

# CHAPTER V

## CONCLUSIONS

### 5. Conclusions

#### 5.1 Formation of self-Organized TiO<sub>2</sub> nanotube arrays by Anodization

Optimum condition of the self-organized formation of TiO<sub>2</sub> nanotube arrays by pulse anodization was found in NH<sub>4</sub>F/glycerol electrolyte (0.36 M) containing 10% water for 3 h with 20 V/-4 V pulse anodization using a pulse duration  $t_0=2$  s at the lower voltage limit. The SEM morphology of the TiO<sub>2</sub> nanotubes indicates that nanotubes are formed in better self-organized arrays under pulse anodization than other nanotubes grown at constant anodization voltage. The photocurrent densities for the nanotubes of TiO<sub>2</sub> films are significantly higher (up to 45%) than other nanotubes grown at constant anodization voltage.

#### 5.2 Metal-modified TiO<sub>2</sub> nanotubes

The successful electrode of the metal-modified TiO<sub>2</sub> nanotube developed by the doping of Li, Ni, Mn, V and Nb into TiO<sub>2</sub>. The doping changed the morphology of the TiO<sub>2</sub> nanotube. The well-define in the nanotube and the formation of characteristic surface structure brought the excellent photoelectrochemical performance. These doping photocatalysts that show significantly enhanced (up to 90%) corresponding to the photospectra extend to visible region from IPCE<sub>max</sub> at 325 nm to 345 nm.

#### 5.3 Dye sensitized TiO<sub>2</sub> nanotube arrays for DSSC application

The self-organized TiO<sub>2</sub> nanotubes can be sensitized with a suitable charge transfer dye to significantly increase the quantitative conversion efficiency of visible light photons into electric current. Photoelectrochemical investigations were carried out with anodic TiO<sub>2</sub> nanotube grown in 0.36 M NH<sub>4</sub>F/ethylene glycol. Clearly sub-band gap sensitization with Zn(II)-5,10,15,20-Tetra (3-carboxyphenyl) porphyrin (acid 4) was successful and led to considerable conversion efficiencies (IPCE up to 52%).

## 5.4 Photocatalysis application for TiO<sub>2</sub> film preparation by anodization

### 5.4.1 Photocatalytic properties of TiO<sub>2</sub> nanostructures using electrolyte composition prepared by anodization technique

The photoreduction kinetics of hexavalent chromium, Cr(VI) (initial concentration of 200  $\mu\text{M}$ ) follows pseudo first-order was observed. The apparent rate constant ( $k_{obs}$ ) value of photoreduction activity of the TiO<sub>2</sub> nanostructure film are as follow; nanotube =  $7.33 \times 10^{-3}$ , nanoporous =  $6.44 \times 10^{-3}$  and non-organized =  $4.03 \times 10^{-3}$   $\text{min}^{-1}$ . The kinetic parameters were strongly depending on the morphology. TiO<sub>2</sub> nanotubes have larger specific surface area than TiO<sub>2</sub> film and could adsorb more substrate matters and more effective separation for the photogenerated electron-hole pairs. Consequently the greater the activity of photocatalyst is, the greater the quantum yield, the photocatalytic activities increase in the order of non-organized form < nanoporous < nanotube.

### 5.4.2 Photocatalysis properties of metal doped TiO<sub>2</sub> nanotube prepared by pulse Anodization

Photocatalytic activity of hexavalent chromium (VI) reduction is varied by types of metal dopant. Each metal dopant provides different film characteristics. The Influence of film characteristic on photocatalytic reduction of Cr(VI) are the small band gap requires less photon energy to promote the excitation of electron from valence band to the conduction band. The second property for photocatalysis efficiency consideration is electronegativity of the doped metal. High electronegativity value leads to high amount of trapped electron and/or hole on the catalyst surface. The best apparent rate constant ( $k_{obs}$ ) value of Cr(VI) up to  $2.37 \times 10^{-2}$   $\text{min}^{-1}$  obtain by film were prepared in 0.36 M NH<sub>4</sub>F with MnF<sub>3</sub> and used ethylene glycol as dopant. Because Mn<sup>3+</sup> owing to smallest band gap (2.85), high electronegativity (1.55) and small diameter of nanotube (66 $\pm$ 2 nm).

## 5.5 Suggestions for future work

The application of photocatalysis has been demonstrated in laboratory scale experiments with synthetic single compound solution which lack of multicomponents studies. The investigation of the obtained film using multi-pollutants should be investigated further. In real environment application, more complicated water with

multiple pollutant contaminants are routinely expected from waste stream, such as contaminated groundwater and industrial wastewater. It is essential that the experiment of this technology at larger scale is need to be compared with other relevant methods on the basis of system performance and cost-effectiveness. The next stage in the development of this technology is an economic feasibility and any such techno-commercial evaluation requires a better understanding of the factors which control electrode efficiency. Due to the high demand of oxidants and energy, the optimization of the condition of a process is essential for economical feasibility. Both studies with synthetic wastewater, where the parameters can controlled and feasibility studies with real water and wastewater have to be conducted before the new promising techniques can be applied successfully.