

NANOSTRUCTURED TITANIUM DIOXIDE FILM PREPARATION USING INORGANIC NANOPARTICLES INSTEAD OF ORGANIC PRECURSOR MATERIALS

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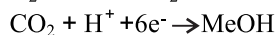
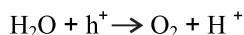
Abstract

Carbon dioxide is a major contributor to global warming. A promising method of reducing the concentration of atmospheric carbon dioxide is by photocatalytic conversion of carbon dioxide into renewable fuels, which has to be done using a photocatalytic film. The nanostructured film preparation method proposed in this study is a preparation of colloidal solution followed by film deposition using manual coating methods, mostly vertical dip-coating. Deposited films were calcined to form a crystalline film on the glass substrate. This method was adopted in case of film preparation from titanium dioxide. Comprehensive study on impact of different factors including temperature, type of surfactants, type of solvents, concentration of surfactants, and concentration of solvents on quality of thin film including band gap, particle size, strength and homogeneity was performed in this work. Material characterisation tests including UV-visible spectroscopy and field emission scanning electron microscopy were carried out to analyse the film characteristics. Mechanical tests including wipe test, rinse test, acetone test, scratch test and scotch tape test were performed to analyse the mechanical strength of obtained thin film. Nanostructured films were successfully prepared with controlled particle size in the range of 70 – 100 nm for TiO₂. Films obtained in this study demonstrate acceptable durability and partial uniformity. The film preparation method used in this study was markedly economical, facile and reproducible.

Keywords: Titanium dioxide, nanostructured film preparation, photocatalytic film

1. Introduction

Nanostructured thin films of titanium dioxide have many important applications including photocatalytic reduction of carbon dioxide into renewable fuels. Carbon dioxide is a major contributor to global warming. Main solution to tackle the problem of global warming is through reduction of atmospheric CO₂ level. Photocatalytic reduction of carbon dioxide to renewable fuels is one method to reduce in atmospheric carbon dioxide concentration. Although in most of the previous researches, particles have been mainly utilized as photocatalysts, applying photoelectrodes or photonanostructured films may improve the efficiency of photocatalytic reduction of carbon dioxide. Titanium dioxide is one of the most favorable photocatalysts which has been utilized in different area of researches because of its properties including low cost, environmental compatibility, efficiency, simple producibility and usability. Titanium dioxide is a semiconductor with a large band gap (E_g) of 3.2 eV in anatase form and band gap of 3 eV in rutile structure which can be stated as the energy required for electrons to be flowed through a material [1]. The fact that anatase structure represents better capability in photocatalytic activities may be due to less chance of electron-hole recombination, in other words photocatalytic activities increase with calcinations since calcinations can transfer the rutile crystal structure form into anatase. Titanium dioxide has been suggested as a semiconductor with photocatalytic properties in CO₂ reduction process. Koci I et al. have utilized suspended TiO₂ in NaOH water solution to reduce carbon dioxide [2]. The photocatalytic property of titanium dioxide is because of its crystal structure, surface area and porosity. Pore and distribution of titanium dioxide are also important for light to be absorbed by TiO₂ and they play an effective role in increasing the accessibility of reactant to the active catalyst sites [3]. As mentioned above, majority of the previous researches have focused on nanoparticles as photocatalysts in application of CO₂ reduction, having said that, recombination of electron-hole is the key barrier in photocatalytic application which cannot be reduced by particles [4]. Replacing nanoparticles with photoelectrode or photonanostructured film has significant benefits. Firstly, since oxidation reaction and reduction reaction occur separately in photonanostructured, electron-hole recombination is lowered which causes an increase in efficiency of CO₂ conversion. Furthermore, organic substances and oxygen will be disconnected applying nanostructured film which avoids the back reaction and producing carbon dioxide and water. Reduction and oxidation reactions are as follow:



The aim of this paper is to introduce an experimental method to prepare nanostructured titanium dioxide film from inorganic commercial nanoparticles of TiO_2 as initial substances, rather than organic precursor materials which are utilized in conventional method of thin film preparation.

2. Experimental

2.1. Materials

Titanium dioxide anatase in a size of 10 nm was supplied by Imperial College London. TWEEN® 80 Polyethylene glycol sorbitan monooleate* from SIGMA-ALDRICH, (FP 113C BP 100), 4-Dodecylbenzenesulfonic acid with 90% purity (mixture of isomers) from Fluka and Triethanolamine with minimum 95% purity from VWR were used as surfactants. Tert-butanol with minimum 99% purity from Merck and distilled water were applied as solvents. Sodium hydroxide white pellets with minimum 98% purity from Fisher Scientific were utilized for treatment of the glass.

Various experiments were carried out to study the effect of surfactant type including polyethylene glycol, triethanolamine and 4- dodecylbenzenesulfonic acid, solvent type including deionised water and butanol, surfactant concentration from 10 to 95%, solvent concentration from 5 to 90% on the quality of thin film. Quality of nanostructured films can be judged by various parameters such as photocatalytic properties, homogeneity, thickness, particle size, mechanical strength and reproducibility.

The following parameters have been analyzed in the paper to estimate the quality of the film.

- Mechanical strength
- Reproducibility
- Homogeneity
- Particle size

Therefore, when the film is said to be of good quality it refers to, that the film has got more mechanical strength, is more homogeneous, has a close band gap to desired one and smaller particle size.

2.2. Preparation of TiO_2 films

Nineteen different colloids were prepared in this study. The difference between colloids was in either type of surfactant or solvent or concentration of surfactant or solvent. In order to examine the effect of surfactant types on obtained thin films, different samples were prepared as follows. In all forms of experiments carried out, certain amounts of TiO_2 as can be seen in table 1, have been measured using the digital lab scale. In the next stage, distilled water and specific surfactants with the volumes mentioned in table 1, were added to the glass beaker containing the previously measured TiO_2 . Examining the effect of surfactant types, in each sample, the type of used surfactants has differed. The prepared solution was stirred and heated to 60 °C for 4 hours by a magnetic stirrer with an approximate speed of 1000 rpm. The obtained colloid was milky in color except colloid SUT1 (Surfactant type on Titania film) in which the obtained colloid was brownish but clear and without precipitate. Manual vertical dip coating was carried out for film to be formed over the glass substrate. In the description of manual dip coating, the glass substrate was held by curved forceps and was immersed into glass beaker containing colloid. After dipping process, the glass was left to dry in ambient conditions for 1 hour and after that it was calcined at 500 °C for another hour.

In table 1, prepared colloids were labeled from SUT1 to SUT7 which means seven colloid were prepared to study the effect of surfactant type on titania film.



Table 1. Change in type of surfactants.

| Colloid | Ingredients |
|-------------------|---|
| SUT1 | 0.45 g TiO ₂ , 3 ml deionized water, 60 ml SDBS |
| SUT2 ¹ | 0.15 g TiO ₂ , 1 ml deionized water, 20 ml TEA |
| SUT3 ² | 0.15 g TiO ₂ , 1 ml deionized water, 20 ml PEG |
| SUT4 ³ | 0.15 g TiO ₂ , 1 ml deionized water, 10 ml PEG, 10 ml SDBS |
| SUT5 | 0.15 g TiO ₂ , 1 ml deionized water, 10 ml TEA, 10 ml SDBS |
| SUT6 | 0.15 g TiO ₂ , 1 ml deionized water, 10 ml TEA, 10 ml PEG |
| UT7 | 0.15 g TiO ₂ , 5 ml deionized water, 5 ml TEA, 5 ml PEG, 5 ml SDBS |

The possible proper combination of surfactant was found based on results obtained from previous sets of experiments. New sets of experiments were carried out in order to find the appropriate range of concentration for solvent and surfactant. To do so, in these series of experiments the concentration of solvent and surfactant have been changed in different ratio including 50:50, 90:10, 80:20, 70:30, 60:40 respectively, when the concentration of TiO₂ was kept constant. After colloid preparation by the 4 hours stirring step, the glass substrate was dip coated manually and vertically in a glass beaker. It is noticeable that all of obtained colloids in these series of experiments were milky in color. The thin layer formed over the glass was calcined at 500 °C for an hour. Details regarding experiments performed with the aid of examining the change in concentration for TiO₂ were listed in table 2. The prepared colloids were labeled from CT1 to CT5 which means five different colloids were prepared to study the effect of concentration of solvents and surfactants on titanium dioxide thin film.

The carried out experiments in previous step were repeated in this step with difference of replacing distilled water with butanol as solvents. In other words, different concentration of solvent and surfactants have been studied including 50:50, 51:49, 90:10, 80:20, 70:30, 60:40 respectively for TiO₂. The prepared solutions were stirred and heated to 60 °C for 4 hours. The color of obtained colloids was darker than the ones using distilled water as a solvent. After that, immersing the glass substrate into colloid was carried out vertically. The thin layer over the glass was calcined at 500 °C for an hour using air recirculation chamber furnace. The more details about these sets of experiments can be found in table 3. The obtained colloids were labeled from SOT1 to SOT7 which means seven different colloids were prepared to study the effect of solvent type on titanium dioxide film.

Table 2. Change in concentration of solvent and surfactants.

| Colloid | Ingredients |
|------------------|--|
| CT1 | 0.15 g TiO ₂ , 10 ml deionized water, 10 ml SDBS |
| CT2 | 0.15 g TiO ₂ , 36 ml deionized water, 2 ml PEG, 2 ml SDBS |
| CT3 ⁴ | 0.15 g TiO ₂ , 32 ml deionized water, 4 ml PEG, 4 ml SDBS |
| CT4 | 0.15 g TiO ₂ , 28 ml deionized water, 6 ml PEG, 6 ml SDBS |
| CT5 | 0.15 g TiO ₂ , 24 ml deionized water, 8 ml PEG, 8ml SDBS |

¹ After first calcination vertical dipcoating was applied and after one hour dryness, deposited film was calcined at 500 °C for another one hour. These procedures were repeated 3 times, the last duration of stay in furnace was 2 hours.

² After first calcination vertical dipcoating was applied and after one hour dryness, deposited film was calcined at 500 °C for another one hour. These procedures were repeated 6 times.

³ After first calcination vertical dipcoating was applied and after one hour dryness, deposited film was calcined at 500 °C for another one hour. These procedures were repeated 10 times, the last duration of stay in furnace was 2 hours.

⁴ After first calcination vertical dipcoating was applied and after one hour drying, film was calcined at 500 °C for another one hour. These procedures were repeated 5 times, the last duration of stay in furnace was 2 hours.

Table 3. Change in solvent types in different concentration.

| Colloid | Ingredients |
|---------|---|
| SOT1 | 0.15 g TiO ₂ , 20 ml butanol, 10 ml PEG, 10 ml SDBS |
| SOT2 | 0.15 g TiO ₂ , 18 ml butanol, 1 ml PEG, 1 ml SDBS |
| SOT3 | 0.15 g TiO ₂ , 3 ml deionized water, 60 ml butanol, 60 ml SDBS |
| SOT4 | 0.15 g TiO ₂ , 36 ml butanol, 2 ml PEG, 2 ml SDBS |
| SOT5 | 0.15 g TiO ₂ , 32 ml butanol, 4 ml PEG, 4 ml SDBS |
| SOT6 | 0.15 g TiO ₂ , 28 ml butanol, 6 ml PEG, 6 ml SDBS |
| SOT7 | 0.15 g TiO ₂ , 24 ml butanol, 8 ml PEG, 8 ml SDBS |

3. Results and discussion

Optical properties

In order to find the optical band gap of TiO₂ films, UV-Visible spectra from 250 nm to 800 nm were taken by UV-2550 spectrophotometer. To measure the absorption of nanostructured film, first a clean glass microscope slide (washed with deionized water, acetone) was positioned into UV spectrophotometer and the amounts of absorption from different wavelengths of incident light were recorded by spectrophotometer as a base line. In the next stage, nanostructure film was placed into the device in the form of a film on a microscope slide. The UV spectrometer was set to absorption mode. The absorption of incident light varies with wave-lengths and is presented to the user in logarithmic form.

Obtained films of TiO₂ are well transparent since for wavelengths above 400 nm (in the visible range) the transmittance approaches 82%. Dramatic fall in transmittance or significant increase in absorption can be found around 300 nm which depends on the quality of TiO₂ films. This increase in absorption corresponds to band to band absorption. The band gap was calculated by two different methods:

Extrapolation

First method to calculate the band gap is the extrapolation of the linear region of the absorption versus wavelength curve, which is called absorption edge. This line where the absorption edge equals zero, gives the wavelength. To calculate the band gap corresponding with obtained wavelength, the following procedures is to be implemented:

To find the energy of this stream of photons with certain wavelength:

$$E = hv = h \frac{c}{\lambda} \quad (1)$$

Where h is Planck's constant, v is frequency, c is the speed of light and λ is the wavelength. Substituting the values of Planck's constant and speed of light, we end up with:

$$E = \frac{(4.13566733 \times 10^{-15} \text{ eVs})(299792458 \text{ m/s})}{\lambda} \quad (2)$$

From the equation 2:

$$E(\text{eV}) \approx \frac{1240 \text{ eV nm}}{\lambda (\text{nm})} \quad (3)$$



Substituting the extrapolated wavelength into above equation is an accurate way to calculate the absorption edge, hence the band gap.

This method results in a band gap of 3.22 eV as can be observed in figure 1. The equation of extrapolation of the absorption edge is $y = -0.014x + 5.383$. Therefore, extrapolation line crossed x axis on wavelength of 384.5 nm. Substituting this value on equation 3 gives the band gap of titanium dioxide thin film as follow:

$$E = \frac{1240}{384.5} = 3.22 \text{ eV}$$

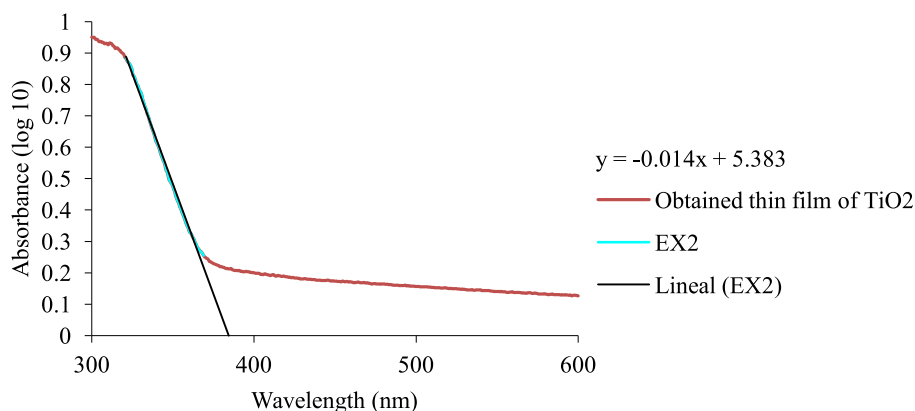


Figure 1 . UV-visible absorption spectrum for thin film of titanium dioxide.

Tauc plot

Use of the Tauc plot to absorption measurements [5,6] is the second method for band gap calculation. In this method, the variation of the absorption coefficient α in the strong absorption range ($\alpha < 10^4 \text{ cm}^{-1}$) is correlated to the energy gap E_g of the material by the following expression:

$$\alpha = B \times \frac{(E - E_g)^m}{E} \tag{4}$$

In equation 4, E presents the photon energy, B indicates a constant and m is 1/2 for an allowed direct transition, 3/2 for a forbidden direct transition and 2 and 3 for an allowed and a forbidden indirect transition respectively. Therefore the value of m for TiO_2 is 2 because TiO_2 is an indirect semiconductor.

Figure 2 shows $(\alpha E)^2$ as a function of the photon energy E for titanium dioxide. The extrapolation of the linear region of the curve was used to obtain band gap. In the extrapolation line where $\alpha = 0$ band gap is calculated which was 3.42 eV.

The tauc plot is the method that normally was used in literature to estimate the band gap and using this calculation method results in an increase in band gap of thin film compared to bulk titania (3.2 eV). Nanocrystalline character of film may change the absorption edge to a shorter wavelength by the result of quantization which is caused an increase in band gap. Mahalingam was reported an indirect band gap of 3.50 eV for film annealed at 500 °C [8]. Average band gap of TiO_2 from the film preparation method used in this study is 3.25 eV. This is very close to the band gap of crystalline titanium dioxide films in anatase phase (3.2 eV) which has been reported by Mahalingam, 2008.

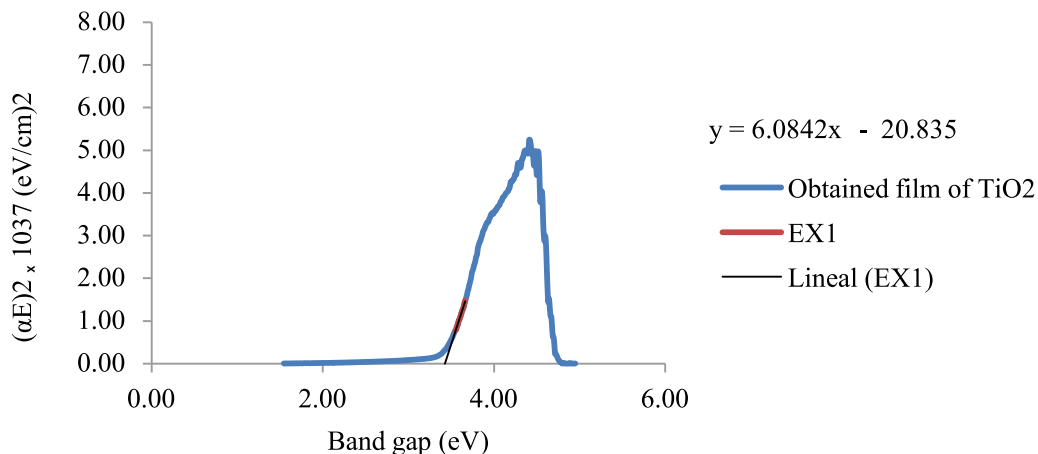


Figure 2. Tauc extrapolation for titanium dioxide thin film

Morphological study of TiO₂ films

Field emission scanning electron microscope (FE-SEM) was utilized to morphological characterization of some obtained films. High resolution images at both low and also high keV range can be obtained by this microscope with the effect of electron gun. The films were coated by a layer of gold using sputtering machine before positioning the specimens in the FE-SEM. Figure 3 shows the FE-SEM images for as-deposited TiO₂ films. Parts a.2, b.2, c.2 and d.2 of the figure 3 are the high magnification images from one region of the parts a.1, b.1, c.1 and d.1 of the figure 3, respectively.

Figure 3 shows two FE-SEM images of colloid CT5 in low and high magnification in part a.1 and part a.2 respectively. This arrangement repeats for films obtained from colloids CT4, CT3 and SOT4 in part b, c and d in that order. FE-SEM analysis revealed that obtained films from colloids CT5, CT4 and CT3 were composed of nanoparticles with narrow particle size of ~ 70 to 100 nm (Figure 3 (a.2, b.2, c.2)). Nanoparticles were aggregated non-uniformly to form clusters in colloids CT5 and CT3 while nearly uniform distribution of cluster can be seen in colloid CT4. The more uniform distribution of clusters was observed in film obtained from colloid SOT4; where the nanoparticles of 10 nm size were agglomerated and make the clusters to form of about 500 nm size. It is beneficial to note that part a and c of Figure 3 exhibit non-spherical particles with the same shape, which is undoubtedly anisometric. It can be drawn from micrograph scans that initial close-to-spherical particles were glued and aggregated together in grape-like and formed non-uniform structure. This may be because of inappropriate surfactant used and/or inappropriate concentration of ingredients used (nanoparticle, solvent and surfactant) that might reduce the stability of colloidal solution. This non-uniform morphology has not observed in film obtained from colloids CT4 and SOT4. The reason might be laid in steady progress in dispersion of nanoparticles. It is possible that non-dispersed nanoparticles which act as glue in the case of films obtained from colloids CT5 and CT3 were consumed and dispersed in films from colloids SOT4 and CT4. This led to the increase in size of the primary particles, jointed with deaggregation process. In part a.6 of Figure 4, high magnification FE-SEM images of film obtained from colloid SOT1 can be observed. Particles start to become glued and grow to create nanoclusters.



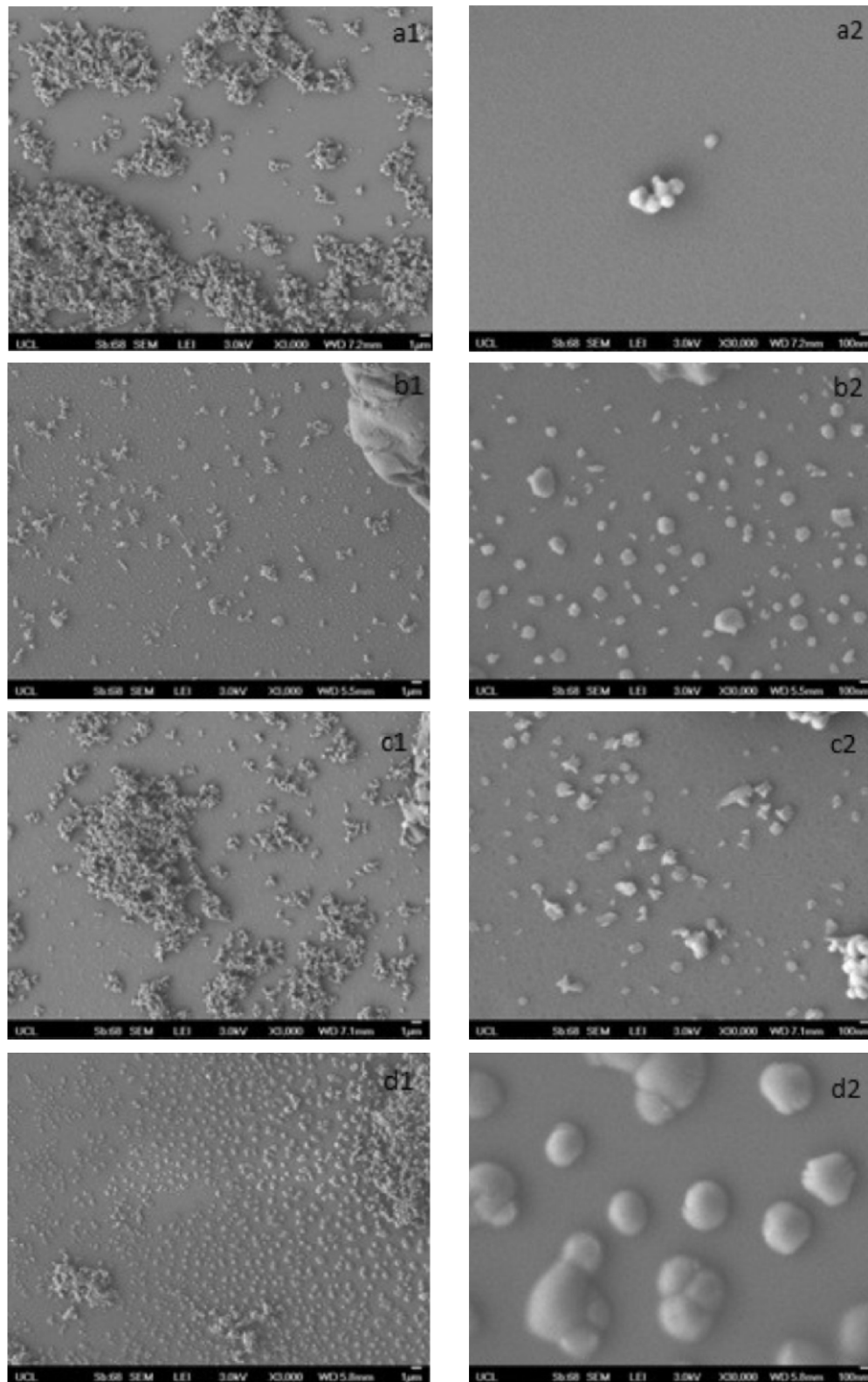


Figure 3. FE-SEM micrographs of titanium dioxide films obtained from different colloids: (a.1, a.2) colloid CT5; (b.1, b.2) colloid CT4; (c.1, c.2) colloid CT3; (d.1, d.2) colloid SOT4.

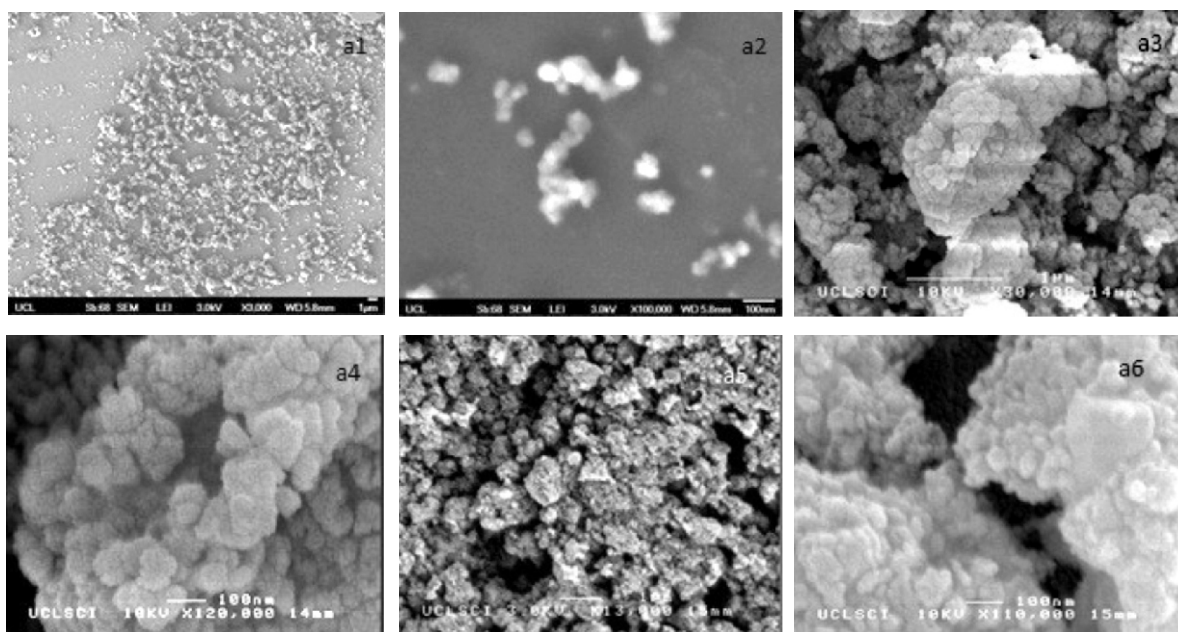


Figure 4. FE-SEM micrographs of obtained titanium dioxide thin film from colloids SUT3 and SOT1: (a.1, a.2) colloid SUT3 using annealed glass as substrate; (a.3, a.4) colloid SUT3 gradual heated from 25 to 500 °C and calcinated at 500 °C for one hour; (a.5) repeating colloid SUT3 using annealed glass as substrate; (a.6) sample SOT1.

Reducing the concentration of surfactant and increasing the concentration of solvent, decreased the viscosity of colloid. As a result the obtained deposited films were thinner. Hence the potential of flaking off in the furnace decreased. Colloids CT3 was obtained from 80:20 ratio of water to surfactant when SDBS and PEG were used as the surfactant (4 ml PEG and 4 ml SDBS). This film was more uniform than other obtained films. When water was replaced with butanol, the proper concentration differed by a 90:10 ratio of butanol to surfactants (2 ml PEG and 2 ml SDBS). possible reason of non-uniformity in most of the obtained films may be the manual dip-coating procedure. There is a margin for human error as the individual decides upon the rate of dip-coating and also the angle of dip-coating, resulting in a lack of consistency on each repeat of the method. It is obvious that if the dip-coating was applied fast the deposited layer is thin in contrast to if the dip-coating was performed slowly, which results in a thick deposited layer. Furthermore, change in the rate of dip-coating can caused deposited film to be thin in one region and thick in another.

Hence the thicker part flaked off in the furnace while the thinner part formed a thin uniform layer over the glass. Non-uniform drying occurred under atmospheric temperature before the calcination process confirmed a change in the dip-coating procedure, since keeping deposited film to be dried partially in ambient conditions proved that glass was dried non-uniformly; thus part of the thin layer was dried but the other part was not dried. The dried part might be thinner as a result of being dried faster. Manual dip-coating has another disadvantage that might cause film to be non-uniform.

Another possible reason could be the calcination process itself. Since the number of experiments conducted were considerable, it was impossible to reduce the temperature of furnace and adjust it to room temperature after reaching 500 °C given time constraints. To do so would have been too time consuming and also the furnace after continuous changes produced errors in temperature and did not always exhibit the real temperature that was inside the furnace. Hence, the majority of samples were directly calcined at 500 °C. Having said that, some non-uniformity were observed in samples which gradually were heated proving that other factors were also present including relatively high heating rate or variable dip-coating speed. Another possible reason behind a non uniform film could have been the low strength of the glass substrate to grow the crystals. As a result because of the low strength of the binding force between the glass substrate and the film the generated thin film after thermal stress was flaked off. To improve the binding force, substrate can be changed and replace with other substrates. Possible substrates which maybe tried include optical fiber and also optically transparent electrodes which have already demonstrated good results even without using any surfactant to disperse the nanoparticles in the solvents [9].



4. Conclusion

Every method of film preparation has its own strengths and weaknesses. Since complicated reactor and/or vacuum system required for chemical vapor deposition method and physical vapor deposition method, these two methods markedly expensive. Unwanted cracks formation, use of precursor and additives, superior hydrolysis and time consuming process are the disadvantages of sol-gel method.

To avoid the disadvantages of other methods, this study focused on exploring a cost-effective method to prepare the photocatalyst nanostructured film. This method involved colloid preparation followed by coating procedure. Comprehensive study on the effects of various parameters including surfactant type, solvent type, surfactant concentration, solvent concentration and annealing temperature was performed. Three different surfactants which were revealed by previous study and showed effective results for dispersion of nano titania powder [7] were utilized in this work including polyethylene glycol (PEG), triethanolamine (TEA) and 4-dodecylbenzenesulfonic acid (SDBS) to disperse nanoparticle TiO_2 in liquid media. All of used surfactants showed very good results in colloid SUT1 in which SDBS was used and also colloid SUT7 in which all three surfactants were used. Both colloid SUT1 and SUT7 were well dispersed and the obtained films from these colloids were well transparent and thin. Also, all of the prepared colloids for zinc oxide films were perfectly dispersed Colloid SUT3 in which PEG was used and also colloid SUT4 in which PEG and SDBS were used showed a smooth and durable thin film although they were not entirely uniform.

Defect in uniformity might be caused by sudden increase in temperature during calcinations process. It was proved by series of experiments in which the calcinations process for different samples of colloid SUT3 were changed. Results showed that gradual increase in temperature improves the quality of film since organic substances are able to evaporate gradually in this condition. Another conclusion can be drawn from this study is that quality of film was enhanced by annealing the substrate which improved coating adhesion, may be due to provide smoother surface. Pre-treatment of glass with acetone and annealing it at 500 °C for 30 min before applying dip coating procedures were effective on control of particle size. Among the series of experiments which were carried out to examine the effect of change in surfactant concentration in the case of using deionized water as solvent, use of 80% deionized water and 20% surfactants including PEG (10%) and SDBS (10%) presented appropriate results (sample CT3) while these concentration changed to 90% butanol and 10% surfactants including PEG (5%) and SDBS (5%) in the case of using butanol as solvent (sample SOT4). Samples obtained in this study were characterized by different methods. UV-visible spectrum showed that obtained films of TiO_2 demonstrated a band gap of 3.22 eV (obtained from extrapolation method).

Obtained band gap values for TiO_2 are well agreed to the reported values in previous studies. The range of particle size of specimens was obtained by field emission scanning microscope. Individual TiO_2 particle was ~ 70 to 100 nm. It can be concluded that change in surfactant type and also change in calcination method affect the particle size which might be due to change in crystalline structure. At the magnification shown, these films appear quite dense and free of large porosities. Further conclusion is that thinner coating provides significantly improved abrasion resistance. Samples obtained from colloid SUT1 and colloid CT3 were proof of this conclusion. Although obtained results are valuable and to well-extent durable there is still further work to be performed to improve the uniformity of films.

5. References

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