The effect of the ionic liquid $BMI.BF_4$ on the production of TiO_2 nanoparticles applied for dye sensitized solar cells

E. Kohlrausch, M. J. L. Santos

Instituto de Química – UFRGS, 91501-970, Porto Alegre, RS, Brazil

emerson.kohlrausch@ufrgs.br

Introduction

One of the major challenges in the development of highly efficient dye sensitized solar cells is the charge recombination at the interface semiconductor/sensitizer. The recombination centers are mainly generated by defects formed during the formation of the crystalline structure of TiO_2, either during synthesis or during post-synthesis thermal treatments. Figure 1 shows and scheme of the excitation and recombination process that takes place in a DSSC. In a simplified way, the higher the recombination rate of the system, lower is the efficiency of the assembled device. Ionic liquids as reaction medium or surfactant has been widely used in the synthesis of metallic nanoparticles, resulting in interesting contributions to the morphology of the obtained material. Within this context, in this work TiO_2 nanoparticles were synthesized in the presence of the ionic liquid (IL) $BMI.BF_4$ aiming to improve the structural properties of TiO_2, since structural defects in the TiO_2 lattice results in high recombination rates [1].

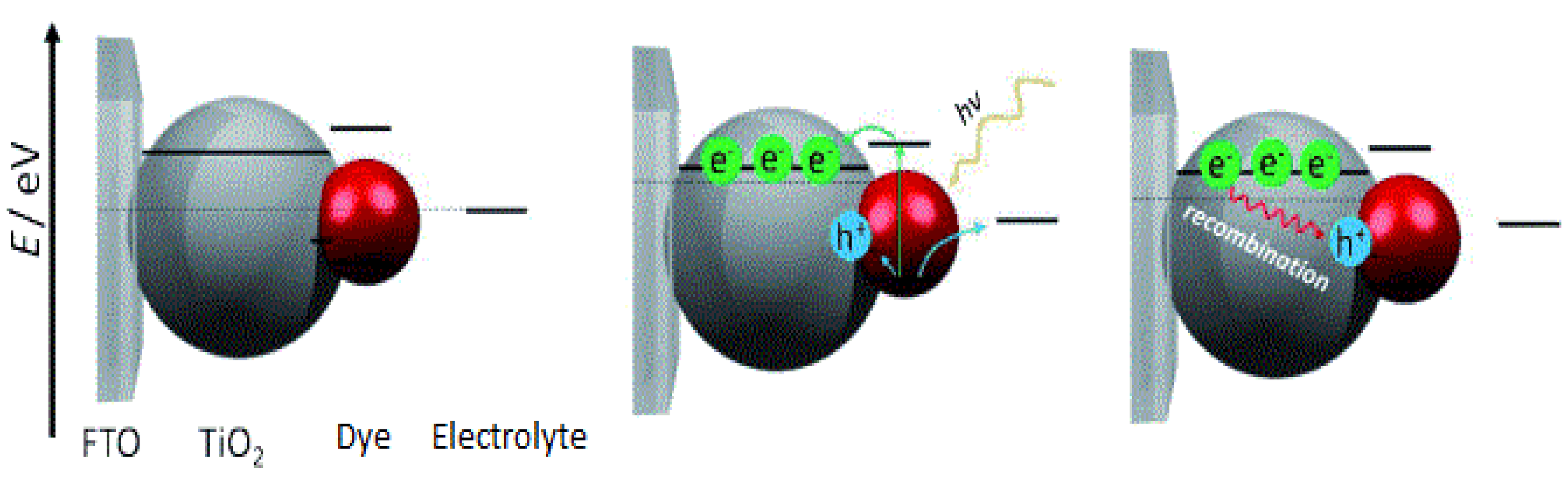

Figure 1. Scheme showing the excitation and recombination process in the DSSC.

Experimental procedure

The complete procedure to obtain the TiO_2 nanoparticles can be found elsewhere [2]. The hydrolysis of titanium isopropoxide was carried out at 80 ºC for 8 hours, followed by hydrothermal growth of the nanoparticles in an autoclave at 230°C for 12 h. Three different TiO_2 pastes were obtained: standard TiO_2 and TiO_2 nanoparticles obtained by using 1% (TiO_2/IL 1%) and 10% (TiO_2/IL 10%) (w/w) of the ionic liquid $BMI.BF_4$ in the synthesis media.

Results and discussion

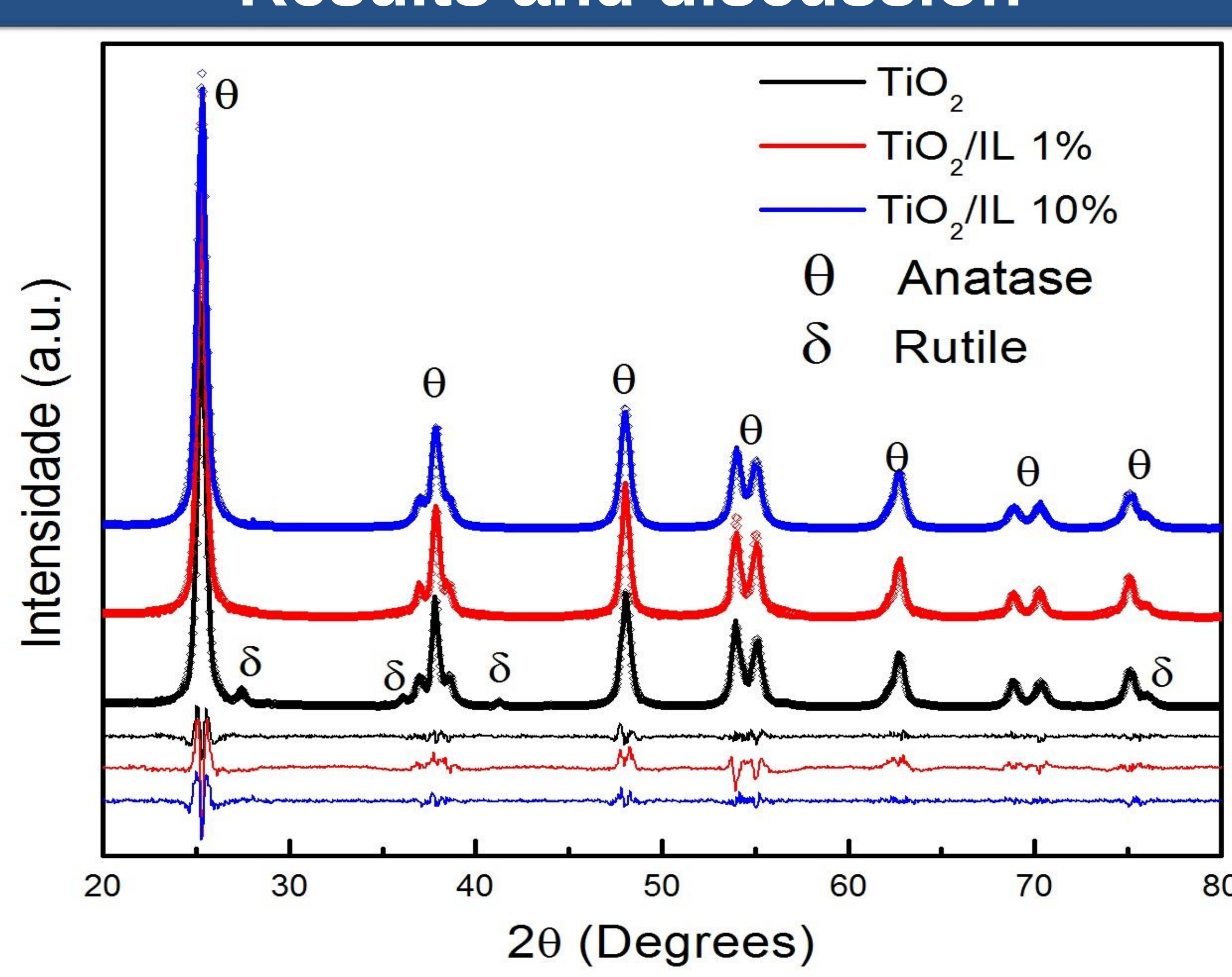

Figure 2: Diffractograms and Rietveld refinement of the samples calcined at 500ºC.

The XRD pattern of the calcined TiO_2 show diffraction peaks related to both anatase and rutile phases (Figure 2). By Rietveld method the phase percentage was calculated as ca. 95.1% for anatase and 4.9% for rutile. An interesting result is the presence of only anatase phase in the samples containing ionic liquid, while the rutile phase vanishes completely. Considering studies in the literature describing the readily formation of oxygen vacancies and Ti interstitials in oxygen poor environment, and the preferential formation of Ti interstitials in the rutile phase, the results obtained in this work suggests a decrease in Ti interstitials related to the presence of ionic liquid.

Figures 3 (a) and (b) present a closer view of the TiO_2/IL 1% and TiO_2/IL 10%, respectively, with the arrows pointing to some of these features inside of the nanoparticles. Based on earlier results in the literature, we suggest that these features might be related to a compositional segregation of Ti or O during the synthesis. Figures 3 (c) and (d) present the high-resolution TEM images, from the samples TiO_2/IL 1% and TiO_2/IL10%, respectively. They show the perfect crystal nature of the synthesized TiO2 in its tetragonal phase (Anatase) characterized by the measurement of the {110} interplanar distance (3.55 Å ±1%).

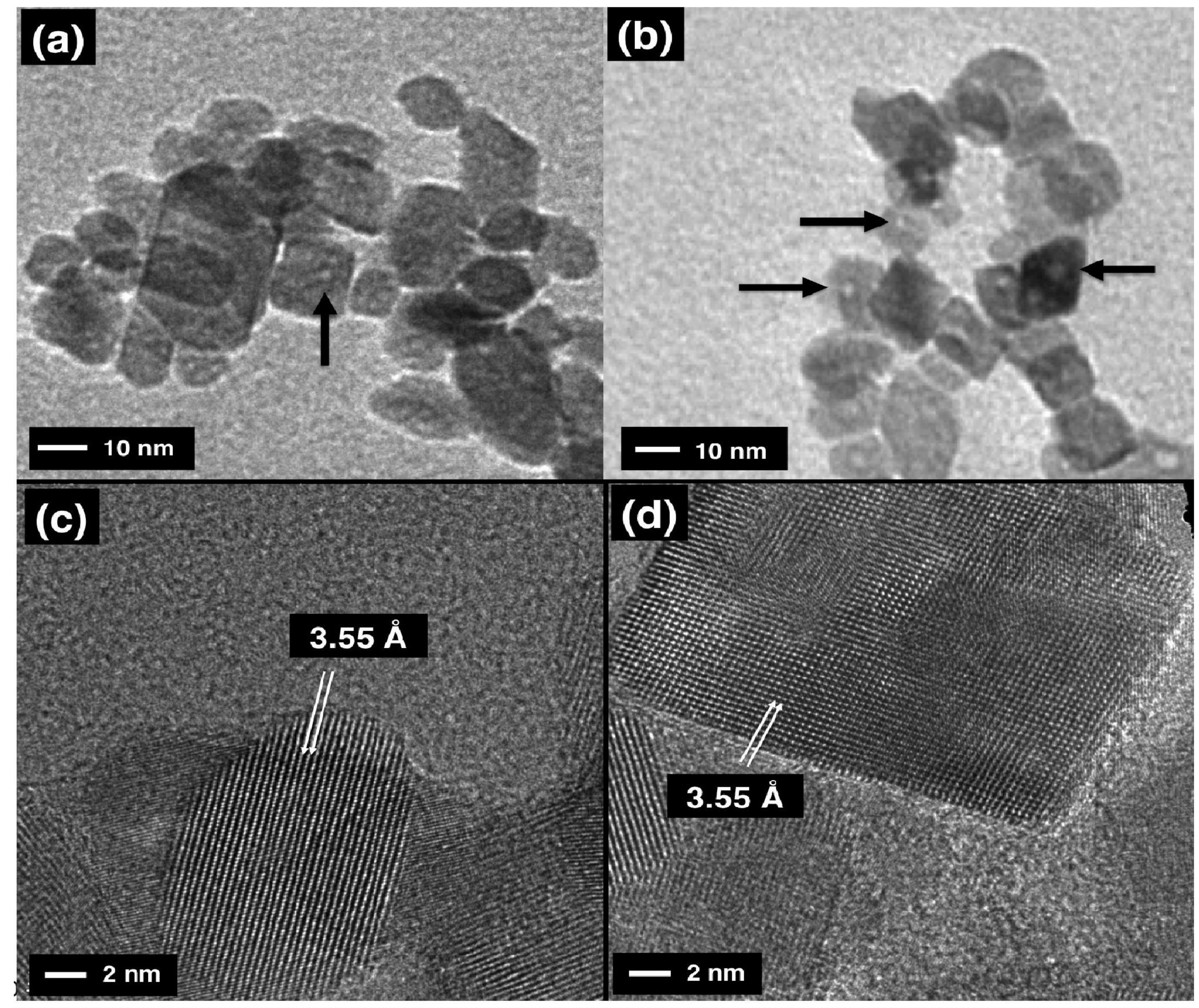

Fig. 3. TEM images(a-b) and HRTEM (c-d) of TiO_2/IL1% and TiO_2/10% respectively.

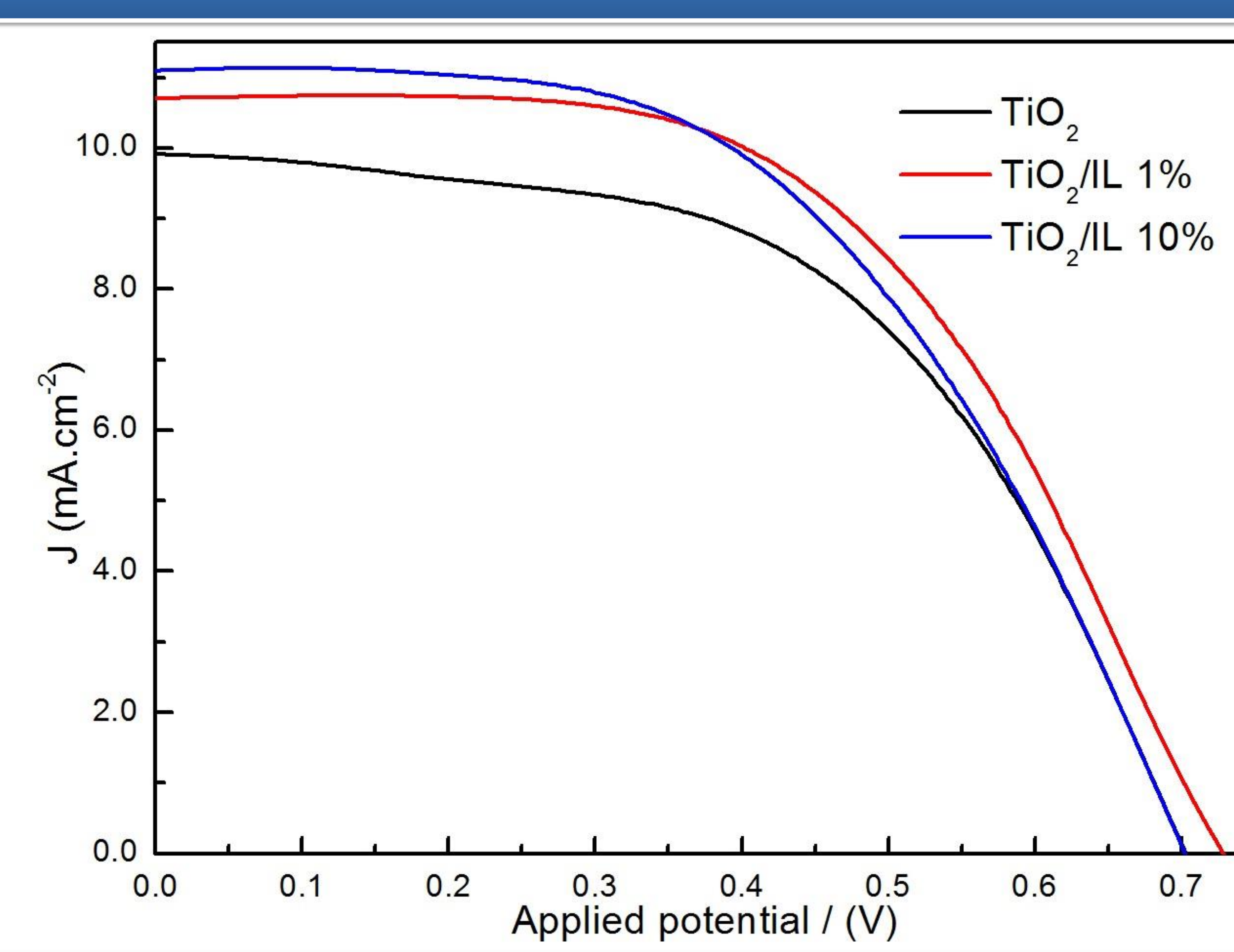

Figure 4. Current *versus* potential curves of samples.

Figure 4 shows the current vs. potential curves obtained under 100 mW.cm^{-2} illumination. The electrical parameters of the cells, the Fill Factor and the efficiency (η) were calculated from these curves and can be observed in the Table 1.

Table 1. Characterization parameters of the cells.

	I_{sc} (mA)	V_{oc} (V)	$I_{max} . V_{max}$	FF	η
TiO_2	9.9	0.70	3.82	55%	3,82%
TiO_2/IL 1%	10.7	0.72	4.32	58%	4.32%
TiO_2/IL 10%	11.1	0.70	4.05	52%	4.1%

Conclusion

In this work we show that introducing small amounts of ionic liquid during the synthesis of TiO_2 favors the formation of the anatase phase, which presents smaller amount of Ti interstitials defects. Resulting in nanoparticles presenting improved optical and morphological properties desirable for DSSCS. The assembled devices using 1 and 10% of ionic liquid in the media presented improved photocurrent and fill factor resulting in a increase of ca. 10 and 30% in efficiency. The results strongly suggests and effect of the ionic liquid decreasing the formation of defects, hence recombination sites.

References

[1] B.O'Reagan e M.Grätzel, *Nature*, ***1991, 353, 737.***

[2] S.Ito, T.N.Murakami, P.Comte, P.Liska, M. K. Nazeeruddin, M.Gratzel. Thin Solid Films, Vol. 516, nº***. 4, (2008), pp. 4613-4619***

Acknowledgments

The authors thanks CNPq, FAPERGS and PROPESQ/UFRGS for their financial support and scholarships.