

Articles

Morphology Effect on Electrocatalytic Activity of TiO₂ Spheres Synthesized by Binary Ionic Liquids in Water ElectrolysisKiwon Hong, Daewon Pak,[†] and Kye Sang Yoo^{*}*Department of Chemical Engineering, Seoul National University of Science & Technology, Seoul 139-743, Korea***E-mail: kyoo@seoultech.ac.kr**[†]Graduate School of Energy and Environment, Seoul National University of Science & Technology, Seoul 139-743, Korea**Received December 9, 2011, Accepted January 18, 2012*

Titania spheres were synthesized using binary ionic liquids to examine the electrocatalytic activity in acid solution. The morphology of TiO₂ particles was significantly different with the composition of ionic liquids. Among the binary ionic liquids, four set of mixtures led to the formation of TiO₂ sphere with various sizes. The morphology and structure of TiO₂ particles were characterized by XRD, N₂ physisorption and SEM analysis. All samples possessed an anatase phase after calcinations at 500 °C. The structural properties of the samples were varied significantly with the morphology. In cyclic voltammograms, the morphology of TiO₂ spheres affected the electrocatalytic activity in water electrolysis. Among the samples, [Omim][BF₄]+[Hmim][BF₄] was the most effective ionic liquid to synthesize TiO₂ sphere with optimum morphology showing the highest electrocatalytic performance.

Key Words : TiO₂ sphere, Ionic liquid, Electrocatalyst

Introduction

Due to the global climate changes and energy crisis by consumption of conventional fossil fuel, many countries have given an effort on the development of new clean fuel.¹ Hydrogen energy is a potential primary source of fuel for automobiles, as well as a potential source of energy for heating buildings and generating electricity. One of the most important processes for hydrogen generation without CO₂ emission is water electrolysis. Moreover, it could convert electrical energy to chemical energy as hydrogen and oxygen production, which can be converted back to electric energy when needed.² However, the main drawback of this process is high energy consumption by the high production and investment cost. Some approaches of the preparation of less expensive electrocatalysts have been considered to overcome those problems; minimizing Pt loading, combining transition metal with Pt to enhance catalytic activity,^{3,4} using mixtures of oxides to improve electrode stability and reducing overpotential.

Titanium dioxide (TiO₂ titania) has received considerable attention due to its numerous applications in, for example, photocatalysis and catalyst support.⁵ Moreover, it shows good stability in acidic solution, and TiO₂ electrode has been used as the support of Pt⁶ or Pt-Ru.⁷ Thus, platinumized titanium anodes have possessed desirable properties in electrochemical technology. Recently, TiO₂ hollow spheres have received significant attention because of their excellent properties as a catalyst and wide range of applications.⁸

Synthesis of TiO₂ hollow spheres with tunable shell thickness, surface area, and void volume is an effective way to develop electrocatalysts with high activities. A numerous methods have been explored to synthesize TiO₂ hollow spheres, and the polystyrene (PS) latex template synthesis is a common technique. Recently, alternative way to the synthesis of TiO₂ hollow spheres involving the direct synthesis of intact titania shells around a soft template, surfactant stabilized non-aqueous emulsion droplets, has been reported.⁹

In last decade, various metal oxides with sphere shape were synthesized using ionic liquid as a new approach. Ionic liquids are a unique type of solvent consisting practically only of ions. They have almost no vapor pressure and possess tunable solvent properties.^{10,11} Nakashima and Kimizuka synthesized hollow TiO₂ microspheres with [C₄mim][PF₆]¹² and Zhou and Antonietti prepared mesoporous TiO₂ spherical aggregates using [C₄mim][BF₄].¹³ After then, ZnO particles with various spherical nanostructures were synthesized with various ionic liquids with [BF₄]⁻ as an anion part.^{14,15} Zheng's group prepared hollow silica spheres using mixture of [C₄mim][BF₄] and surfactant.¹⁶ Dong's group synthesized SnO₂ microspheres with [C₄mim][BF₄] through a rapid hydrothermal process heating by microwave.¹⁷ In our previous work, we have found possibility to synthesize TiO₂ hollow sphere with anatase phase using binary ionic liquid mixture.¹⁸ Among the various ionic liquids, [BF₄]⁻ component was crucial to form TiO₂ particle with spherical shape. In this study, various binary ionic liquid mixtures were used to prepare TiO₂ spheres. The properties of binary ionic

liquid mixtures gave a synergetic effect on the formation of the sphere. Here TiO₂ spheres with various sizes were successfully synthesized using binary ionic liquid mixtures. The prepared samples have been characterized to identify their properties. Moreover, the samples were examined by cyclic voltammetry under identical conditions to investigate the effect of morphology on electrocatalytic performance.

Experimental Section

For the synthesis, titanium isopropoxide (98%), toluene (99.5%) and methanol (99.5%) were supplied by Daejung Chemical & Metal (Korea). The ionic liquids were purchased from Sigma-Aldrich and C-Try as illustrated in Table 1. The purity of all ionic liquids is over 97% and all chemicals used as purchased without any purification. Initially, 3.6 mL of binary ionic liquid mixture with sample mole ratios and 0.4 mL of anhydrous toluene solution containing 0.2 M titanium tetraisopropoxide were mixed under vigorous stirring for 10 mins. After then, 6 mL of methanol was added, and the diluted mixture was centrifuged at 1000 rpm for 10 min. After filtration, the TiO₂ samples obtained was dried and calcined at 500 °C in furnace.

The powder XRD patterns of the catalysts were recorded using a X-ray diffractometer (Shimadzu XRD-6000) operated at 40 kV and 30 mA using Cu KR ($\lambda = 0.15418$ nm) radiation to determine the crystal structure. The surface area of sample was measured using N₂ sorption method with a BELSORP-MINI II instrument (BEL Co.). The sample images were confirmed using scanning electron microscopy (SEM, JEOL, JSM-6700F).

The catalyst ink was prepared by mixing the catalyst powder, Nafion solution (Dupont, 5% solution, equivalent to 110 g/mol) and solvent (mixture of water and isopropyl alcohol) under sonication for 20 min. The catalyst ink was cast onto waterproof carbon cloth (1 cm × 1 cm) and dried at 70 °C in air to remove solvent (water and alcohol). The casting process was followed repeatedly to load approximately 2 mg of catalyst onto the carbon cloth. Cyclic voltammetric

measurement was carried out in a three-electrode cell with Potentiostat/Galvanostat (Princeton Applied Research, Parastat 2273). Ag/AgCl electrode and Pt plate (1 cm × 1 cm) were used as reference and counter electrodes, respectively. A H₂SO₄ solution of 0.01 N concentration was used as electrolyte in the experiment. The cyclic voltammetry data were recorded in the potential range of 0 to 2 V vs. Ag/AgCl electrode with a scan rate of 100 mV s⁻¹. The anodic polarization curves were recorded with a potential scan rate of 0.5 mV s⁻¹.

Results and Discussion

In our previous work,¹⁸ TiO₂ particle with various shapes was synthesized by binary ionic liquid mixtures. In the method, the particles were formed with spherical, hexagonal pyramid and amorphous, respectively. The results were mainly attributed to the properties of the ionic liquids. Especially, ionic liquid with [BF₄]⁻ as an anion part was relatively effective to form anatase TiO₂ particle with regular shape. However, Ionic liquid with [CF₃SO₃]⁻ component gave negative effect. Moreover, ionic liquids with shorter alkyl chain than buthyl- were inadequate in the synthesis as well. Hence, TiO₂ particles were prepared with 15 different binary ionic liquids using 6 ionic liquids as listed in Table 1. Among the 15 samples, 4 samples with anatase phase, high crystallinity and sphere morphology were selected for further investigation in this study. The particle "pure" was used as the control sample for comparison with other particles. It was prepared with the sample method described above, except ionic liquid addition. The phase and purity of the samples were determined by XRD, and the diffraction patterns are shown in Figure 1. All the peaks in the pattern are assigned to anatase TiO₂ phase, Miller indices of (101), (004), (200), (105) and (211), without any indication of impurities. Moreover, the crystallinity of all samples was

Table 1. List of ionic liquids used in this study

Symbol	Full name	Vender
BBF4	1-Butyl-3-methylimidazolium tetrafluoroborate	Sigma-Aldrich
HBF4	1-Hexyl-3-methylimidazolium tetrafluoroborate	C-Try
OBF4	1-Octyl-3-methylimidazolium tetrafluoroborate	C-Try
BPF6	1-Butyl-3-methylimidazolium hexafluorophosphate	Sigma-Aldrich
HPF6	1-Hexyl-3-methylimidazolium hexafluorophosphate	Sigma-Aldrich
OPF6	1-Octyl-3-methylimidazolium hexafluorophosphate	C-Try

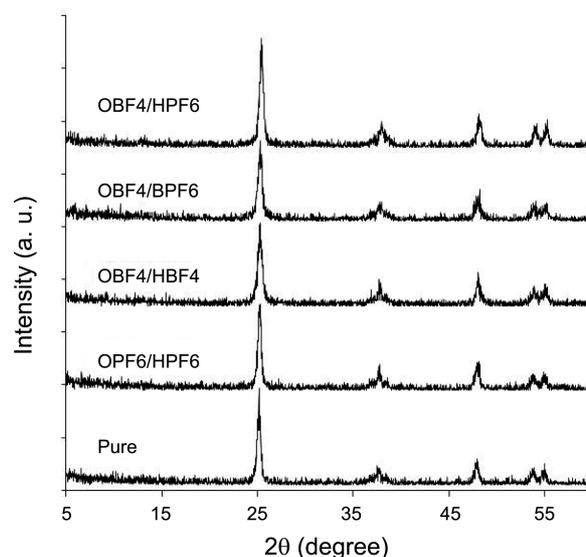


Figure 1. XRD patterns of TiO₂ particles prepared by various ionic liquids after calcinations at 500 °C.

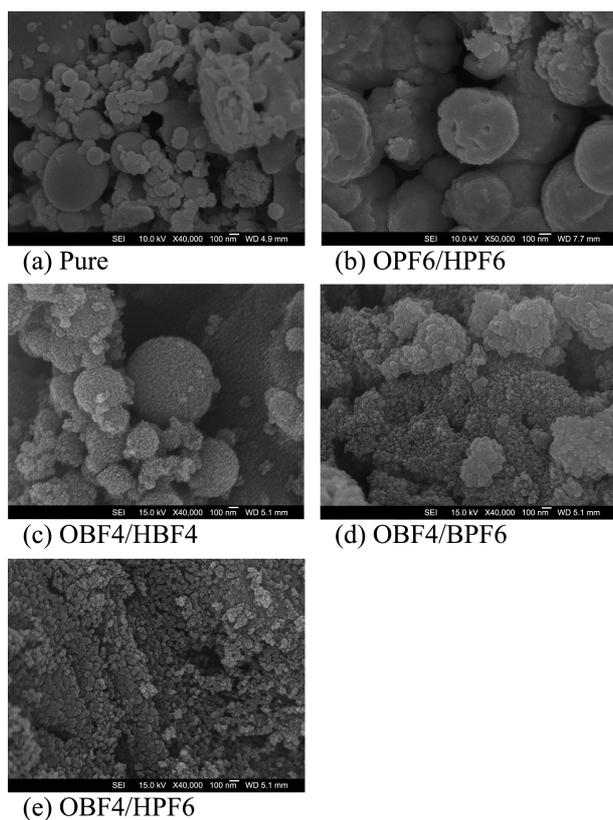


Figure 2. SEM images of TiO₂ particles prepared by various ionic liquids after calcinations at 500 °C.

comparable. This means all samples possessed a similar phase structure as a catalyst.

The morphology of the samples prepared with various binary ionic liquid mixtures was characterized by SEM. Interestingly, various sizes and shapes of TiO₂ nanostructure were formed as shown in Figure 2. The morphology of pure sample prepared without ionic liquid was relatively irregular (see Fig. 2(a)). The result could support the fact that ionic liquid plays a role to form regular structure of TiO₂ particle.^{13,19,20} About 1 μm diameter of sphere with less polydispersity was obtained using OPF6/HPF6 as shown in Figure 2(b). On the other hand, sample consisted of sub-microspheres and submicrosphere aggregates with diameter of less than 500 nm was formed using OBF4/HBF4 (see Figure 2(c)). Moreover, Sample 3 showed better porosity than sample 2, even though it was formed with more polydispersity. For the sample 5 prepared with OBF4/HPF6, hollow sphere shape of submicrosphere aggregates was hardly formed. Only submicrosphere shape was observed over the sample 5. Obviously, the particle is composed of a large amount of submicrosphere and constitutes a disordered wormlike framework. This is a typical characteristic of mesoporous structures. Interestingly, the morphology of the sample 4 is the shape possessed both sample 3 and sample 5 as shown in Figure 2(e). Based on the above results, it was found that [Omim][BF₄] is crucial to obtain the desirable particles, especially in the binary ionic liquids. This is mainly attributed to the different interaction between TiO₂

nuclei and ionic liquids. Over ionic liquid with hydrophobic, the interaction between TiO₂ nuclei and ionic liquid is weak to prevent TiO₂ nucleation and growth. The strong interaction between TiO₂ nuclei and ionic liquids could lead to the disordered shape of particle due to the rapid nucleation and growth.

The N₂ isotherms of samples are illustrated in Figure 3. In the isotherm pattern of sample 2, N₂ was hardly adsorbed on the sample. However, a drastically increasing for adsorbed volume at P/P₀ = 0.9 was observed as shown in Figure 3(b). It is a typical isotherm of wide pore materials. The samples 3 showed a typical N₂ isotherms pattern of hollow sphere. In low pressure ranges, N₂ was slightly adsorbed on the sample, however, a significant increasing for adsorbed volume at P/P₀ = 0.7 as shown in Figure 3(b). The isotherm pattern of sample 5 exhibit hysteresis loop which is a characteristic of mesoporous materials based on the IUPAC classification.²¹ A sharp inflection of adsorbed volume at P/P₀ = 0.45 and a relatively steep desorption branch was observed over the sample with mesopore particle as shown in Figure 3(d). This means the existence of mesoporosity with similar sized entrances in the materials, being in agreement with SEM image in Figure 2(e). The isotherms type of sample 4 is in between the type of sample 3 and sample 5 as shown in Figure 3(c). The result is in a good agreement with SEM results as described above. The structural properties of the samples are illustrated in Table 2. The surface area of the samples was significantly different with their morphology. With decreasing the size of sphere, the surface area of the sample was increased gradually. The trend of pore volume was contrary to that of surface area. The properties of sample 2 were comparable with pure sample but considerably different with sample 5. Thus, the effect of ionic liquids was significant to the structural properties of the samples.

The electrocatalytic performance of the samples was investigated with cyclic voltammetric (CV) analysis. The results are different with the samples as shown in Figure 4. In the CVs, three anodic peaks (*a*₁, *a*₂ and *b*₁) and two cathodic peaks (*a*₃ and *b*₂) were observed. The peak *b*₁ represents oxygen evolution and *a*₃ is the peak of hydrogen production. The peaks *a*₁, *a*₂, *a*₃ are attributed to the hydrogen atoms bonded weakly and strongly on the catalyst surface.^{3,22-24} In the anodic region, the peak *a*₁ represented the hydrogen desorption from the bulk of catalyst, and the peak *a*₃ represented the hydrogen evolution in cathodic sweep. Similarly, the peak *b*₂ is attributed to the oxygen reduction during cathodic sweep. Considering the peak *b*₁, the value of anodic peak current density, the capability of oxygen production of the samples is strongly dependent on their morphology.

The oxygen adsorption-desorption potential gives an effect on the oxide reduction potential value and the charge passed because of the adsorption of oxygen. Oxygen and hydrogen are adsorbed to a great extent on the large surface of spheres. Especially, the oxygen deficient nature of TiO₂ can create oxygen vacancies resulting in the oxygen adsorption and diffusions on the surface of catalyst. The

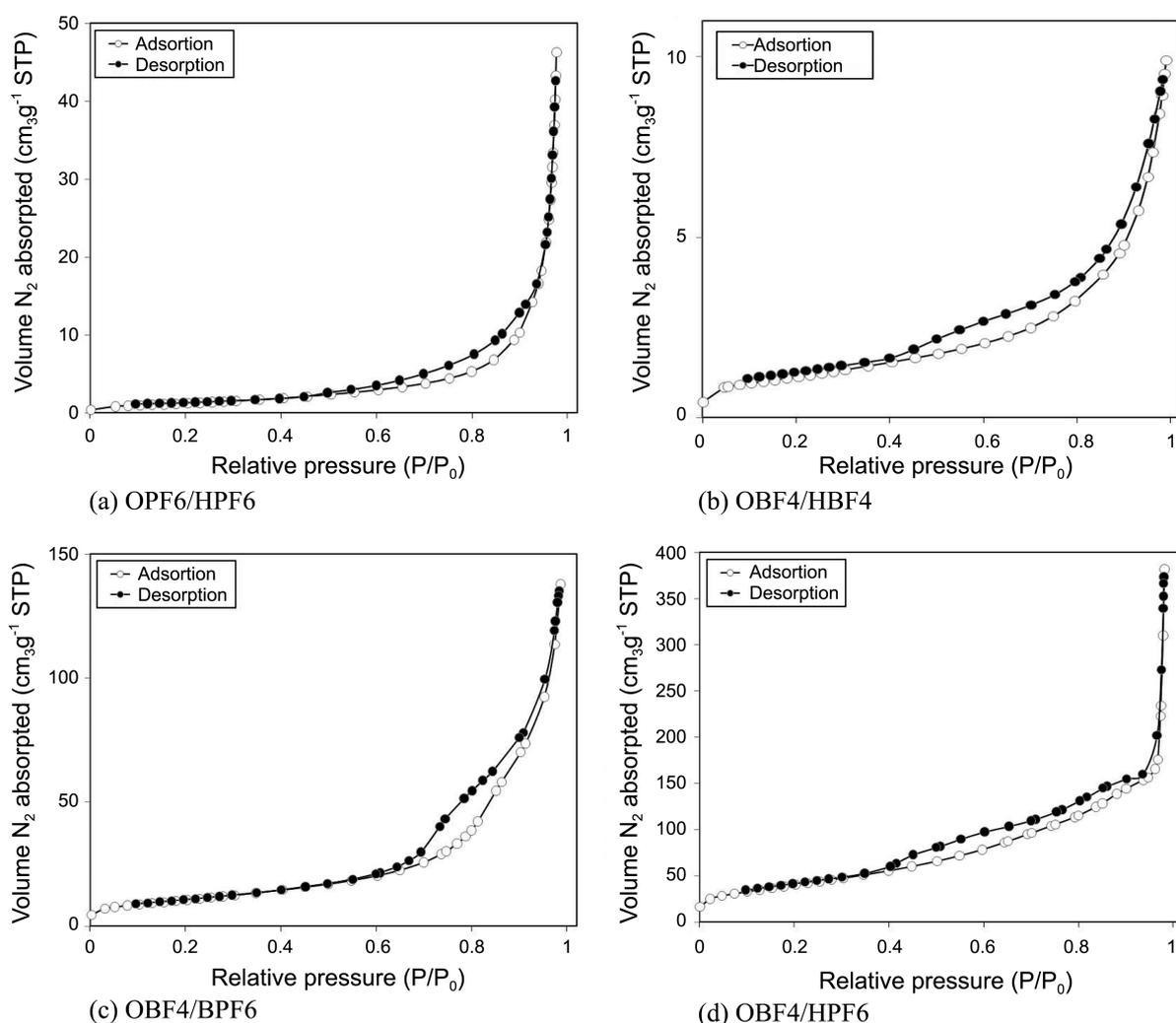


Figure 3. N_2 adsorption-desorption isotherm of TiO_2 particles prepared by various ionic liquids after calcinations at $500\text{ }^\circ\text{C}$.

Table 2. The structural properties of TiO_2 samples

Sample No.	Name	Surface area (m^2/g)	Pore Volume (cm^3/g)
1	Pure	4.3	0.095
2	OPF6/HPF6	5.1	0.085
3	OBF4/HBF4	36.3	0.213
4	OBF4/BPF6	88.9	0.447
5	OBF4/HPF6	147.1	0.590

adsorption processes create charge shifting and alteration at the local electronic structure. During the cathodic potential sweep, reduced Ti^{3+} is present on the surface and creates unsymmetrical bonding with only one oxygen atom, results in the reduction of oxygen. This oxygen reduction phenomenon therefore precedes the hydrogen evolution during the process. Furthermore, the favorable morphology of catalyst is crucial to determine the electrocatalytic performance in water hydrolysis. This is mainly attributed to the balance of oxygen mass-transfer and evolution rate. Even though, the rate of oxygen generation is high, the oxygen should diffuse out rapidly through the catalyst layers on the

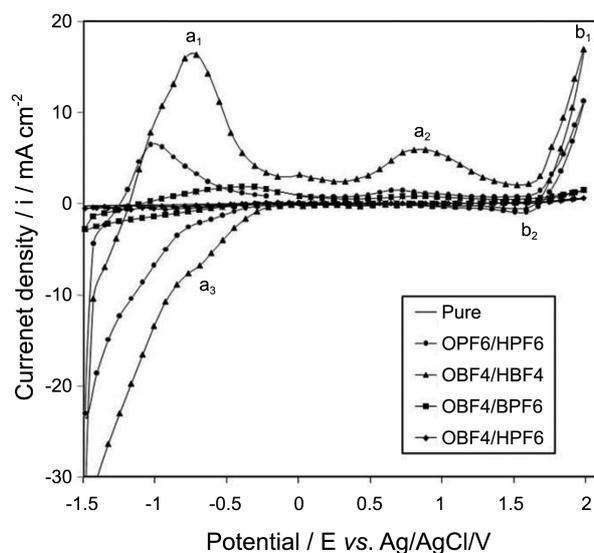


Figure 4. Cyclic voltammograms of TiO_2 particles prepared by various ionic liquids after calcinations at $500\text{ }^\circ\text{C}$.

electrode to maintain desirable overall rate. Over the electrocatalyst with small size, the produced oxygen hardly moved

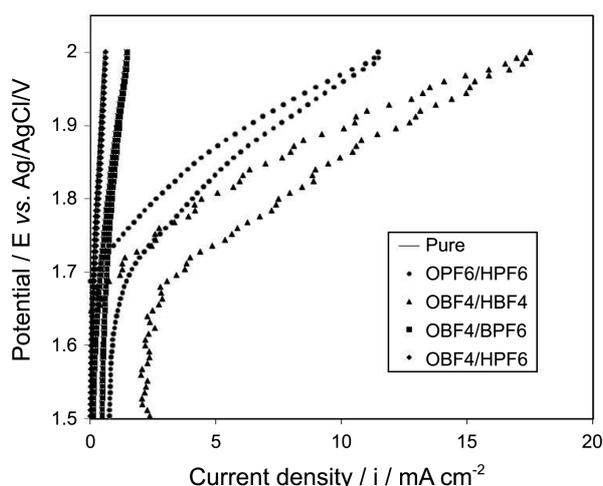


Figure 5. Anodic polarization curves of TiO₂ particles prepared by various ionic liquids after calcinations at 500 °C.

through the catalyst layers. On the contrary, the rate of oxygen was relative slower over the electrocatalyst with large size.

The performance of the samples as anode electrocatalysts was evaluated by anodic polarization. The anodic polarization curves were recorded to investigate the electrocatalytic performance of the spheres towards the oxygen evolution reaction. The performance of the sphere samples was evaluated up to current densities of 20 mAcm⁻² as shown in Figure 5. The potential at 1 mAcm⁻² is used to exhibit the performance of the electrocatalysts without the influence of ohmic resistivity and high bubble formation, therefore the majority of the overpotential will be due to anode reaction at this current density. Contrastingly, the potential at higher current densities will be affected by ohmic resistivity and bubble formation, and thus show the performance under real operating conditions.²⁵ Thus, the OBF4/HBF4 electrocatalysts possessing optimum morphology for oxygen mass transfer have shown the highest overpotential value in oxygen evolution process.

Conclusions

Controlling materials at a nano-level can promote the synthesis of new products with improved properties and functionality for numerous applications. In this study, anatase TiO₂ spheres with various morphologies were prepared by binary ionic liquid mixtures. Ionic liquids played a crucial role in determining the morphology of TiO₂ materials. Specific ionic liquids supported to the formation of spheres

due to their properties. The addition of ionic liquids in the synthesis changed the shape of submicrosphere aggregates. In cyclic voltammetric studies, the peaks for both hydrogen and oxygen evolution were present. Among the samples, TiO₂ prepared with [Omim][BF₄] and [Hmim][BF₄] mixture outperformed in oxygen evolution reaction, and showed the highest anodic density at lower over-potential value during anodic polarization measurements.

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References

- Zanganeh, K.; Shafeen, A. *Int. J. Greenhouse Gas. Cont.* **2007**, *1*, 47.
- Borresen, B.; Hagen, G.; Tunold, R. *Electrochim. Acta* **2002**, *47*, 1819.
- Garcia, I.; Torres, M.; Crespo, M.; Rodriguez, C.; Estrada, E. *J. Alloy. Comp.* **2007**, *434*, 764.
- Hwang, J.; Chung, J. *Electrochim. Acta* **1993**, *38*, 2715.
- Fujishima, A.; Hashimoto, K.; Watanabe, T. *TiO₂ Photocatalysis, Fundamentals and Applications*; Bkc Inc.: Tokyo, 1999.
- Hayden, B. E.; Malevich, D. V.; Pletcher, D. *Electrochem. Commun.* **2001**, *3*, 395.
- Drew, K.; Girishkumar; Vinodgopal, G. K.; Kamat, P. V. *J. Phys. Chem. B* **2005**, *109*, 11581.
- Hagfeldt, A.; Gratzel, M. *Chem. Rev.* **1995**, *95*, 49.
- Collins, A. M.; Spickermann, C.; Nann, S. *J. Mater. Chem.* **2003**, *13*, 1112.
- Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.
- Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- Nakashima, T.; Kimizuka, N. *J. Am. Chem. Soc.* **2003**, *125*, 6386.
- Zhou, Y.; Antonietti, M. *J. Am. Chem. Soc.* **2003**, *125*, 14960.
- Wang, J.; Cao, J.; Fang, B.; Lu, P.; Deng, S.; Wang, H. *Mater. Lett.* **2005**, *59*, 1405.
- Wang, L.; Chang, L.; Zhao, B.; Yuan, Z.; Shao, G.; Zheng, W. *Inorg. Chem.* **2008**, *47*, 1443.
- Zhao, M.; Zheng, L.; Li, N.; Yu, L. *Mater. Lett.* **2008**, *62*, 4591.
- Dong, W. S.; Li, M. Y.; Liu, C.; Lin, F.; Liu, Z. *J. Colloid Interface Sci.* **2008**, *319*, 115.
- Hong, K.; Yoo, K. S. *Res. Chem. Intermed.* **2011**, *37*, 1325.
- Yoo, K.; Choi, H.; Dionysiou, D. D. *Chem. Commun.* **2004**, 2000.
- Liu, Y.; Li, J.; Wang, M.; Li, Z.; Liu, H.; He, P.; Yang, X.; Li, J. *J. Cryst. Growth Des.* **2005**, *5*, 1643.
- Sing, K. S. W. *Pure Appl. Chem.* **1982**, *51*, 2201.
- Woods, R. In *Electroanalytical Chemistry*; Bard, A., Ed.; Marcel Dekker: New York, U.S.A., 1976; Vol. 9, p 24.
- Czerwinski, A. *J. Electroanal. Chem.* **1994**, *379*, 487.
- Czerwinski, A.; Marassi, R.; Zamponi, S. *J. Electroanal. Chem.* **1991**, *316*, 211.
- Marshall, A.; Sunde, S.; Tsyppin, M.; Tunold, R. *Int. J. Hydrogen Energy* **2007**, *32*, 2320.