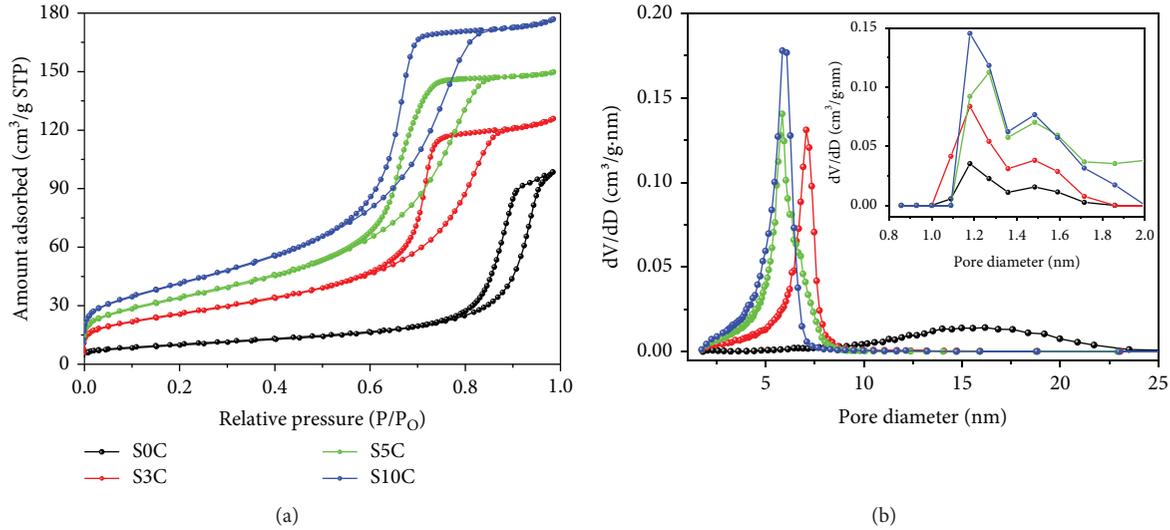


FIGURE 2: (a)  $N_2$  adsorption-desorption isotherms and (b) BJH pore size distribution of S0C, S3C, S5C, and S10C (thermally treated at  $500^\circ\text{C}$ ). Inset in (b): the DFT pore size distribution.

TABLE 1: Surface area and pore volume from the samples thermally treated at  $500^\circ\text{C}$ .

Sample	Surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{g}^{-1}$ )
S0C	$36 \pm 3$	$0.153 \pm 0.001$
S3C	$93 \pm 3$	$0.194 \pm 0.001$
S5C	$124 \pm 4$	$0.233 \pm 0.001$
S10C	$150 \pm 4$	$0.276 \pm 0.001$

presents a smaller surface area than  $\text{TiO}_2/\text{SiO}_2$  samples. In addition, the surface area and pore volume is found to increase along with the increase of  $\text{SiO}_2$  content, from S3C to S10C. This result corroborates with the literature, indicating that silica affords a surface area to  $\text{SiO}_2/\text{TiO}_2$  [6]. For S0C, the pore size is related to the agglomeration of large particles, as observed in the TEM images (Figure 1(e)) [9]. For S3C, S5C, and S10C, the average pore diameter 8 nm corroborates with the size of the particles observed by TEM images.

In order to evaluate the influence of  $\text{SiO}_2$  content in the anatase-to-rutile phase transition, XRD patterns were obtained from S0, S3, S5, and S10 before and after thermal treatment at  $300$ ,  $400$ ,  $500$ ,  $600$ ,  $700$ ,  $800$ ,  $900$ , and  $1000^\circ\text{C}$  (Figure 3). S0 presents diffraction peaks corresponding to the anatase phase (JCPDS# 84-1286) in addition to incipient peaks related to the brookite phase (JCPDS# 29-1360). Anatase-to-rutile phase transition (JCPDS# 76-0649) in the S0 (Figure 3(a)) starts at ca.  $400^\circ\text{C}$ , and the complete conversion is observed at temperatures higher than  $700^\circ\text{C}$ . Meanwhile, for S3, phase transition only starts at ca.  $800^\circ\text{C}$  (Figure 3(b)); for S5 at  $900^\circ\text{C}$  (Figure 3(c)) and for S10 at  $1000^\circ\text{C}$  (Figure 3(d)). The typical XRD pattern of amorphous  $\text{SiO}_2$ , which presents a broad peak near  $22^\circ$ , was not observed, strongly suggesting that  $\text{SiO}_2$  domains are so small and well dispersed that could not be detected by XRD.

Table 2 shows the change in anatase crystallite size related to the thermal treatment temperature and the  $\text{SiO}_2$  content. The crystallite size in S0 was measured as 11 nm at  $400^\circ\text{C}$ ; meanwhile, in S5 and S10, such crystallite size was only obtained after  $700^\circ\text{C}$ . These results show that  $\text{SiO}_2$  amorphous domains hinder or delay the grain growth in anatase phase, and this behaviour is more significant for higher concentrations of  $\text{SiO}_2$  [9]. Although in S0 the anatase crystallites maintain the size of 11 nm at  $500^\circ\text{C}$ , the TEM images (Figure 1) show particles larger than 20 nm for this sample. These results can be explained by the formation of rutile phase after thermal treatment, with crystallite size calculated as 29 nm. The crystallite size exerts a significant influence on the anatase-to-rutile solid-solid phase transition. According to the literature, for this transition to occur, the anatase particles need to grow to a size of approximately 35 nm [26, 27]. Up to this size, the anatase phase has a more stable thermodynamic equilibrium, and the grain grows to decrease the total energy. However, the contribution of bulk energy to total energy increases along with particle size and the anatase phase collapses to decrease the total energy. The transition to the rutile takes place in a reconstructive process, where the Ti-O bonds are ruptured, followed by a structural rearrangement and subsequent formation of new Ti-O bonds in the rutile phase [28, 29]. In this way, the  $\text{SiO}_2$  dispersed in the  $\text{TiO}_2/\text{SiO}_2$  prevented the phase transition by inhibiting the growth of the primary particles [30]. Indeed, these results confirm that a single-anatase phase is obtained even after thermal treatment at  $500^\circ\text{C}$ , due to the presence of  $\text{SiO}_2$ .

Figure 4 shows the Raman spectra of S0, S3, S5, and S10 as synthesized and after thermal treatment at  $500^\circ\text{C}$  (as in Figure 2, the samples thermally treated at  $500^\circ\text{C}$  are labelled as S0C, S3C, S5C, and S10C). The peaks observed at  $163$ ,  $406$ ,  $514$ , and  $635\text{ cm}^{-1}$  are related to vibrational modes  $E_g$ ,  $B_{1g}$ ,  $A_{1g}$  or  $B_{1g}$ , and  $E_g$ , respectively, characteristic of anatase phase (Figure 4(a)). As one can observe, the intensity of these peaks decrease along with the increase in  $\text{SiO}_2$  content. According to literature, the strongest  $E_g$  mode at

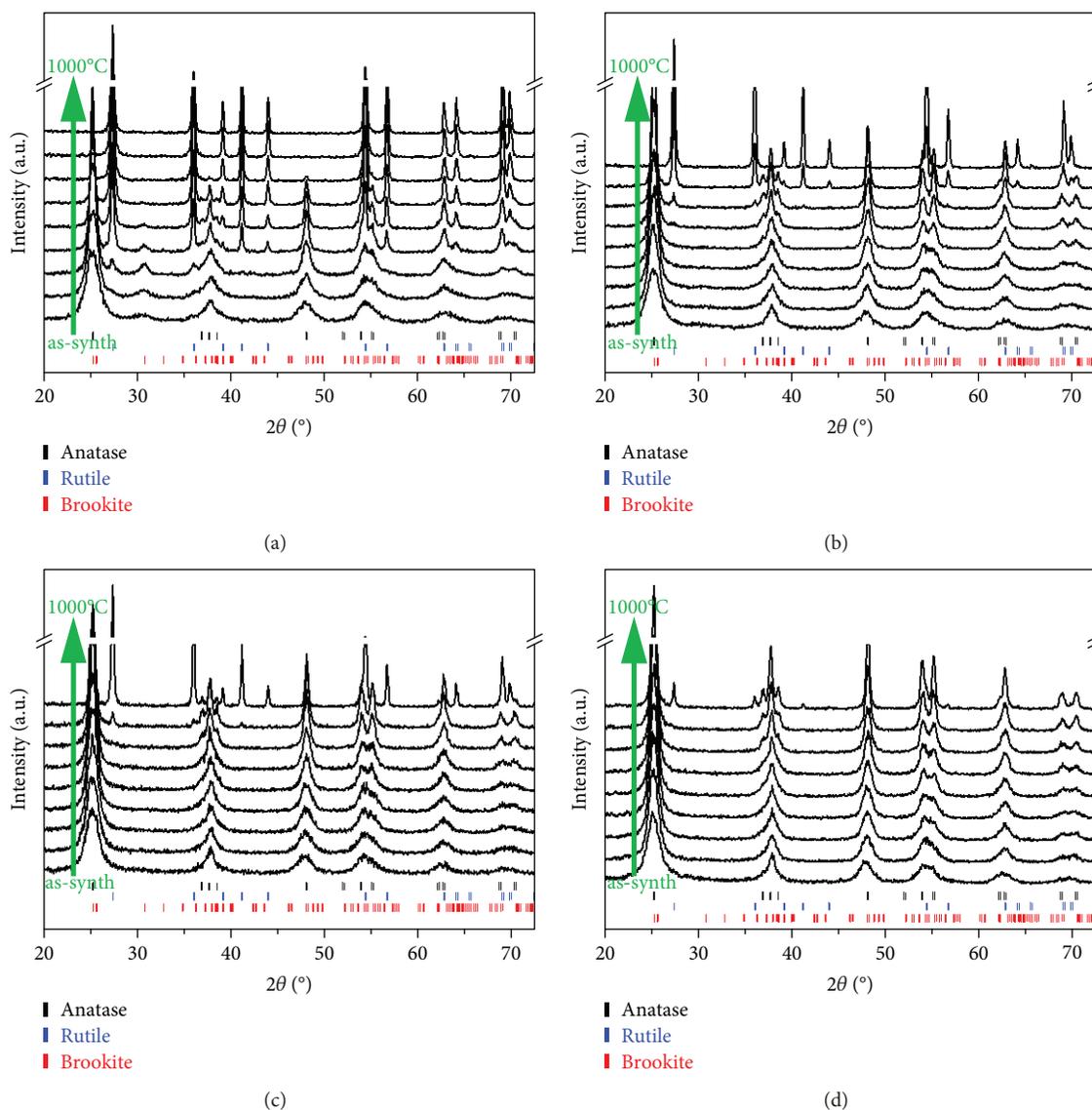


FIGURE 3: XRD patterns of as-synthesized and thermally treated samples at 300, 400, 500, 600, 700, 800, 900, and 1000°C (a) S0, (b) S3, (c) S5, and (d) S10.

TABLE 2: Crystallite size for S0, S3, S5, and S10 thermally treated at different temperatures, calculated by using Scherrer's equation.

Temperature (°C)	S0 (nm)	S3 (nm)	S5 (nm)	S10 (nm)
25	6 ± 1	5 ± 1	6 ± 1	5 ± 1
300	8 ± 1	7 ± 1	6 ± 1	8 ± 1
400	11 ± 1	9 ± 1	7 ± 1	9 ± 1
500	11 ± 1	10 ± 1	8 ± 1	9 ± 1
600	—	13 ± 1	9 ± 1	10 ± 1
700	—	16 ± 1	11 ± 1	12 ± 1
800	—	21 ± 1	16 ± 1	13 ± 1
900	—	28 ± 1	21 ± 1	17 ± 1
1000	—	—	—	28 ± 1

163  $\text{cm}^{-1}$  is related to the external vibration of the anatase structure, showing that the anatase phase was formed in the as-synthesized  $\text{TiO}_2$ . After thermal treatment, this peak shifts to lower frequency at 153  $\text{cm}^{-1}$ , becoming more well defined and the linewidth decreases [31].

For the S0, the peak characteristic of rutile are observed as a shoulder at 447  $\text{cm}^{-1}$  and a peak at 638  $\text{cm}^{-1}$ , corresponding to vibrational modes  $E_g$  and  $A_{1g}$ . Some peaks of rutile and anatase are very similar, such as the ones at 638 and 635  $\text{cm}^{-1}$ ; therefore, the presence of rutile in the S0C can be identified mainly by the shoulder at 447  $\text{cm}^{-1}$  [32]. This shoulder is observed only in S0 corroborating with the early discussion that phase transformation to rutile occurred at 500°C only in the pristine  $\text{TiO}_2$ . The spectra of S3C, S5C, and S10C are very similar to the spectra of S3, S5, and S10, only showing more well-defined and narrow peaks indicating

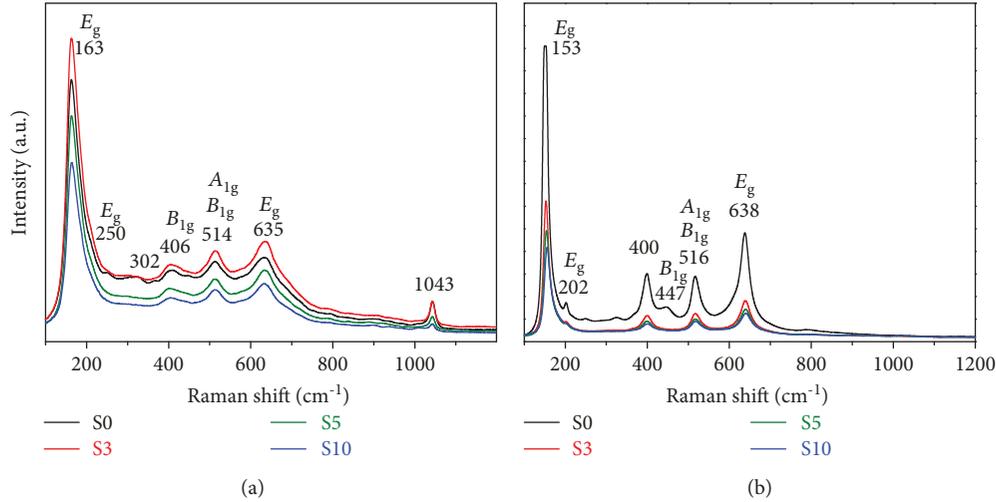


FIGURE 4: Raman shift of S0, S3, S5, and S10 (a) and S0C, S3C, S5C, and S10C (b).

a better crystallization of anatase in the thermally treated samples (Figure S3).

The UV–visible absorption spectra of as-synthesized and thermally treated samples (Figure S4) present similar optical behavior [33]. The measured reflectance  $R$  is not directly proportional to the absorption coefficient,  $\alpha$ ; so Kubelka-Munk was used to extract  $\alpha$ , where  $f(R)$  is the Kubelka-Munk function and  $S$  is the scattering coefficient,

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{S}. \quad (1)$$

By assuming the scattering coefficient to be wavelength independent,  $f(R)$  is proportional to  $\alpha$ , and the Tauc plots were obtained by plotting  $f(R)$  in place of  $\alpha$  as a function of the incident radiation energy ( $h\nu$ ), where  $\alpha$  is the absorption coefficient and  $m$  is equal to 1/2 for a direct gap and 2 for an indirect gap. Extrapolating values of  $f(R)$  to zero, the band gap values were determined (Table S2). In general, the band gap values obtained in the present work are similar to the values for  $\text{TiO}_2$  earlier described in the literature and were not affected by the presence of the  $\text{SiO}_2$  [34, 35]. An interesting result is the tail at around 400 nm decreasing along with the  $\text{SiO}_2$  content. Earlier studies have demonstrated that a very thin layer of  $\text{SiO}_2$  can passivate defects or trapping states on the  $\text{TiO}_2$  surface [36, 37]. Hence, one can suggest that  $\text{TiO}_2$  in S3, S5, and S10 presents less defect concentration, which would result in a decrease of charge recombination and improvement of DSSC efficiencies. The spectra of the photoanodes assembled with S0, S3, S5, and S10 and sensitized with the ruthenium complex (Figure S5) show an increase in dye loading depending on the  $\text{SiO}_2$  content. The results corroborate with data presented in Table 2, once larger surface areas allow larger dye loading, which ultimately should result in improved photocurrent.

Figure 5 shows the current versus potential curves of the DSSCs assembled with S0C, S3C, S5C, and S10C. The obtained electrical parameters, Fill Factor (FF), and efficiency

( $\eta$ ) are described in Table 3. The FF of the devices assembled with S3C, S5C, and S10C presents a slight improvement when compared to S0C. Hence, corroborating with XRD data, the formation of  $\text{SiO}_2$  in very small domains does not seem to affect series or parallel resistance of the devices. On the other hand,  $V_{oc}$  decreased with the amount of silica.  $V_{oc}$  results from the difference between the redox potential of the electrolytes and the quasi-Fermi level of electrons in  $\text{TiO}_2$ , under illumination. Once the high density of photoexcited electrons can negatively shift the quasi-Fermi level and  $\text{SiO}_2$  domains would behave like insulators dispersed into the  $\text{TiO}_2$  matrix, we suggest that the presence of result in a small impediment for charge transfer, displacing the quasi-fermi level and resulting in a short open circuit potential [38, 39]. The obtained power conversion efficiencies (at AM 1.5 G illumination) were 2.25%, 3.3%, 2.45%, and 2.1% for the devices based on S0C, S3C, S5C, and S10C, respectively. Therefore, only a small percentage of silica results in some improvement in efficiency, as observed from sample S3.

Figure 6 shows the Nyquist plots of the assembled DSSCs. These plots consist of three components: ohmic resistance  $R_0$  (associated with the series resistance ( $R_s$ ) of the electrolytes and electrical contacts in the DSSCs), the short arcs ( $R_1$ ), and the larger arcs ( $R_2$ ). The arcs in the high frequency ( $R_1$ ) correspond to the charge-transfer resistance at the Pt counter electrode/electrolyte interface while the arcs at a lower frequency ( $R_2$ ) are attributed to the charge-transfer resistance at the  $\text{TiO}_2$ /dye/electrolyte interface. Table 4 summarizes the results obtained by fitting the experimental data, using an equivalent circuit containing a combination of constant phase element (CPE) and resistance components (inset of Figure 6), where  $\text{CPE}_1$  and  $\text{CPE}_2$  correspond to  $R_1$  and  $R_2$ , respectively. These impedances showed an apparent effect on the charge transport in the DSSCs [40–42].

#### 4. Conclusions

Small silica domains dispersed in a  $\text{TiO}_2$  matrix were found to delay the temperature of anatase-to-utile phase transition,

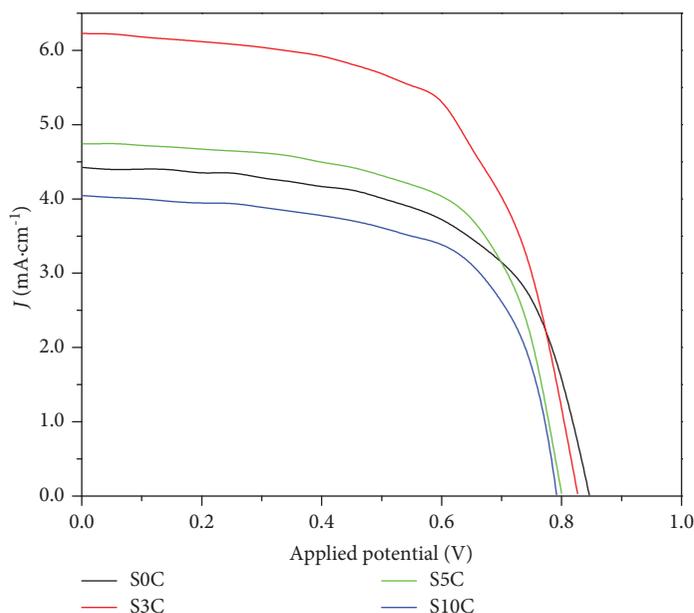


FIGURE 5: Current versus applied potential curves from DSSCs assembled with S0C, S3C, S5C, and S10C.

TABLE 3: Electrical parameters of the assembled devices.

Devices	$I_{sc}$ (mA)	$V_{oc}$ (V)	$I_{max} \cdot V_{max}$	FF	$n$
S0C	4.42	0.85	2.25	60%	2.25%
S3C	6.22	0.84	3.30	63%	3.30%
S5C	4.73	0.81	2.44	64%	2.45%
S10C	4.05	0.80	2.10	65%	2.10%

TABLE 4: EIS parameters from the devices determined by fitting the data according to the equivalent circuit model (see Figure 6).

Devices	$R_0$ ( $\Omega$ )	$R_1$ ( $\Omega$ )	$R_2$ ( $\Omega$ )	$R_{total}$ ( $\Omega$ )
S0C	20.5	42.0	222	284.5
S3C	23.7	46.8	109	179.5
S5C	23.6	39.9	133	196.5
S10C	22.0	68.7	126	216.7

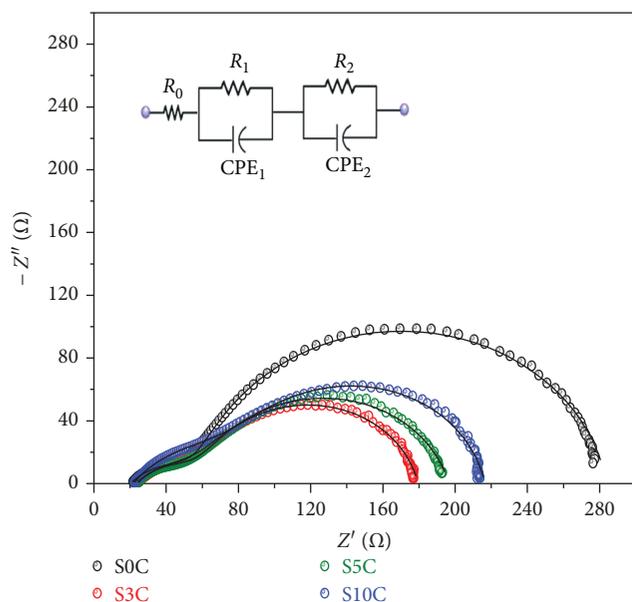


FIGURE 6: Impedance measurement from DSSCs assembled with S0C, S3C, S5C, and S10C.

to temperatures above the ones usually applied to assemble dye-sensitized solar cells. Hence, more efficient DSSC photoanodes presenting single-anatase phase were obtained. The

TiO<sub>2</sub>/SiO<sub>2</sub> samples present very high surface areas, enabling large dye loading and hence improved photocurrents. The delay in phase transition was related to the inhibition of anatase crystallite growth by the presence of SiO<sub>2</sub>. Although all of the samples containing SiO<sub>2</sub> presented larger surface areas than pristine TiO<sub>2</sub>, only the photoanodes based on TiO<sub>2</sub>/SiO<sub>2</sub> with low concentration of SiO<sub>2</sub> resulted in improved power conversion efficiency.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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## Supplementary Materials

Figure S1: scanning electron microscopy images of (a) S0, (b) S3, (c) S5, and (d) S10. Figure S2: diffraction patterns of the samples (a) before and (b) after thermal treatment at 500°C. Figure S3: Raman Shift of S0, S3, S5, and S10 before and after thermal treatment. Figure S4: direct (left) and indirect (right) Tauc plots for S0, S3, S5, and S10. Figure S5: UV-Visible spectra of S0, S3, S5, and S10 thermally treated at 500°C and sensitized with N-719. Table S1: carbon elemental analysis of the samples. Table S2: direct and indirect band gaps of the samples thermally treated at 500°C. (Supplementary Materials)

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