Photophysicochemical Properties of Chlorophyll-*a* Adsorbed on Mg-containing Mesoporous Silica

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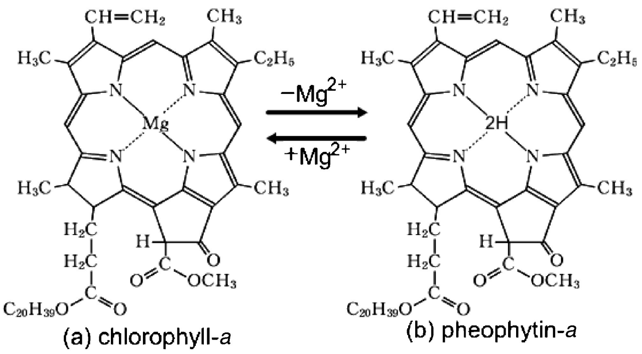
Chlorophyll-*a* (chl-*a*) was found to easily change to pheophytin-*a* during its adsorption on hexagonal mesoporous silica (HMS) since the centered Mg ions of chl-*a* easily react with silanol groups as Brønsted acid sites (pheophytinization). This pheophytinization process could be suppressed by adding small amounts of Mg species into the frameworks of HMS. The highly dispersed Mg species work as adsorption sites for chl-*a* and/or the porphyrin ring of pheophytin-*a*, resulting in the formation of an original chl-*a* like complex species.

Chlorophyll-*a* (chl-*a*) dye plays an important role in photosynthesis, one of the most efficient photochemical processes in converting sunlight energy into chemical energy. In recent years, researchers in organic chemistry have tried to develop artificial photosynthetic processess by using photofunctional dyes, fullerene derivatives and carbon nano-tubes[1,2] while the immobilization of these photofunctional compounds onto the solid surfaces has been actively investigated,[3–8] since pioneering works[9] by Turro et al. and Anpo et al. The chl-*a* itself is unstable and easily changes to pheophytin-*a* owing to the lack of centered Mg ions in acidic conditions, as shown in Scheme 1.[3] Kuroda et al. have used mesoporous silica (e.g., C_{18}FSM) as a host material to adsorb chl-*a* and reported that the C_{18}FSM modified with diol can stabilize the chl-*a* adsorbed on such solid surfaces.[10] In the present work, we have investigated the stabilization of chl-*a* on Mg-containing mesoporous silica.

The hexagonal mesoporous silica (HMS) was prepared by procedures in previous literature.[11] Tetraethoxyorthosilicate (TEOS) as a SiO_2 source, dodecylamine (DDA) as a template, 2-propanol, ethanol, H_2O, and HCl were mixed at a molar ratio of TEOS:DDA:EtOH:*i*-PrOH:HCl:H_2O = 1:0.27:6.54:1:0.02:36.3. The mixture solution was stirred at 295 K for 24 h and then filtered. The obtained white powders were thoroughly washed with distilled water, dried at 373 K for 24 h, crushed with an agate mortar and then calcined in air at 873 K for 6 h in order to remove the template. Mg-HMS was prepared using the same procedure by adding $MgCl_2$ into a precursor solution. Mg-HMS100, thus, refers to HMS including Mg in its framework structure with a Si/Mg ratio of 100.


(a) chlorophyll-*a* (b) pheophytin-*a*

Scheme 1. Molecular structure of: (a) chlorophyll-*a*; and (b) pheophytin-*a*.

The adsorption of chl-*a* on the mesoporous silica was carried out by adding HMS powders into 0.5 mL of 1.0×10^{-4} M chl-*a*/toluene solution. After stirring at 295 K under dark conditions for 2 h, the samples were dried at 323 K for 24 h to evaporate the toluene solvent. Characterization studies were carried out by XRD (Shimadzu, XRD–6100) and UV–vis absorption (Shimadzu, UV–2200A) measurements in air at 295 K.

Figure 1 shows the XRD patterns of HMS and Mg-HMS100. A diffraction peak at around 2 degrees attributed to the hexagonal mesoporous structure can clearly be observed, however, the peak width was quite broad, showing that the wall of HMS is much wider as compared to MCM-41 and FSM-16. Using the Sherrer's equation, the pore sizes of HMS and Mg-HMS100 were estimated to be 5.09 and 4.80 nm, respectively. Since the size of chl-*a* is estimated to be ca. 2 nm, both HMS and Mg-HMS can be considered to be good host materials to adsorb and incorporate chl-*a* in their pores. The incorporation of Mg ions within the HMS matrices was found to decrease the intensity of the diffraction peak. Mg-HMS10 (Si/Mg = 10) did not show any diffraction peaks. The BET surface areas are summarized in Table 1. The surface area of Mg-HMS100 became smaller than that of the original HMS of ca. 580 m^2/g by the incorporation of Mg into its framework. These results clearly indicate that some part of the mesoporous structure of HMS has collapsed by including Mg ions within the SiO_2 matrices, although the mesostructure of the Mg-HMS100 has been maintained.

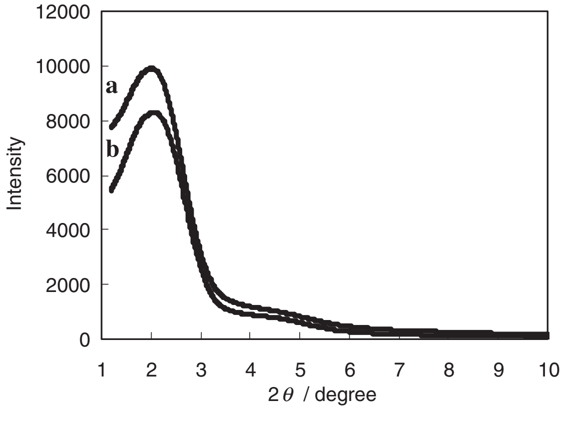


Figure 1. XRD patterns of: (a) HMS and (b) Mg-HMS100.

Table 1. Specific surface area of HMS and Mg-HMS100

Sample	Surface area/$m^2\ g^{-1}$	Pore size/nm
HMS	850.1	5.09
Mg-HMS100	583.0	4.80

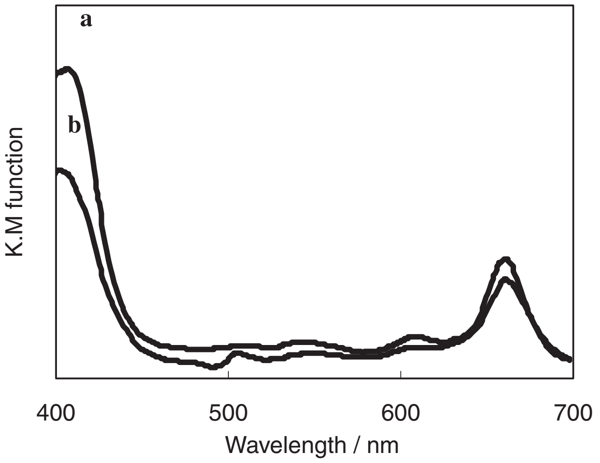
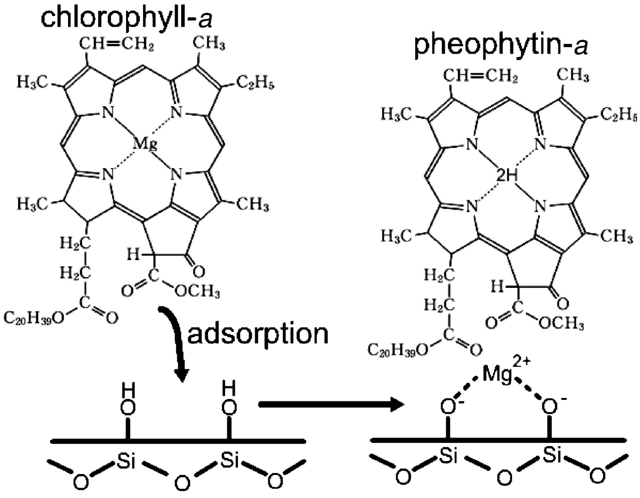


Figure 2. UV–vis absorption spectra of chlorophyllous dyes adsorbed on: (a) HMS and (b) Mg-HMS100.

Figure 2 shows the UV–vis absorption spectra of the chl-*a* adsorbed on: (a) HMS and (b) Mg-HMS100. The chlorophyllous dye has two main absorption bands at around 400–450 nm due to the Soret band and the red light regions of 650–700 nm due to the Q_y band. The Soret/Q_y ratio of chl-*a* in the toluene solution and the chl-*a* adsorbed on HMS and Mg-HMS are shown in Table 2. The Soret/Q_y ratio of chl-*a* and pheophytin-*a* in organic solvents is generally known to be 1.1–1.3 and 2.2–2.9, respectively.[12] The Soret/Q_y ratio of the chl-*a* adsorbed on HMS was much higher, suggesting that the chl-*a* changed to pheophytin-*a* due to the lack of centered Mg ions. As shown in Scheme 2, the chl-*a* adsorbed on HMS was found to easily change into pheophytin-*a* by the loss of Mg through the reaction with the Brønsted acid sites on the HMS surfaces. Meanwhile, the chl-*a* adsorbed on Mg-HMS100 was found to show a Soret/Q_y ratio of 1.97 which is similar to the value of 1.51 for chl-*a* in toluene solution. Photoluminescence measurements also revealed that the chl-*a* dye adsorbed on HMS was easily pheophytinized, however, chl-*a* adsorbed on Mg-HMS100 remained stable (spectra not shown). These results suggest that the less acidic Mg-HMS surfaces suppress the conversion of chl-*a* into pheophytin-*a*. Another possibility is that the pheophytin-*a* interacts with the Mg sites on Mg-HMS100 to form the chl-*a*-like complex showing a similar Soret/Q_y ratio to chl-*a* dye in the toluene solvent. However, such a stabilization of the chl-*a* could not be observed on Mg-rich-HMS (Mg-HMS10). These results indicate that the highly dispersed Mg sites on HMS play an important role in the stabilization of the chl-*a* dye. Also, the lifetime of photoluminescence of chlorophyllous dyes adsorbed on HMS and Mg-HMS showed about 5.0 ns which is similar to that of chlorophyll-*a*/toluene solution.

Table 2. Soret/Q_y ratio of chlorophyll-*a*/toluene solution, chlorophyllous dyes/HMS, and Mg-HMS100

Sample	Soret/Q_y ratio
Chlorophyll-*a*/toluene solution	1.51
Chlorophyllous dyes/HMS	2.60
Chlorophyllous dyes/Mg-HMS100	1.97



Scheme 2.

In conclusion, the chl-*a* dye was found to be pheophytinized by the Brønsted acid sites on the HMS surfaces. The conversion of chl-*a* into pheophytin-*a* could be suppressed on the Mg-containing mesoporous silica since the porphyrin ring of pheophytin-*a* can interact with the highly dispersed Mg sites. Thus, chl-*a* was successfully stabilized on Mg-HMS100 without modification of the HMS surfaces by the organic functional groups.

References

1 H. Imahori, S. Fukuzumi, *Gendai Kagaku* **2002**, *375*, 46.
2 S. Fukuzumi, H. Imahori, *Molecular and Supramolecular Photochemistry*, in *Photochemistry of Organic Molecules in Isotropic and Anisotropic Media*, **2003**, Vol. 9, pp. 227–273.
3 H. Scheer, *Chlorophylls*, CRC Press, Boca Raton, FL, **1991**.
4 K. Y. Yoon, *Chem. Rev.* **1993**, *93*, 321.
5 T. Shinoda, Y. Izumi, M. Onaka, *J. Chem. Soc., Chem. Commun.* **1995**, 1801.
6 K. Moller, T. Bein, *Chem. Mater.* **1998**, *10*, 2950.
7 B. T. Holland, C. Walkup, A. Stein, *J. Phys. Chem. B* **1998**, *102*, 4301.
8 T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.
9 *Photochemistry on Solid Surfaces*, ed. by M. Anpo, T. Matsuua, Elsevier, Amsterdam, **1989**, and references therein.
10 S. Murata, H. Hata, T. Kimura, Y. Sugahara, K. Kuroda, *Langmuir* **2000**, *16*, 7106.
11 H. Yang, N. Coombs, G. Ozin, *Nature* **1997**, *386*, 692.
12 H. J. Perkins, D. W. A. Roberts, *Biochim. Biophys. Acta* **1964**, *79*, 20.

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