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Raman Measurements as a Fast and Efficient Technique for Characterisation of TiO_2 and Quantum Dots on TiO_2 Substrate for Photovoltaic Application

P. Kwaśnicki[a,b,*] and M. Inglot[c]

[a]Department of Physical Chemistry and Physicochemical Basis of Environmental Engineering, Institute of Environmental Engineering in Stalowa Wola, John Paul II Catholic University of Lublin, E. Kwiatkowskiego 3A, 37-450 Stalowa Wola, Poland

[b]ML System S.A, Zaczernie 190G, 36-062 Zaczernie, Poland

[c]Department of Physics and Medical Engineering, Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

In this work we focus on the characterization methods allowing fast, cheap, and easy identification of photoanode TiO_2 layer as well as quantum dots on the TiO_2 surface for photovoltaic application. Application of the colloidal quantum dots material for the production of quantum dots solar cell is a key issue for mass production. At the same time there is a demand for a method to control the production steps for the deposition process for both photoanode and nanomaterial. The method has to be fast and cheap as well as efficient in order to meet the requirements imposed by production processes. For this purpose we propose to use a micro Raman spectroscopy as an efficient method to verify the presence of QDs. In this work we compare the results obtained by scanning electron microscopy with the Raman spectroscopy in theme of the pros and cons of these techniques.

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1. Introduction

Energy generation is one of the key issues in the modern world, where almost everything rely on devices needed to be constantly electrically powered. To supply energy, we generally use conventional sources which are limited in terms of resources such as oil, gas, or radiative elements, or what is being now more and more commonly used as green sources such as wind farms, hydroelectric power plants, or photovoltaic (PV) [1]. Nowadays photovoltaic gains more and more attention due to new materials used for PV cells such as quantum dots [2–4], reducing the price of the PV devices and at the same time increasing the conversion efficiency, as well as expanding the place of application [5]. New materials however, before being applied into PV, needs to be characterized in order to determine their parameters [6]. One way to characterize them is to use a micro-Raman spectroscopy.

In this work we focus on the Raman characterization of quantum dots material on TiO_2 substrate and the substrate itself in order to determine their presence, distribution, and homogeneity and the quality of the substrate before and after the deposition process. The Raman spectroscopy is a spectroscopic technique based on the measurement of the Raman scattering radiation, i.e. inelastic photon scattering, similarly to infrared absorption spectroscopy, and belongs to the techniques for testing the oscillation spectra of materials. The symmetry of the molecule determines which vibrations are active in the Raman scatter spectrum, which is expressed by the selection rules determining the probability of observation (intensity) of a given band. According to the rule of choice in the Raman spectrum, in this spectrum only those vibrations appear in which the polarizability changes so that it has no extreme in the equilibrium position. It was shown that the Raman spectroscopy is a useful method to characterize different parameters of nanomaterial such as quantum dots [7].

2. Experimental

2.1. Raman

The measurements were made using the integrated Raman LabRam spectroscope. The source used for the measurements was a helium–neon laser with wavelength of 632.8 or 532 nm at 17 mW power. The whole system was complemented by a confocal microscope coupled with a 800 nm focused lens and a two-dimensional multichannel CCD detector. Additionally, the system is equipped with an automatic Czerney-Turner spectrograph with a slot width of 30 mm for a wide flat field of view. The measurements were taken at room temperature for the ML System of samples prepared at the laboratory.

*corresponding author; e-mail: kwasnickipawel@gmail.com

2.2. SEM

Measurements were done using FEI Quanta 3D FEG with a dual beam system equipped with multiple analytical and manipulative tools to use different techniques and methods. Instrument was equipped with a number of high-resolution imaging and surface analysis methodologies, such as low vacuum backscatter electron imaging (BSE), secondary electron (SE) imaging, and ion induced secondary imaging (ISE), and energy dispersive X-ray detector (EDS). The range of the accelerating voltage varied from 1 to 2 keV and working distance between 2 and 4 mm depending on the samples and expected resolution. Magnification of 300k× allowed to observe low-dimensional structure such as quantum dots.

2.3. PVD

For the deposition of TiO_2 material a PVD system with magnetron sputtering and glove box was used. The glove box was equipped with gloves dismounted from the safety front window and made of high quality butyl rubber with low gas permeability. Two-port glovebox system was connected to the Adapterbox from the left through the T-shaped vestibule, and on the right side, was connected by a collar with a four-port glovebox. The system was equipped with a thermal evaporation and a magnetron with 2 sources allowing for deposition of thin layers with very good homogeneity both in terms of thickness and chemical composition. Magnetron sources of a power supply 300 W for an RF source and a DC power supply with a power of 1 kW with the ability to control the arc for DC source equipped with pneumatically controlled separators effectively eliminating cross-contamination between neighbouring sputtering sources. The substrate was mounted on a rotating plate with variable speed equipped with a PID controller. In addition, it is possible to adjust the substrate temperature to 350 °C using a quartz lamp.

3. Results and discussion

The structure of investigated samples consisted of three different layers all made on glass substrate [8]. In this work we used 2.2 mm thick float glass covered by TCO layer. On the glass substrate the layer of transparent conductive oxide (TCO) was deposited using chemical vapor deposition (CVD) technique. In this work we used FTO layer since it is widely available on the market, cheap, and has good conductive parameters. The surface resistance was found to be less than 8 Ω/cm^2 [2, 9]. On the top of the FTO layer the TiO_2 layer was made using physical vapor deposition (PVD)technique. Finally, above the TiO_2, quantum dots (QDs) were deposited using spin coating technique. The inhomogeneity of this method was found to be less than 2% on the substrate of the diameter up to 10 mm QDs layer. The examined low-dimensional structures were applied to the TiO_2 substrate, which was the reference matrix. A typical surface topography of TiO_2 is shown in Fig. 1. Measurements were done using scanning electron microscopy (SEM) in order to obtain the information about the topography of photoanode layer of TiO_2.

Measured layer was made using magnetron sputtering. The deposition time was set at 5400 s and the thickness was estimated to be in a range of 450 nm. On the surface one can see clusters of the material on the height of few tens of nm and diameters, from 50 nm up to 1.5 μm. Their bright colours suggested that they protruded above the surface. These clusters were formed during the deposition process and most probably were due to too low temperature on the substrate during the growth process. Measurements done in higher magnification showed that indeed the clusters are the TiO_2 crystallites material cumulated. Figure 2 shows the surface of TiO_2 in higher magnification. One can clearly see the porous surface topography and the rounded shape clusters. Here the clusters are in the range of 150 nm.

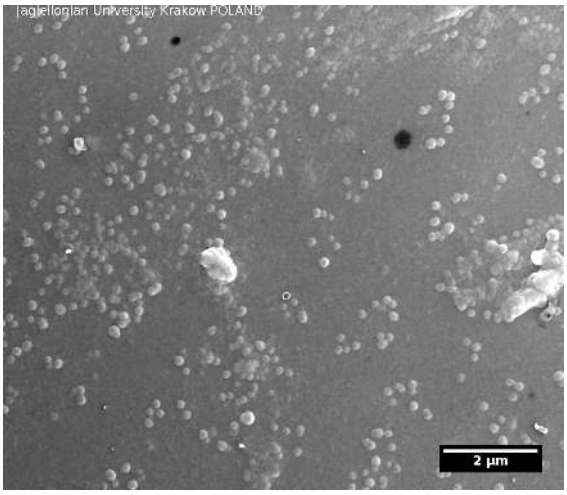

Fig. 1. SEM image of the surface of TiO_2 acquired using SE detector.

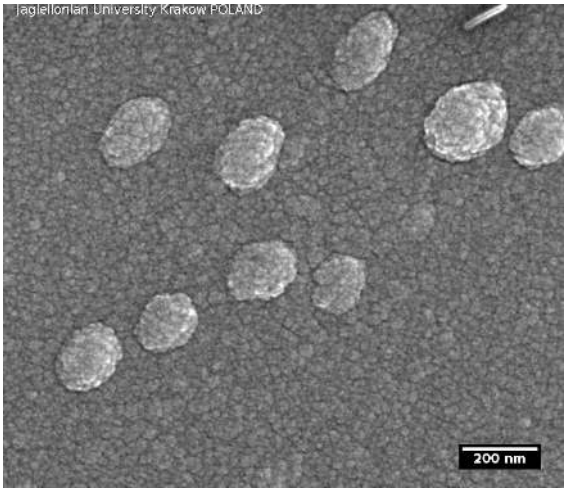

Fig. 2. High magnification SEM image of TiO_2 surface made using PVD technique.

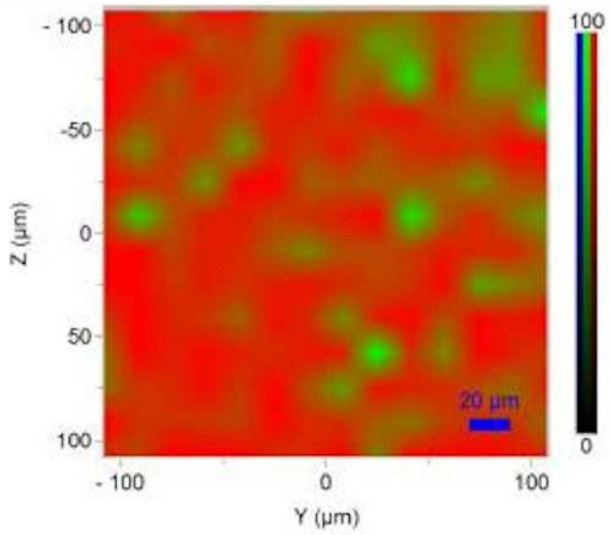

Fig. 3. The surface map of the TiO_2 photoanode is made using the Raman spectroscopy.

Combining these results with the measurements done using the Raman spectroscopy one can notice that these clusters are the reason of different stresses present in the material. This stress can cause the cracks of the photoanode layer and performance degradation of the photovoltaic cell. Cracks can appear especially after the thermal treatment. Figure 3 presents the surface map of the TiO_2 photoanode made using the Raman spectroscopy. In red and green colour different stresses are marked resulting most probably from the deposition process. Green colour corresponds to the places where the stress is higher and mostly is related to the places where the clusters of the TiO_2 are present.

The appearance of inhomogeneities in the context of stresses may affect the properties of both the substrate and the low-dimensional structure deposited on the surface. Since for deposition process of quantum dots we use spin coater technique, these small clusters can be a reason of the inhomogeneity of the QDs layer. Quantum dots can be accumulated near the protruding islands of TiO_2 clusters causing thick and not well attached clusters of quantum dots which in turns can easily fall off. Further examination using the Raman spectroscopy and SEM measurements were needed to verify the assumption. On the top of the TiO_2 layer a thin film of quantum dots material was deposited using spin coating method. Next, SEM measurements were done in order to verify the presents of QDs. The results of SEM investigation in high resolution is presented in Fig. 4.

A typical structure of TiO_2 layer made by using PVD system is visible, and one can also notice presence of the cluster of TiO_2. Since the size of used QDs is estimated to be in range of few nanometre (4 to 6 nm), using such a high magnification, we assume to be able to identify QDs. Nonetheless we did not observe any trace of the quantum dots. Next, micro Raman measurements were performed on the same samples in order to verify presence

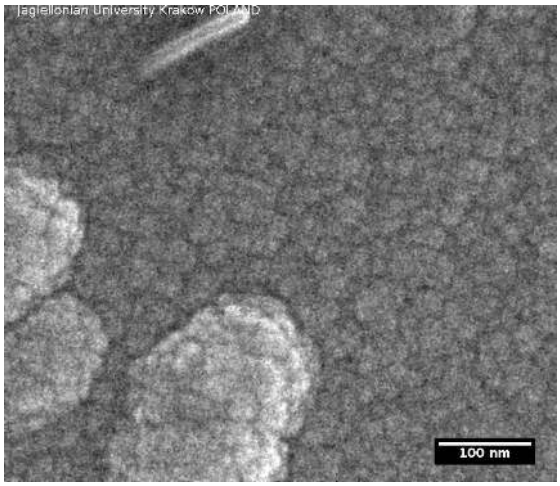

Fig. 4. High resolution SEM image of the surface of the TiO_2 layer after the deposition of quantum dots material.

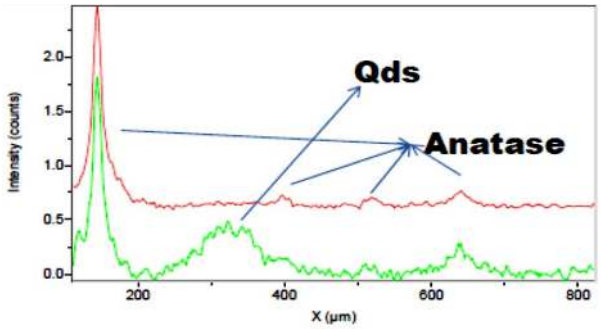

Fig. 5. Raman spectra of the investigated samples, red line (top) TiO_2, green line (bottom) TiO_2 with quantum dots layer on the top.

of QDs. For this purpose a 532 nm wavelength laser was used with the objective of 100× and 600 gr/mm grating. Measurements were done in confocal configuration with confocal hole of 50 μm and step of 1 μm. The results are shown in Fig. 5. One can clearly see typical spectra of TiO_2 material. The peaks appearing are typical for anatase phase of TiO_2. Red line corresponds to TiO_2 without QDs and green line corresponds to the samples with QDs layer on the top.

One can clearly notice the difference between two spectra. For the spectrum taken on the sample with quantum dots a broad peak in the range of 200–400 cm^{-1} appears. This peak is assigned to the presence of quantum dots and appears only for the samples and places where QDs were deposited. Additionally, the intensity of this peak is higher for the samples where we expect to have higher concentration of QDs.

4. Conclusion

In this work we showed that the Raman spectroscopy is a fast and effective way for determination of the quantum dots' presence on the TiO_2 substrate. In addition,

in some cases it provides more information in easier way than commonly used SEM characterization. It is possible not only to define the material (in this case TiO_2) but also obtain the information about the polytype. Additionally it was also established that Raman spectroscopy is a good method to verify the stress of the TiO_2 layer made by PVD. For this case the results obtained by the Raman spectroscopy are in good agreement with SEM results. Furthermore, the Raman spectroscopy is a good method for identification of the nanomaterial such as quantum dots on the TiO_2 surface.

Acknowledgments

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