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Effect of microwave power irradiation on TiO₂ nano-structures and binder free paste screen printed dye sensitized solar cells

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Abstract:

Titanium dioxide (TiO₂) nanostructures (nanorods and nanoparticles) were prepared using a low-cost microwave irradiation method from a polyol medium of glycerol. Titanium glycerolate and TiO₂ powders were obtained in the glycerol medium for the first time with four different power densities (240W, 480W, 720W, 960W) of irradiation using a domestic microwave oven of 2.45 GHz, to understand the impact of power on morphology tuning. The structural and morphological features of the titanium glycerolate and TiO₂ powders were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Raman spectra analysis. The TiO₂ was successfully used in the fabrication of photovoltaic devices and as a proof-of-concept binder free paste was prepared and successfully employed for photo-anode using screen printing on the fluorine-doped tin oxide substrate.

Keywords:

Titanium glycerolate, TiO₂, microwave processing, binder free paste, screen printing, dye sensitized solar cell

Introduction:

Dye sensitized solar cells (DSSC), which are one of the potential candidates for the replacement of conventional silicon-based p-n junction photovoltaic (PV) devices, has become of both academic and commercial interest [1,2]. Metal oxide semiconductors are extensively explored for many applications in photo catalysis, sensors, high speed memory devices and most importantly for the purposes of this study, applications around dye sensitized solar cells [3-6]. Among several semiconductor metal oxides, anatase titanium dioxide (TiO₂) has proven to be the better material for photo-conversion efficiency, depending on the sensitizer adopted [7]. Photovoltaic conversion efficiency of DSSC also depends on the factors like quantum confinement of nanostructures, thickness of the layer, coating method, sensitizer, electrolyte and counter electrode [8-12].

For the preparation of TiO₂ nanostructures, a variety of synthesis methods such as hydrothermal, solvothermal, sol-gel, direct oxidation, chemical vapor deposition, electro deposition, sonochemical, and the microwave method have been used [13-20]. The preferred nanostructure are one dimensional nanostructures such as nanorods, nanowires and nanotubes as they offer a unidirectional electrical path ways for photogenerated electrons through the cell. In general, the hydrothermal method is considered the preferable method to obtain such 1-D nanostructures as they grow directly on the substrate [21-24]. The microwave method reduces the processing time rapidly from 12 or 24 hours to minutes for synthesizing nanostructure [25, 26]. And this microwave-based synthesis method is proven to be one of the cost effective, easiest, energy saving, and fastest way for the synthesis of TiO₂ nanostructures. Hence, it is a potentially useful route for synthesis of TiO₂ and results in higher yields within shorter reaction time [27, 28].

Very few research findings have been reported for the synthesis of TiO₂ nanomaterial in pure glycerol medium and with supporting solvents. Fiber like titanium glycerolate and anatase nanorods were obtained using condenser based experimental setup heated to 190°C about 24 hours [29]. Titanium glycerolate (TiGly) nanoribbons were synthesized by the solvothermal method in glycerol

medium and the obtained gel-like substance was dried in rotary evaporator followed by three different calcination processes to attain TiO₂ powder for photocatalytic activity [30]. Titanium glycerolate microspheres with the granules of nanobelts, which results in flower-like morphology were prepared by solvothermal method with the supporting solvents. The porous anatase TiO₂ powder maintained with same structure after the calcination process and it was also used for photocatalysis [31, 32]. With the help of the supporting solvents in additions to the glycerol medium, the 1-D rod-like nanostructure to hedgehog-like 3-D nanostructures were attained in single microwave power irradiation at 450W for photovoltaic device fabrication [33].

To build on this work, in this study we report, a simple and economically-attractive microwave route for synthesis of TiO₂ rod-like structures and nanoparticles using a domestic microwave oven with a polyol medium of glycerol with different microwave powers. This glycerol medium is amenable for microwave assisted synthesis and this medium can play multiple roles as the solvent, reducing agent and capping agent [34-36]. By systematically altering the microwave power at normal pressure and the boiling temperature of the solvent, one can probe the effects of processing on the microstructural and electrical properties of the nanomaterials fabricated. This method is also attractive because it can be used for large-scale synthesis. To demonstrate the utility of the materials they are used in a solar PV devices along with a proof-of-concept binder free paste employed for the photo-anode using screen printing on the fluorine-doped tin oxide (FTO) substrate.

Materials and Methods/Experimental Details

Titanium isopropoxide (TIP, Aldrich, 97%) and glycerol (Emparta, Anhydrous), ethanol AR (99.9 %), N719 –dye (Sigma), FTO plate (Sigma Aldrich) was used as received.

Preparation of Titanium Glycerolate and TiO₂:

Titanium glycerolate powders were synthesized with the microwave method using a domestic microwave oven without any modification. In a typical procedure, the reaction solution were prepared by dissolving TIP as a precursor in glycerol medium and kept in ultrasonication to make the solution homogeneously clear. The transparent solution was treated with a domestic microwave irradiation of frequency 2.45GHz with four different irradiation power density of 240W, 480W, 720W and 960W respectively, until the optical transformation from clear solution to white was observed. Then it was allowed to cool down for ambient temperature. The white precipitate was separated by filtration and washed with distilled water and ethanol several times to obtain the titanium glycerolate powders. This powder was dried at 80°C followed by the annealing of 450° C for 3 hours to obtain the TiO₂ powder.

Working electrode preparation:

The fluorine-doped tin oxide (SnO₂:F) coated glass substrate was used as a current collector (13Ω/Sq, Aldrich). It was cleaned with distilled water and acetone using an ultrasonic bath. Conventional TiO₂ paste preparation depends on the binders (e.g. ethyl cellulose and alpha teriphenol), which takes four hours to three days [1, 37, 38]. Here, we report binder free paste for screen printing as this route significantly reduces the paste preparation time as detailed in

experimental section. Binder-free TiO₂ paste was made by grinding TiO₂ powder and glycerol using a mortar. A layer of prepared paste was coated on the SnO₂:F- glass substrate using a screen printer(AT-45PA). The coated substrate was annealed at 450° C for 30 minutes in a muffle furnace. The substrate was pre and post treated with the 90 mM of TiCl₄ solution at 70° C for 30 minutes, subsequently it was washed and sintered at 450°C for 30 minutes.

PV device fabrication

The prepared photo anode was immersed into the 0.5mM of N719 dye in anhydrous ethanol and it is kept at room temperature for 16 hours. The platinum counter electrode was prepared by chloroplatinic acid solution using drop casting method and the substrate was sintered at 450° C for 30 minutes.

The dye incorporated TiO₂ working electrode and Pt counter electrode was sandwiched together using binder clips in the standard configuration [39, 40]. The electrolyte solution was prepared by mixing 4-tert-butylpyridine, lithium iodide (LiI), iodine (I₂) in the molar ratio of 0.3:0.5:0.05 with acetonitrile. The electrolyte solution was injected between the two electrodes. The device is assembled in an open configuration without aid of any commercially available paste, powder or blocking layer.

Characterization:

The structural analysis was carried out by Rigaku ultima IV X-ray diffractometer. The surface morphology of TiO₂ samples was characterized by field emission scanning electron microscopy (FESEM) Hitachi S-4800. The photovoltaic performance of the fabricated device was investigated by I-V measurements under illumination of AM1.5G (100mW/cm²) using Keithly 2400 source measurement unit.

Results and Discussion

The microwave irradiation on titanium isopropoxide in a glycerol medium results in the formation of a titanium glycerolate complex. The XRD patterns for as-synthesized titanium glycerolate powder in various microwave powers are shown in Fig.1 and denoted as TG240W, TG480W, TG720W, and TG960W, respectively. A single broad peak of TG240W reflects the amorphous nature of the sample. Sharp intense peaks are obtained with an increase in microwave power confirming that the samples are crystalline in nature. The peaks are existing at 2θ of around 10.85°, 11.79°, 15.95°, 21.43°, 23.49°, 28.59°, 37.45°, and 39.0°. The pattern could not be indexed through the survey of crystal data bases. However, it matches with the already reported pattern excluding the fluctuation of intensity in the facets, which was indexed under P2/c space group symmetry of monoclinic crystal system [29]. The XRD pattern confirms that increase in microwave power does not alter the structure of the crystalline because there is no emergence of new peak and vanished of existing peaks. The relative intensity ratios are tabulated in Table 1 were found by correlating the high intensity peak (I₁) at 11.79°, 11.65°, and 11.54° with the intensity of other

existing peaks (I_2, I_3, I_4, I_5, I_6). Table 1 shows that the increase of microwave power promotes the growth of plane standing around 10.85° , 10.66° and inhibits the other facets. The calcination at 450°C consequences the total disappearance of titanium glycerolate and formed TiO₂ with higher symmetry. The diffraction patterns recorded on the annealed powder samples are shown in Fig.2. For all samples the strongest peak is observed around 25.3° is assigned to (101) plane of anatase phase. This primary diffraction peaks in all the samples are very sharp indicating the significant crystalline nature of the TiO₂ samples. The other exhibited strong diffraction peaks occurred around $48.04, 37.81, 55.11, 53.94, 62.74, 38.49, 75.10, 36.95, 70.36, 68.90, 76.05^\circ$ for the reflection at (200), (004), (211), (105), (204), (112), (215), (103), (220), (116), (301) are noted from powder diffraction data base (JCPDS: 73-1764), respectively for the anatase phase. In addition, the peaks around 27.4 and 41.2° are attributed to the plane (110) and (111) of the rutile phase in the prepared samples (JCPDS: 89-4920). The secondary phase trace has not been observed in the sample prepared at 480W. The patterns shows the considerable variation in area and full width half maximum (FWHM) for all the samples. The Debye Scherer formula is used to estimate the crystallite size corresponds to (101) planes and it was found that 18.6 nm, 17.5 nm, 18 nm, 17.8 nm respectively for the 240W, 480W, 720W, 900W processed samples [41]. The standing planes confirm the formation of tetragonal structures. The crystallite sizes of rutile phase at (110) plane for 240W, 720W, 900W sample are 14.2 nm, 21.1 nm, 16.7 nm, respectively. The peaks corresponds to (101) and (110) plane for all the samples are fit with CMPR to find integrated intensity of the strongest anatase reflection (I_A) and to the intensity of the strongest rutile reflection (I_R). The ratio between I_A to I_R was estimated and percentage content of rutile in all the samples are calculated using the formula [42]:

$$W_R = \frac{1}{1 + 0.886 \left(\frac{I_A}{I_R} \right)} \quad (1)$$

The results were 3.67 %, 4.49 %, 5.82 % rutile in the 240W, 720W, and 980W processed samples, respectively. The lowest intensity of the diffraction peaks, highest value of FWHM and slight peak position shift to lower angle for (101) of 480W sample has been observed when compared to the other samples.

Fig. 3 represents the FESEM images of the obtained titanium glycerolate powder at different microwave powers. It clearly indicates that microwave power during processing has a strong influence on the morphology of the materials. The energy given in the period of time as detailed in the experimental section is enough to form titanium glycerolate nanoparticles. At 240 W the particles form titanium glycerolate spheres. When the microwave power is further increased to 480W, it forces the 1D growth and results in another morphology of more rod-like structures. This rod like morphology has been formed due to the stacking of the self-attached titanium glycerolate sphere shaped nanoparticles in the proper orientation of the particular direction [43]. Moreover, individual rods are having rough surfaces for the entire length and the diameter is in order of 37.5 nm of the rough surfaces. At 720W one can find a combination of rod like structure and spherical nanoparticles, which are nucleated on the surfaces of the rods. The morphology changes to hierarchical 3-D flower-

like structure at 960W for the titanium glycerolate powder samples. Here the diameter of rod-like granules are not uniform in their length and thus forms a thorn like structure. At the tip of the thorn, the dimension is around 166 nm. Several self-assembled nanothorns are aggregated in a common center resulting in the formation of uniform 3-D flower-like structures. This may be the result from multiple spontaneous nucleation sites, the nuclei growth in multiple oriented direction. The whole morphology evolution processes with respect to microwave power is summarized in Fig. 4. As the compositional changes occurred in the samples were given in XRD, the morphology and sub-structures are observable in FESEM images of TiO₂ powder in Fig. 5. It should be noted that there is particle agglomeration in all samples.

After the annealing process, the sphere like shape is not maintained completely for the 240W TiO₂ sample when compared to 240W titanium glycerolate precursor. Fig. 5 (a) has combination of rods with the sphere-like particles. During the annealing process sphere-like particles appeared to combine through aggregation. Rod-like morphology is conserved before and after annealing in the 480W samples, however, it shows a variation in the diameters of the TiO₂ rod-like structures, which ranges from 255–500 nm. The samples processed at 720W and 960W contains agglomerated rods and particles. The 3-D flower-like structure was not conserved during annealing in this work. Agglomeration of crystallites may result for the deviation with calculated crystallite size from XRD to the present analysis.

Raman spectra for synthesized TiO₂ nanopowder by four different microwave powers and the peaks are displayed in Fig. 6. The phase of TiO₂ is further confirmed by Raman spectroscopy. The active modes of the sharp intense peak at 144cm⁻¹, the weakest peak is around 198cm⁻¹ and at 638 cm⁻¹ can be attributed to E_g vibrational modes of symmetric stretching vibrations of O-Ti-O bond. The B_{1g} peak at 400cm⁻¹ is due to symmetric bending vibration of O-Ti-O and A_{1g} peak at 514 cm⁻¹ is assigned to the anti-symmetric bending vibration of O-Ti-O for TiO₂ anatase phase. These peaks exactly matches with the active mode of anatase phase TiO₂ [44, 45].

The Raman active mode of sharp intense peak E_g for 480W sample occurred at 145.75 cm⁻¹. This mode is slightly shifted to the lower wave number side for the other samples compared to the 480W samples. Occurrence of both anatase and rutile phases are confirmed in XRD, but only the anatase peaks are attained in Raman. The discrepancy results from XRD and Raman analysis are attributed due to the percentage of rutile content is less than 6 % in all the samples.

Fig. 7. portrays a schematic illustration of structure and working mechanism of the DSSC. When the photons hit the dye molecules through the transparent conductive substrate, the dye molecules get excited. These photoexcited electrons from the sensitizer of lowest unoccupied molecular orbitals are injected into the conduction band of TiO₂. They then move through the load and eventually reach to the platinum counter electrode. Meanwhile the oxidized dye molecules are regenerated by the redox couples in the electrolyte in order to continue the cycle.

Fig. 8 depicts the current density–voltage curves of the DSSC devices for all the samples. The performance parameters of the devices are extracted from the J-V curves are listed in the inset. The device with 480W microwave power irradiated sample shows the highest short circuit current density

and open circuit voltage and highest output power with the efficiency of 2.84%. This is not overly surprising based on the morphology of the 480W samples. They have the advantages compared to other samples of having a rod-like morphology (Fig. 5) and are made up of the pure anatase phase. This anatase 1-D rod like nanostructure may offers an effective unidirectional electron transport pathway between the dye and TiO₂ to the transparent conducting substrate. In addition, it also provides an optimum surface area for dye loading, when compared to other samples.

This efficiency is comparable with the already reported (2.8% at light intensity of 100 mW/cm²) glycerol based solvothermal method synthesis of TiO₂ [29]. The other reported work from glycerol based microwave synthesis method, a 3-D hedgehog structure with an efficiency of 5.37% was achieved with supporting solvents and binders of Triton X-100, alpha teriphenol used for the paste preparation [30]. It also needs a modified microwave oven. With these results being taken into account it appears that further effort is warranted in this area to optimize the processing in an unmodified microwave oven as described here to improve the cell efficiency.

Conclusions

In summary, a novel and rapid microwave-driven method is adopted for the synthesis of TiO₂ nanopowder. Glycerol was used as the medium with titanium tetraisopropoxide as the precursor for the formation of titanium glycerolate complex. After calcination titanium glycerolate was transformed to TiO₂ nanopowder. The morphology of the synthesized titanium glycerolate and TiO₂ nanopowders as a function of domestic microwave power irradiation was characterized using FE-SEM. The results found that 480W irradiation power creates more one dimensional growth than the powers for the synthesis and it maintains same morphology after annealing. A rod like morphology was formed due to the stacking of the self-assembled sphere shaped nanoparticles in a particular direction. Pure anatase phase of TiO₂ is witnessed in 480W and anatase with secondary rutile phases are identified in the other samples. Working electrodes are screen printed from binder free glycerol based paste and the novel mTiO₂ materials were successfully used in photovoltaic devices.

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Fig.1 XRD patterns for as-synthesized titanium glycerolate powder having been processed at various microwave powers.

MICROWAVE POWERS	Relative Intensity Ratio				
	I_1/I_2	I_1/I_3	I_1/I_4	I_1/I_5	I_1/I_6
480W	1.211	1.823	2.732	3.190	5.767
720W	1.193	3.691	4.106	7.319	11.571
960W	1.083	2.667	7.319	5.872	7.016

Table 1. Relative intensity ratio for titanium glycerolate XRD

Fig. 2 XRD patterns of TiO₂ powder samples synthesized by microwave power of 240W, 480W, 720W, and 960W.

Fig. 3 FESEM image of titanium glycerolate powder samples synthesized by the microwave power at (a) 240W, (b) 480W, (c) 720W, and (d) 960W.

Fig. 4. Morphology evolution summary as a function of power for titanium glycerolate.

Fig.
5 FESEM image of TiO₂ powder samples synthesized by the microwave power at (a) 240W, (b) 480W, (c) 720W, and (d) 960W.

Fig. 6 Raman spectra of TiO₂ powder samples synthesized by different microwave powers at 240W, 480W, 720W, and 960W

Fig 7. Schematic of DSSC.

Fig. 8 J-V curves as a function of microwave power irradiation density performed using simulated sunlight

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