Journal of Photochemistry and Photobiology A: Chemistry 341 (2017) 1–11

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Invited feature article

Photo-induced electron transfer of carotenoids in mesoporous sieves (MCM-41) and surface modified MCM-41: The role of hydrogen bonds on the electron transfer

Yunlong Gao[a,*], Hanjiao Chen[b], Sefadzi Tay-Agbozo[b], Lowell D. Kispert[b,*]

[a] College of Sciences, Nanjing Agricultural University, Nanjing, 210095, China
[b] Department of Chemistry, BOX 870336, University of Alabama, Tuscaloosa, AL, 35487, United States

ARTICLE INFO

Article history:
Received 29 October 2016
Received in revised form 4 March 2017
Accepted 12 March 2017
Available online 16 March 2017

Keywords:
Carotenoids
MCM-41
Hydrogen bonds
Electron transfer

ABSTRACT

Two types of hydrogen bonds (H-bond) can be formed when a carotenoid containing a hydroxy group, such as retinol, interacts with a silanol group on the surface of MCM-41. H-bond **1**, the oxygen atom of the carotenoid interacts with the proton of the —SiOH group on the surface of MCM-41, and H-bond **2**, the proton of the —OH group of the carotenoid interacts with the oxygen atom of —SiOH group on the surface of MCM-41. DFT calculations show that the formation of the H-bond **1** decreases the LUMO of the carotenoid and stabilizes the neutral species more than the radical cation, and thus disfavors the photo-induced electron transfer (ET) from the carotenoid to MCM-41. The opposite is true for the formation of H-bond **2**. This conclusion is confirmed by the EPR study of the photo-induced ET of retinol imbedded in MCM-41 and the surface modified MCM-41. Although the formation of H-bond **1** results in low ET efficiency, the efficiency is much higher than that of the same carotenoid physisorbed on the surface of MCM-41. These results are relevant for improving the low solar-light-to-energy conversion efficiency in dye-sensitized solar cells.

1. Introduction

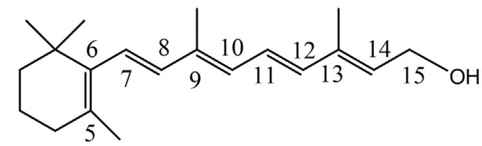
Dye-sensitized solar cells (DSCs) are attractive as an alternate class of solar cells, and extensive studies have been carried out in recent years [1]. The use of DSCs have gained attention because they have some advantages over other solar cells. These are low cost, flexibility and lightweight, potential for indoor application, and color (with choice of different colors of dyes) availability [2]. However, DSCs have not been widely used owing to their low solar-light-to-energy conversion efficiency and long-term stability.

The performance of DSCs can be improved by increasing the incident photon-to-current conversion efficiency (IPCE). IPCE is determined by four factors: (1) the light-harvesting efficiency, (2) the electron injection efficiency (Φ_{inj}) from the dye to the semiconductor, (3) the efficiency of the regeneration of the oxidized dye by the redox system, and (4) the charge collection efficiency from the device to the external circuit [1]. Of all these processes, the mechanism for the electron injection is the least understood. Three important factors are found to control Φ_{inj}: the free energy change ($-\Delta G_{inj}$) for electron injection, the surface geometry and adsorption characteristics of the adsorbed dyes on the semiconductor surface, and the presence of fast charge recombination (electron back transfer) [2]. $-\Delta G_{inj}$ can be evaluated from the energy difference between the lowest unoccupied molecular orbital (LUMO) of the dye and the conduction band edge of the semiconductor. A positive value of $-\Delta G_{inj}$ is necessary, but not sufficient, to achieve high Φ_{inj}. Surface treatment of the semiconductor and a more detailed understanding of fast charge recombination are also significantly important to realize high-performance devices.

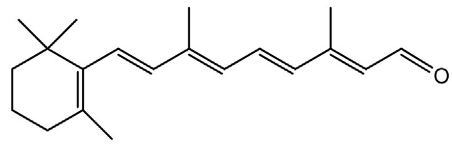
The importance of investigating the type of anchoring between the sensitizer molecules and the surface of the semiconductor is emphasized by the fact that the bonding mechanism and the electron coupling between semiconductor and dye directly impacts electron transfer and the performance of the dye-sensitized photoanode [3]. A complete understanding of the interaction between the dye and the semiconductor is essential for the design of a DSC. When dyes adsorb on the surface of a semiconductor, chemical bonds, such as coordination bonds and hydrogen bonds, can form. It is important to know how the bond formation affects Φ_{inj}. A previous study[4] has shown that the formation of H-bonds between the carotenoid canthaxanthin

* Corresponding authors.
E-mail addresses: yunlong@njau.edu.cn (Y. Gao), lkispert@ua.edu (L.D. Kispert).

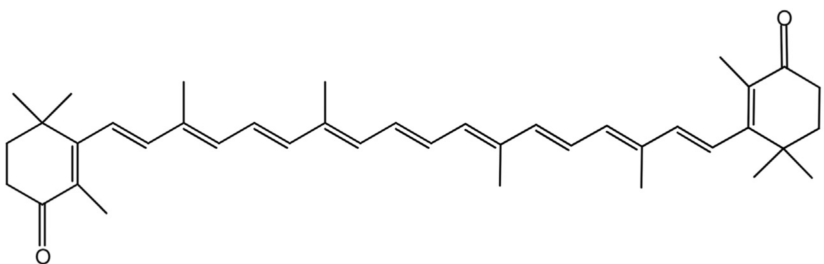
http://dx.doi.org/10.1016/j.jphotochem.2017.03.013
1010-6030/



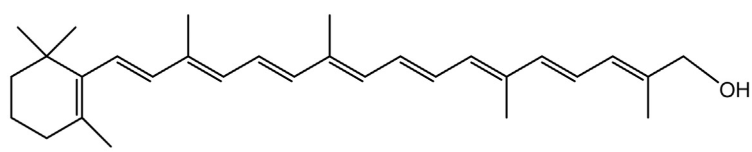
Retinol (**ROL**)



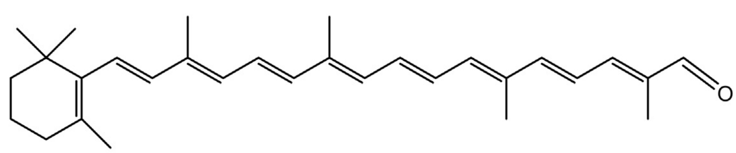
Retinal (**RAL**)



Canthaxanthim(**CAN**)



8'-Apo-β-caroten-8'-ol (**COL**)



8'-Apo-β-caroten-8'-al (**CAL**)

Scheme 1. The structures and names of the carotenoids mentioned in the paper.

(**CAN**) (see Scheme 1) and the silanol groups on the surface of MCM-41 decreases the HOMO and LUMO energies of CAN, and stabilizes the neutral species more than its radical cation. This results in lower electron transfer (ET) efficiency for **CAN** versus that for β-carotene.

Carotenoids as natural dyes have been used in the construction of DSCs [5–7]. The use of natural dyes has become of interest recently because of their ease of preparation, low cost, biodegradability, availability, purity, environmental friendliness, and most importantly, significant reduction of noble metal and chemical synthesis cost [8–10]. Kispert [7] and co-workers fabricated a DSC, for the first time, using β-apo-8′-carotenoic acid as a sensitizer and hydroquinone as a reductant. It exhibited a reasonably high IPCE of 34% at the absorption maximum at 426 nm, the open-circuit voltage (Voc) of 0.15 V, and no bleaching of the dye even after 12 h. In order to further understand the electron transfer (ET) process of carotenoids, Kispert's group has studied the ET reactions of carotenoids imbedded in mesoporous molecular sieves MCM-41 and metal ion substituted MCM-41 (Ni-MCM-41 [11], Fe-MCM-41 [12], Ti-MCM-41 [13], and Cu-MCM-41 [14]). Understanding the mechanisms of these ET reactions are useful in the design of DSCs. MCM-41 is a mesoporous silica containing a regular array of uniform cylindrical pores. The pore size ranges from 15 to 100 Å depending on the chain length of the template used in the synthesis [15]. Previous studies [11–14,16,17] have shown that such material provides a microenvironment appropriate for retarding back ET and thus increase the lifetime of photo-produced radical ions.