Interactions of tio2 nanoparticles with carotenoids

Role of TiO_2 semiconductor nanoparticles on photodegradation of carotenoids: stability of carotenoids in solution.

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Abstract:

Introduction

Carotenoid (Car) molecules as a sensitizer in Dye-sensitized solar cells (DSSC) with optimum photo conversion efficiency have recently been widely investigated by several researchers [1-3] . Car are one of the most widespread naturally occurring pigments which are of great interest due to their biological functions in living organisms [4] . The most striking feature of the long chain car molecules is absorbing visible light in the electromagnetic spectrum, and therefore act as light harvesting pigments in green plants. The optical absorption of car molecules is occurred in the range of 400 nm to 550 nm with a very high molar absorptivity coefficient. Besides their light harvesting and photo-protecting actions in plants, they play major roles as good antioxidants on preventing degenerative diseases and some of them are important dietary source of vitamin A.

Light harvesting ability of car is responsible for their attractive colours and which is associated with the long conjugated double bond system, composed of light absorbing chromophore [5] . Although the *all-trans* configuration of car is most stable in nature, several of *mono-cis* and *di-cis* isomers are possible during photodegradation of car. *Cis-trans* geometrical isomerization of double bonds in chromophore may cause the loss in colour of car molecules as well as appearing a *cis* peak in UV-region (Amaya et al. 2001). This colour loss may imparts the structural variations to the dye molecule and hence the performance of DSSC. Light Irradiation of car molecules is studied by several researchers [6-8] and the photocatalyzed degradation of car on semiconductors such as TiO_2 , CdS and ZnO are studied by (kispert et al. 1998), he revealed that a rapid photodegradation of car are occurred in the presence of the semiconductors.

Recently the application of wide band gap semiconductors mainly TiO_2 are greatly under investigations for Photovoltaic (PV) solar cells over the last few years. TiO_2 plays a major role in development of higher conversion efficiency solar cells that is because due to its good photoactive properties [9, 10] , as well as its biological and chemical inertness for more suitability for many environmental applications. PV solar cells provide an attractive alternative to high cost energy sources for harnessing and converting free, unlimited solar energy into clean electricity [10-12] . However the expensive raw materials and high manufacturing cost for silicon and Ru-based solar cells have led to develop viable alternative for sensitizers in solar cells with new molecular materials using naturally occurring plant materials. Dye-sensitized solar cells (DSSC) assembled by natural dyes extracted from plant materials as a sensitizer have made considerable attention due to their low cost and environmental friendliness [13] . DSSC composed of nanostructured, mesoporous, wide-bandgap semiconductor to which the dye molecules (sensitizers) are adsorbed, a counter electrode and an electrolyte. In DSSC the dye molecule absorb visible light, and inject electron from photo-excited state of dye molecule to conduction band of semiconductor. [12, 14] The performance of a dye-sensitized solar cell is mainly based on the structure of the visible light absorbing dye/ sensitizer.

Several researches were focused to enhance the conversion efficiency of solar cells by improving the photovoltaic properties of dye-sensitized semiconductor solar cells [15, 16]. Recently (Polivka et al. 2002) studied the dynamics of photoinduced electron transfer and recombination between car and a TiO_2 nanoparticle by means of transient absorption spectroscopy [6]. On the other hand utilization of several natural dyes extracted from natural plant sources as sensitizers have been reported by several workers [14, 17]. Besides that the interactions of human serum albumin, porphyrin and natural pigments with colloidal TiO_2 were studied by several researchers [18-21] with the use of absorption and fluorescence spectroscopy. However the photochemical behavior and the stability of car containing terminal carboxylic groups adsorb on to a surface of semiconductor in a solvent mixture has not been extensively investigated to our knowledge.

The present study involves the use of mono and di-carboxylic carotenoids bixin and norbixin respectively to investigate the interactions of TiO_2 nanoparticles with carotenoids extracted from annato (*Bixa orellana*) seeds. The chemical structures of bixin and norbixin are shown in Fig. 1.

Here we irradiate the car solution in MeOH in the presence of spray coated and non-coated TiO_2 semiconductor glass plate to investigate the photodegradation behavior of car. Further the effect of colloidal TiO_2 on the fluorescence quenching of car was also studied to attain better understanding on the interception of the excited state of car on the TiO_2 surface. UV-vis absorption and UV-Vis diffuse reflectance spectra were also obtained to characterized the car dye adsorb semiconductors.

2. Experimental methods.

2. 1 Sample preparation and materials

Titanium (IV) 2-propoxide at 21 nm in diameter was purchased from Sigma Aldrich. All solvents were HPLC grade obtained from Aldrich.

The outer coating of the Annatto seeds of the *Bixa orellana* tree (50 g) were removed by ultra sonication and washed with hexane to extract the bixin [14] , followed by solvent removal by rotary evaporation. The crude residue was washed with cold solvent, further purified and dried. Norbixin was extracted by adding aqueous alkali to one part of the bixin residue obtained previously then heated for hydrolysis, followed by cooling. An aqueous solution was filtered and acidified with 5 M HCl to precipitate norbixin, washed with cold hexane, purified and then dried to obtain solid norbixin [22] . All of the samples were N_2 purged and stored at -20 °C. Compounds were characterized using UV-vis spectrophotometry and HPLC techniques. A HPLC series 1200 (Agilent, Waldbronn Germany) apparatus equipped with a multiwavelength/ photodiode array detectors was used for chromatographic analysis. The mobile phase consisting acetonitrile, methanol and ethyl acetate with 0. 05% (v/v) triethylamine was used at a flow rate 0. 5 ml/min.

2. 2 UV-vis, UV-vis DRS and fluorescence spectroscopy

Electronic absorption spectra were recorded using a Perkin-Elmer…….., Spectro UV-vis double beam spectrophotometer Model …………

UV-Vis diffuse reflectance (UV-Vis DRS) were obtained in the range of 200-900 nm with………BaSO4……… as the background on the Perkin-Elmer……. spectrophotometer equipped with a integrating sphere.

Fluorescence spectra were obtained at room temperature using Thermo Scientific Lumina spectro-fluorophotometer, using 10/10 nm slit widths. The excitation wavelength was 350 nm and the emission spectra were recorded between 460 and 660 nm. Fluorometric titrations were carried out by successive addition of 26. 3 mg dm $^{-3}$ of TiO_2 NPs colloid in EtOH with a micropipette. The fluorescence spectra were recorded under 300 K.

Photodegradation study of Car on TiO_2 coated and non-coated glass plates were investigated by irradiating the samples with broadband UV source Xenon arc lamp (……W) at a distance ……. A spray coating method was used to prepare TiO_2 coated glass plates having 2 cm×2 cm surface area. During irradiation, the solutions were stirred magnetically and the effect of carotenoid degradation in pure MeOH, O_2 purging and N_2 purging were analyzed by measuring the absorbance of the solution at 460 nm for each 10 min intervals.