## Fabrication and Visible Light Photocatalytic Activities of TiO<sub>2</sub> Nanomaterials Incorporated with Tin(IV) Porphyrins

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## **Extended Abstract**

Photocatalytic processes using  $TiO_2$  as photocatalyst have been introduced in the seventies. However, despite lots of advantages,  $TiO_2$  must be excited in the UV region, which means that it can absorb only 3% of solar energy it receives. The majority of solar energy is concentrated in the visible region. Therefore, a photocatalyst that is active under visible light is of paramount importance as an essential element of solar photoenergy utilization. A variety of approaches has been attempted in search of visible light active materials. Porphyrins and metalloporphyrins have been widely investigated for their photochemical activity for various applications such as environmental photocatalysis, hydrogen production, and solar cell. The electrochemical potentials for the porphyrin ring being the redox center is readily dependent on the kind of central metal ions. Among a series of metalloporphyrins, tin(IV)-porphyrin has a strong oxidative capacity (porphyrin ring reduced easily) owing to the high charge on tin(IV) and the excited tin-porphyrin exhibits a high activity for the photooxidation of organic compounds under visible light [1]. We have interests in the photocatalysts based on tin-porphyrin with strong visible light absorption as an efficient visible light photocatalyst for an environmental remediation [2-4] and  $H_2$  production [5,6]. We here present  $TiO_2$  hybrid nanomaterials incorporated with tin(IV) porphyrins exhibiting visible light activities: (i) Tin(IV)porphyrins incorporated-TiO<sub>2</sub> nanotubes with 152 m<sup>2</sup>/g of surface area and 0.44 cm<sup>3</sup>/g of porosity showing visible-lightactivated photocatalytic production of H<sub>2</sub>. (ii) A ternary hybrid material of semiconductor/polymer/porphyrin in which the surface of TiO<sub>2</sub> particles coated with perfluorosulfonate polymer (Nafion<sup>®</sup>) binds water-soluble cationic tin(IV) porphyrins within the Nafion layer through electrostatic attraction. H<sub>2</sub> evolution activity in this ternary hybrid material was estimated to be 1.5 times higher than that in TiO<sub>2</sub>-porphyrin without Nafion<sup>®</sup>.

## References

- J. H. Jang, K.-S. Jeon, S. Oh, H.-J. Kim, T. Asahi, H. Masuhara, and M. Yoon, "Synthesis of Sn-Porphyrin-Intercalated Trititanate Nanofibers: Optoelectronic Properties and Photocatalytic Activities," *Chem. Mater.*, vol. 19, pp. 1984-1991, 2007.
- [2] W. Kim, J. Park, H. J. Jo, H.-J. Kim, and W. Choi, "Visible Light Photocatalysts Based on Homogeneous and Heterogenized Tin Porphyrins," *J. Phys. Chem. C*, vol. 112, pp. 491-499, 2008.
- [3] H. Kim, W. Kim, Y. Mackeyev, G.-S. Lee, H.-J. Kim, T. Tachikawa, S. Hong, S. Lee, J. Kim, L. J. Wilson, T. Majima, P. J. J. Alvarez, W. Choi, and J. Lee, "Selective Oxidative Degradation of Organic Pollutants by Singlet Oxygen Photosensitizing Systems: Tin Porphyrin versus C<sub>60</sub> Aminofullerene Systems," *Environ. Sci. Tech.*, vol. 46, pp. 9606-9613, 2012.
- [4] H.-Y. Yoo, S. Yan, J. W. Ra, D. Jeon, B. Goh, T.-Y. Kim, Y. Mackeyev, Y.-Y. Ahn, H.-J. Kim, L. J. Wilson, P. J. J. Alvarez, Y. Lee, W. Song, J. Kim, and J. Lee, "Tin Porphyrin Immobilization Significantly Enhances Visible-Light-Photosensitized Degradation of Microcystins: Mechanistic Implications," *Appl. Catal. B*, vol. 199, pp. 33-44, 2016.
- [5] W. Kim, T. Tachikawa, T. Majima, C. Li, H.-J. Kim, and W. Choi, "Tin-porphyrin sensitized TiO<sub>2</sub> for the production of H<sub>2</sub> under visible light," *Energy Environ. Sci.*, vol. 3, pp. 1789-1795, 2010.
- [6] C. Li, K.-M. Park, and H.-J. Kim, "Ionic assembled hybrid nanoparticle consisting of tin(IV) porphyrin cations and polyoxomolybdate anions, and photocatalytic hydrogen production by its visible light sensitization," *Inorg. Chem. Commun.*, vol. 60, pp. 8-11, 2015.