CHAPTER 7

SUMMARY

The modified TiO$_2$ and ZnO coatings exhibited higher photocatalytic activity. The following summarizes the results of work carried out.

**P-block elements (C, N and F) doped TiO$_2$ coatings**

P-block elements (C, N and F) doped TiO$_2$ coatings were developed by MAO technique for visible light photocatalytic applications. MAO produced porous coatings increased the surface reactive area which enhanced the photocatalytic activity. Surface roughness increases in the order of pure TiO$_2$ < F-TiO$_2$ < N-TiO$_2$ < C-TiO$_2$. The obtained band gap energies were 3.03, 3.04 and 3.02 eV for C-TiO$_2$, N-TiO$_2$ and F-TiO$_2$ coatings respectively, whereas for pure TiO$_2$ coating was exhibited 3.15 eV. The reduced band gap energy and appropriate percentage of anatase and rutile phase structure of doped TiO$_2$ samples resulted in higher photocatalytic activity under visible light. The photo-generated electron-hole pair’s recombination rate was effectively inhibited by doping of C, N and F into TiO$_2$ which attributes enhanced photocatalytic efficiency. Doped TiO$_2$ showed enhanced photocatalytic activity with MB dye compared to pure TiO$_2$. Particularly, F-TiO$_2$ revealed maximum photocatalytic activity among all other doped TiO$_2$. 


Nitrogen doped porous TiO$_2$ coatings

N-TiO$_2$ porous coating was developed by combined technique of plasma nitriding and MAO on Cp titanium. Doping nitrogen into TiO$_2$ facilitates to increase the surface reactive area of N-TiO$_2$ and extend the visible light responsiveness as evidenced from surface optical profilometer amplitude parameters and DRS UV-Visible absorbance spectra respectively. XRD analysis showed the additional phase TiN$_{0.30}$ existed in N-TiO$_2$ along with anatase and rutile phases. In addition, N-TiO$_2$ consists of the appropriate amount of anatase and rutile phases which could increase the separation of photo-generated charge carriers. UV-Visible absorption study showed that the band gap energy is reduced as 2.93 eV compared to pure TiO$_2$. Photoluminescence study explains that the recombination rate of photo-generated charge carriers of TiO$_2$ is suppressed with nitrogen doping. The N-TiO$_2$ coating exhibited higher solar photocatalytic activity compared to pure TiO$_2$ coating. The methylene blue dye degradation follows pseudo first order kinetics and the calculated apparent reaction rate constants of N-TiO$_2$ and TiO$_2$ coatings are 0.0202 min$^{-1}$ and 0.0087 min$^{-1}$ respectively. The recyclability of N-TiO$_2$ coating was conducted and the result shows good repeatability.

TiO$_2$ coated nano-porous silicon

TiO$_2$ coated porous silicon was prepared by the combined technique of stain etching and ALD for efficient solar photocatalytic activity. DRS UV-Vis absorbance spectrum of TiO$_2$/PS$_3$ solar absorber shows that it has the ability to absorb the complete wave length range (300-800 nm) of solar light. TiO$_2$ coated porous silicon exhibited higher solar photocatalytic activity compared to TiO$_2$ coated on glass. This remarkably enhanced photocatalytic activity is attributed to the visible light absorption of TiO$_2$/PS. Moreover, the layer by layer solar absorption mechanism explains that the
electrons created in porous silicon by visible light will be injected into TiO$_2$ via hetero junction interface which leads to efficient charge separation even though porous silicon is not participating in any redox reactions in direct. In addition, the degree of photocatalytic activity of TiO$_2$/PS depends on the etching time of the silicon. Higher the etching time, higher visible light absorption and photocatalytic activity and vice versa.

**ZnO coated nano-porous silicon**

ZnO coated nanoporous silicon was prepared by combined technique of stain etching and ALD. The surface roughness of the nanoporous silicon increases continuously with etching time of silicon, which could be a consequence of increased active surface area. ZnO coated nanoporous silicon exhibited very strong visible light absorbance around 526 nm. The photocatalytic and photoelectrocatalytic activity of ZnO/PS is investigated by degrading aqueous MB dye solution. The result shows that ZnO/PS exhibited higher photocatalytic activity compared to ordinary ZnO coating. The enhanced photocatalytic activity is attributed to visible light absorption of ZnO/PS. Even though porous silicon is not participating any redox reactions, it injects the photogenerated electrons effectively into the ZnO layer which enhances the photocatalytic activity. It is identified that both negative and positive biased ZnO/PS exhibited higher photocatalytic activity compared to unbiased ZnO/PS. Particularly, negative biased ZnO/PS shows higher photocatalytic activity compared to unbiased and positive biased ZnO/PS. In addition, the recyclability of ZnO/PS study shows that the variation in photocatalytic efficiency is negligible after 5$^{th}$ run.
7.1 FUTURE WORK

- To develop semiconductor coupled TiO$_2$ coatings one over another in the form of layer by ALD using various low band gap semiconductors such as WO$_3$, CdS and etc. for efficient solar photocatalytic activity.

- To characterize the semiconductor coupled TiO$_2$ coatings by FESEM, XRD, FTIR, XPS, PL and DRS UV-Vis absorbance spectrometer.

- To optimize the low band gap semiconductor and TiO$_2$ coating thickness, crystal phase and particle size by controlling ALD processing parameters such as deposition cycle, temperature and etc.

- To investigate photocatalytic activities of ALD coatings with a model pollutant under the solar light illumination.