Heteropolyacid-encapsulated TiHY zeolite as an inorganic photosynthetic reaction center mimicking the plant systems

Sambandam Anandan, Minjoong Yoon*

Department of Chemistry, Chungnam National University, Taejon 305-764, South Korea

Abstract

A tremendous breakthrough was required for the researchers trying to find a way to photodecomposition of water by using semiconductor photocatalysts without electricity. In this regard, we attempted to prepare the heteropolyacid (HPA)-encapsulated TiHY zeolite a new photocatalyst mimicking the plant photosynthetic system. This photocatalyst (0.3 g/40 ml) was observed to generate hydrogen (4.08 ± 0.7 µl/h) and oxygen (6.86 ± 0.7 µl/h) from the aqueous solutions upon illumination by two photon reactions (UV and visible lights), which is quite analogous to the "Z-scheme" mechanism for plant photosynthetic systems. The turnover number of the photocatalyst was determined to be 11 with the quantum yield of the water splitting about 27 ± 6% at 352 nm. Thus, this inorganic material must be very useful as a reaction center mimicking the plant photosynthetic system without electrical energy.
© 2003 Elsevier Science B.V. All rights reserved.

Plants capture the energy from sunlight and thus grow. During this process, they produce oxygen by oxidizing water and reducing carbon dioxide. In other words, the oxidation of water and reduction of CO_2 are achieved with solar energy. A number of research groups have studied the photoelectrolysis of water using light energy by analogy with natural photosynthesis, which is considered as a possible novel source of energy for the future [1–8]. Their research results have shown that the TiO_2 colloids are useful for the photodissociation of water into H_2 and O_2 as well as the photodestruction of organic contaminants in water [1]. The photoinduced electron transfer reactions of the liquid-junction photovoltaic cells have shown a resemblance to the plant photosynthetic process [1]. However, this system used electrical energy as well as light energy. In this regard, many authors [9–14] surveying new photocatalysts and investigating factors dominating photocatalytic activities give useful information on the development of photocatalyst materials under the visible light irradiation, but the activity is very low. Thus, the observed overall quantum yield of the water splitting reaction in the "Z-scheme" system was 0.1% [14]. This is because TiO_2 shows very high activity under UV irradiation, but the photocatalytic activity is not observed under visible light irradiation. Similarly, a perspective class

of compounds in the search for photocatalytic system for water cleavage seems to be that of heteropolyacids (HPA) [15] because these compounds have charge transfer absorption bands in the UV region, and their redox potentials can be varied over a wide range by changing their composition and they can act as donors or acceptors of several electrons [16]. However in this case, the photon-to-electron conversion efficiency remained very low. Hence, it is worthwhile to attempt to make a novel photocatalytic system operated by the two photochemical reactions mimicking the plant photosynthetic process without electrical energy.

In this work, we attempted encapsulation of both TiO_2 and HPA into the nano-porous zeolite (Y-zeolite) of high surface area in order to effectively increase the number of surface active sites of the nano-sized TiO_2 as shown below. The structure of the prepared HPA-encapsulated TiHY was already characterized in our previous experiment [17] (see Scheme 1). The above-prepared photocatalyst irradiated simultaneously by both UV and visible lights was found to enhance the photoreduction of Methyl Orange dissolved in water. In the previous experiment, the UV light induces the generation of electrons from semiconductor which in turn enhances the photocatalytic activity of the HPA-encapsulated TiHY zeolite to generate heteropolyblue (HPB), whose absorption is in the visible region. This is the main reason why we are in need of visible light as well as UV light. Thus, simultaneous irradiation of the photocatalyst

* Corresponding author. Tel.: +82-42-821-6546; fax: +82-42-823-7008.
E-mail address: mjyoon@cnu.ac.kr (M. Yoon).
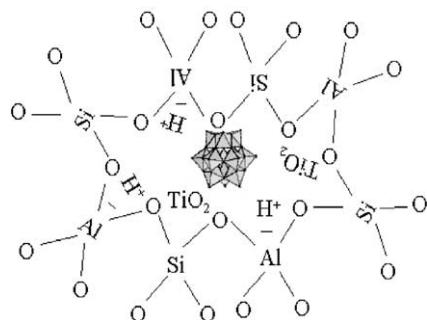
Scheme 1.

with UV and visible light is expected to enhance the photo-catalytic activity to photolysis water to generate the liberation of H_2 and O_2 as observed in the natural photosynthetic systems.

In order to confirm the expectation, the following experiments were performed. In a 100 ml capacity quartz vessel, about 0.3 g of the above catalyst was dissolved in 40 ml of ethanol (sacrificial electron donor):water (1:1) mixture (Sample 1) and sealed with a silicone rubber septum at 25 °C. Before irradiation, the sample solution was deaerated with argon gas for an hour to prevent the contamination of the reactor by the atmosphere. The sample was illuminated simultaneously by both UV light (Rayonet Photochemical reactor, USA, 8.124×10^{-8} einsteins/(cm^2 s)) and visible light (150 W Xenon arc lamp, 2.443×10^{-9} einsteins/(cm^2 s)), and the samples were checked for H_2 and O_2 by using GC (Donam Instruments Company, Korea) stainless steel column and argon as the carrier gas (Fig. 1). Similar results

were observed with the same amount of the catalyst containing 0.1% PVA (sacrificial electron donor) in 40 ml of water (Sample 2). The sacrificial electron donors are required to photoreduce HPA to HPB as previously observed in the TiO_2 colloidal systems [18] (see Scheme 2). Actually, the amount of H_2 evolved is $4.08 \pm 0.7\,\mu l/h$ and the quantum efficiency (Φ) observed at 352 nm is $27 \pm 6\%$ whereas the amount of H_2 evolved (0.24 μl/h) is very less in the absence of the sacrificial electron donors.

Quantum efficiency is difficult to determine for each wavelength in this study because (a) the reactor is irregularly shaped and (b) the heteropolyacid solutions are not optically thick at all wavelength studied. So the quantum efficiency was calculated at 352 nm, which initiates the catalytic activities by using the Planck relation as follows

$$E_i = n_i h \nu_i = \frac{n_i hc}{\lambda_i} \tag{1}$$

$$n_i = \frac{E_i \lambda_i}{hc} \tag{2}$$

quantum efficiency (%)

$$= \frac{\text{number of photoreduced HPA}}{\text{total number of absorbed photons}} \times 100 \tag{3}$$

where E_i is the light intensity of selected wavelength, n_i the number of photons, h the Planck constant and c is the velocity of the light.

Indirectly, we observed action spectrum for this system by photoreduction of methyl orange in the presence of HPA-adsorbed TiO_2 colloids [18], in which the pho-
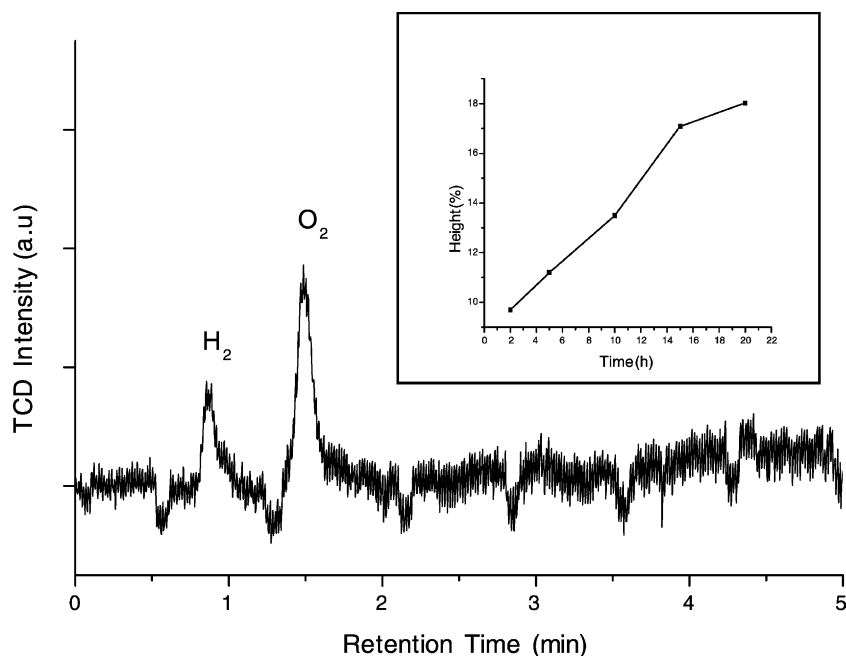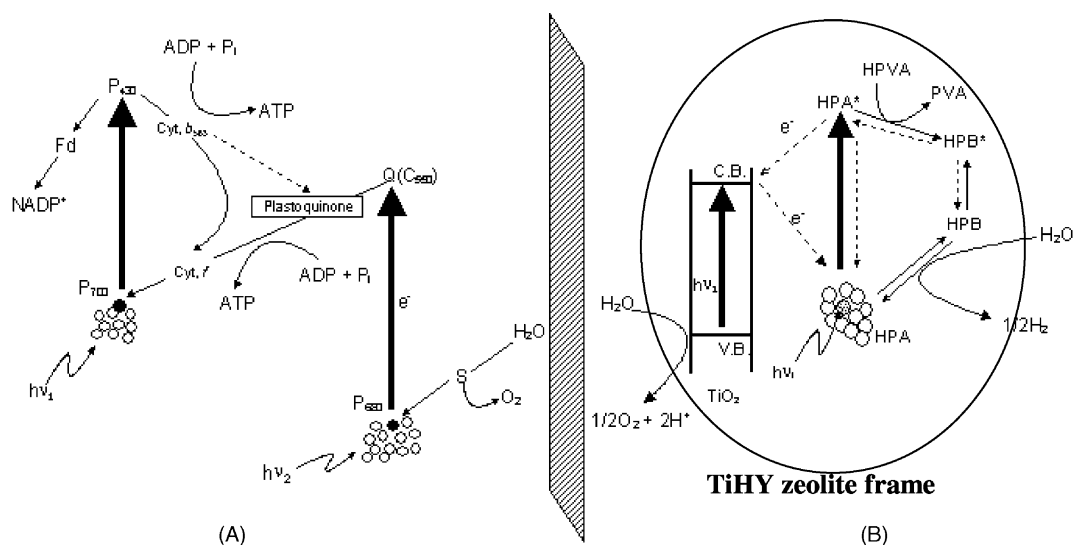

Fig. 1. Gas chromatogram of H_2 and O_2 evolved from ethanol:water (1:1) mixture after 15 h irradiation by both UV and visible light in the same time. Inset shows increase in the evolution of H_2 gas as the irradiation time increases.

Scheme 2. Energy diagram: (A) photosynthesis in green plants [18]; (B) photoinduced electron transfer at the HPA encapsulated TiHY zeolite for the generation of H_2 and O_2.

toinduced electron transfer processes are similar to those in the present zeolite systems. The turnover number is the essential information on photocatalytic processes and it was determined according to Schiavello et al. [19] by assuming 2.656×10^{12} active sites based on the number of TiO_2 molecules in the nano-sized super cage of zeolite (see).[1] The calculated turnover number was of at least 11.

The liberation of H_2 and O_2 can be explained based on the proposed mechanism similar to "Z-scheme" for the plant photosynthesis (see Scheme 2) according to our previous studies in the HPA-adsorbed TiO_2 colloidal systems [18,20]. When the samples are illuminated, HPA encapsulated in the zeolite cavities is reduced to so-called heteropoly blues showing new absorption at 750 nm (Fig. 2), due to the inter-valence charge transfer $(W(VI) \rightarrow W(V))$ [21]. The formation of HPB is induced by direct electron transfer from the TiO_2 conduction band to the ground state HPA in addition to photoreduction through the excited state of HPA. Such processes have been already proved to be reversible in the HPA-adsorbed TiO_2 colloids [18] and the photocatalysts are very stable to be used repetitively. Thus, all the reactions favors the oxidation and reduction of water without electricity by using both visible light and near-UV light which includes the whole spectrum of sunlight on Earth. This inorganic material must be very useful as a reaction center mimicking the natural plant photosynthetic reaction center containing photosystems I and II. Further work is under scrutiny in our lab in order to improve the mass production of the liberated gases.

Fig. 2. Absorbance spectrum of HPB formed upon UV irradiation of the mixture of HPA and TiO_2.

References

[1] M. Gratzel, Energy Resources Through Photochemistry & Catalysis, Academic Press, New York, 1983.
[2] A. Fujishima, K. Honda, Nature 238 (1972) 37.

---

[1] From the surface area (669 m^2/g), vacant space in super cage of zeolite (827 Å) and each unit cell containing 7.2 Ti, we find total active sites is equal to 2.656×10^{12}.
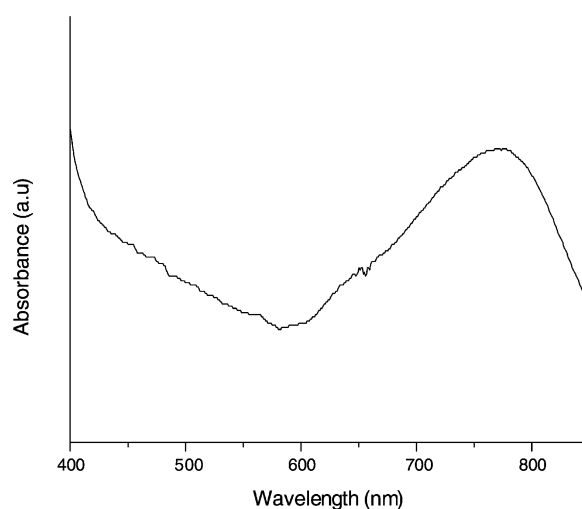
[3] T. Kawai, T. Sakata, Nature 286 (1980) 474.

[4] V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta, M. Gleria, Science 189 (1975) 852.

[5] A. Kudo, H. Kato, S. Nakagawa, J. Phys. Chem. B 104 (2000) 571.

[6] P. Keller, A. Moradpour, E. Amouyal, H. Kagan, J. Mol. Catal. 7 (1980) 539.

[7] M. Hara, C.C. Waraksa, J.T. Lean, B.A. Lewis, T.E. Mallouk, J. Phys. Chem. A 104 (2000) 5275.

[8] A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Am. Chem. Soc. 124 (2002) 13547.

[9] Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature 414 (2001) 625.

[10] C. Konigstein, J. Photochem. Photobiol. A: Chem. 90 (1995) 141.

[11] J. Yoshimure, Y. Ebina, J. Kondo, K. Domen, J. Phys. Chem. 97 (1993) 1970.

[12] Y. Inoue, Y. Asai, K. Sato, J. Chem. Soc., Faraday Trans. 90 (1994) 797.

[13] Z. Zou, J. Ye, H. Arakawa, Chem. Phys. Lett. 332 (2000) 271.

[14] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, J. Photochem. Photobiol. A: Chem. 148 (2002) 71.

[15] E.N. Savinov, S.S. Saidkhanov, V.N. Parmon, K.I. Zamaraev, React. Kinet. Catal. Lett. 17 (1981) 407.

[16] M.T. Pope, G.M. Varga, Inorg. Chem. 5 (1966) 1249.

[17] S. Anandan, S.Y. Ryu, M. Yoon, W. Cho, J. Mol. Catal. A: Chem. 195 (2003) 201.

[18] M. Yoon, J.A. Chang, Y. Kim, J.R. Choi, K. Kim, S.J. Lee, J. Phys. Chem. B 105 (2001) 2539.

[19] M. Schiavello, V. Augugliaro, L. Palmisano, J. Catal. 27 (1991) 332.

[20] K.C. Smith, The Science of Photobiology, Plenum Press, New York, 1977.

[21] T. Yamase, N. Takabayashi, M. Kaji, J. Chem. Soc., Dalton Trans. (1984) 793.