Enhancement of the Photocatalytic Activity of TiO₂ Nanoparticles by Water-Soluble Complexes of Carotenoids[†]

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Received: September 4, 2009; Revised Manuscript Received: November 5, 2009

Photoirradiation of TiO₂ nanoparticles by visible light in the presence of the water-soluble natural polysaccharide arabinogalactan complexes of the hydrocarbon carotenoid β-carotene leads to enhanced yield of the reactive hydroxyl (OH) radicals. The electron paramagnetic resonance (EPR) spin-trapping technique using α-phenyl-*N-tert*-butyl nitrone (PBN) as the spin-trap has been applied to detect this intermediate by trapping the methyl and methoxy radicals generated upon reaction of the hydroxyl radical with dimethylsulfoxide (DMSO). The free radicals formed in this system proceed via oxygen reduction and not via the reaction of holes on the TiO₂ surface. As compared with pure carotenoids, carotenoid−arabinogalactan complexes exhibit an enhanced quantum yield of free radicals and stability toward photodegradation. The observed enhancement of the photocatalytic efficiency for carotenoid complexes, as measured by the quantum yield of the desired spin adducts, arises specifically from the decrease in the rate constant for the back electron transfer to the carotenoid radical cation. These results are important for a variety of TiO₂ applications, namely, in photodynamic therapy, and in the design of artificial light-harvesting, photoredox, and catalytic devices.

Introduction

Titanium dioxide is widely used in photocatalysis due to its ability to absorb UV light, producing active electron−hole pairs.[1−6] In an air-saturated aqueous solution, photoirradiation results in the formation of hydroxyl (OH) and superoxide radicals.[6,7] The hydroxyl radical is assumed to be the key species in the photocatalytic oxidation of organic materials deposited on TiO₂. These reactions are important in the field of water decontamination[8] as well as in photodynamic therapy.[9−14]

For medicinal applications, it is very important to extend the wavelength range of the irradiation to longer wavelengths since UV light has a lower penetration through living tissues. Various approaches have been attempted to enhance the visible-light utilization of TiO₂.[15−17] Recently, the carotenoid-modified TiO₂ was investigated as a potent system for photodynamic therapy and the design of artificial solar cells.[18−22] Effective photocurrent generation was demonstrated with visible light using the carotenoid-sensitized TiO₂ nanocrystalline mesoporous electrode.[20] Also, an increase in the yield of superoxide radicals was observed during irradiation of a TiO₂ suspension in organic solvents in the presence of carotenoids.[21]

Recently, we reported the study of the water-soluble complexes of carotenoids that formed with arabinogalactan (AG), a branched polysaccharide polymer with a molecular mass of 15 000−20 000[23] whose structure is given in Figure 1. Arabinogalactans are found in a variety of plants but are more abundant in the *Larix* genus, primarily Western and Siberian Larch.[24,25] Larch arabinogalactan is approved by the U.S. Food
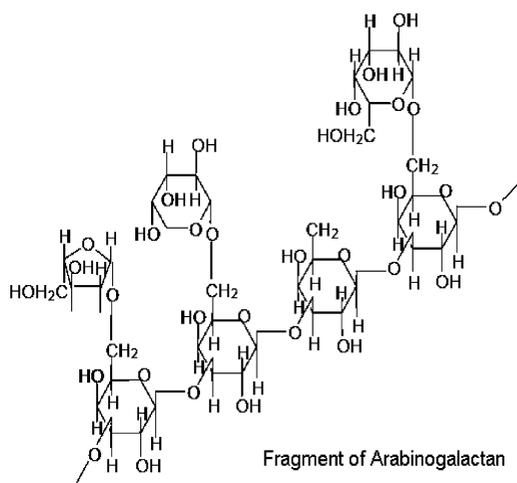
Figure 1. Fragment of the structure of the natural polysaccharide arabinogalactan with a molecular mass of 15 000−20 000.

and Drug Administration (FDA) as a source of dietary fiber but also has potential therapeutic benefits as an immune-stimulating agent and cancer protocol adjunct. Moreover, complexes of carotenoids with arabinogalactan show enhanced stability toward photodegradation as well as toward oxidation by reactive oxygen species in solution.[23] The advantages of carotenoids as sensitizers are their high extinction coefficients in the visible region (400−600 nm) and the stability of their radical cations.[23] In our previous study, it was found that the yield of O₂•⁻ radicals increased during irradiation of a suspension of TiO₂ in organic solvents at low (<30 μM) carotenoid concentration.[21] The additional advantage of complexes of carotenoids is the water solubility, which allows their use in many pharmaceutical formulations.

The main goal of this paper is to demonstrate that the presence of a β-carotene$-$AG complex in a water suspension of TiO_2 nanoparticles enhances the yield of reactive hydroxyl radicals during visible-light irradiation of this system.

Experimental Section

β-Carotene was provided by Fluka and was kept at -18 °C.

β−Carotene
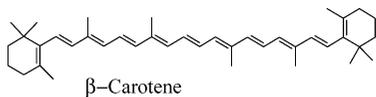
Arabinogalactan was extracted from *Larix sibirica*.[26] Pharmaceutical-grade larch arabinogalactan is a fine, dry, off-white powder with a slightly sweet taste and mild pine-like odor. It dissolves completely in water or juice, exhibits a low viscosity, and is therefore easy to administer, even to children. For preparation of the complex, we used a mechanical treatment of the solid mixture of β-carotene carotenoid crystals with the arabinogalactan powder. Typical mechanical reactions are achieved by cogrinding or milling the powder materials. These preparations are usually carried out either manually, in an agate mortar, or electromechanically, as in ball milling. In all of these cases, the crystal lattice is destroyed and re-formed through recrystallization. In such processes, hydrogen bonds, π-stacking, van der Waals, ion pairing interactions, and so forth, are broken and formed through the reaction process, leading to formation of supramolecular compounds or hybrid molecular crystals.[27,28] In the present study, the samples were prepared electromechanically. Cogrinding of solid material results in penetration of the carotenoid molecules into the arabinogalactan polymer without using any organic solvents. This approach allowed us to prepare water-soluble composites of the β-carotene water-insoluble hydrocarbon for the first time. The estimated solubility of this complex exhibited a molar stoichiometry of 1:1 and, by HPLC analysis, was 1.4 mM in a water solution. X-ray diffraction analysis of the solid complex was performed using a conventional X-ray diffractometer DRON-3 with Cu Kα radiation. Differential scanning calorimetry (DSC) of these samples was also performed using DSC-550 (Instrument Specialists Inc.) in an argon atmosphere ($20 < T < 250$ °C).

Free radicals were photogenerated by visible-light irradiation ($\lambda > 380$ nm) of a water suspension of the TiO_2 powder (7 nm particles from Ishihara Sangyo Kaisha, Ltd., Japan) in a quartz EPR capillary (0.7 mm). Free radicals were detected by the EPR spin-trapping technique.[21] The spin adducts of *N-tert*-butyl-α-phenylnitrone, PBN (Aldrich), were detected with a Bruker ELEXSYS E-680 W/X FT/CW pulse X-band spectrometer equipped with a MD5-W1 dielectric resonator. The spectrometer is controlled through a Linux workstation with Xepr, the Bruker data acquisition and manipulation software.

Results and Discussion

Preparation of the β-Carotene$-$Arabinogalactan Composites. Complex formation was established by use of differential scanning calorimetry (DSC) techniques and X-ray diffraction phase analysis. The results of these measurements were similar (compare Figures S1 and S2 in the Supporting Information) as those reported earlier for the canthaxanthin$-$AG complex.[23] Namely, the characteristic peaks of the crystal
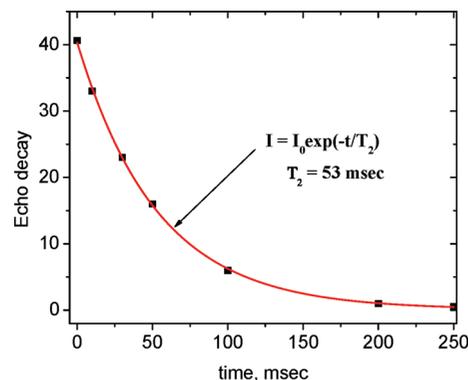
Figure 2. Changes in the NMR echo signal intensity of the 5-substituted methyl protons of β-carotene versus time delay ($t = 2\tau \times n$; see Experimental Section) in a D_2O solution of a β-carotene$-$AG complex.

structure of the carotenoid β-carotene and arabinogalactan disappear after mechanical treatment of the mixture. It is suggested that the absence of a crystal structure is due to the molecular penetration of the carotenoid into the arabinogalactan polymer matrix. The penetration of the carotenoid deep into the arabinogalactan matrix does not occur when we try to prepare the complex by addition of a carotenoid solution to an arabinogalactan solution. This is consistent with the significant increase in the solubility of the complex prepared mechanically as compared with that of traditional solvent-mediated methods.

These results suggest that the complex formation occurs in the solid state but not during further solubilization. The important advantage of this mechanical method over solvent-mediated methods is the possibility of preparing complexes without using any toxic organic solvents.

The formation of the β-carotene$-$AG complex in a water solution was confirmed by the measurement of the relaxation time (T_2) of the carotenoid methyl protons by high-field NMR techniques (Figure 2).

It is well-known that the T_2 values of the protons are very sensitive to the mobility of the molecule. The restricted mobility of the "guest" molecule in a complex results, as a rule, in an increased relaxation rate. To measure T_2 relaxation, the Carr$-$Purcell$-$Meiboom$-$Gill pulse sequence was utilized from the Advance version of the Bruker pulse sequence library, $p(90°) - (\tau - p(180°) - \tau)_n - $ acquisition, where $\tau = 0.6$ ms and n varied from 0 to 4028. The time dependence of the resulting NMR echo signal intensity ($t = 2n\tau$) is given in Figure 2 for the 5-substituted methyl protons (1.18 ppm). This time dependence is described by a monoexponential decay function, $I(t) = I_o \cdot \exp(-\tau/T_2)$.

A T_2 value of 53 ± 1.5 ms was calculated by fitting the experimental data shown in Figure 2 to the monoexponential decay function. The T_2 value measured for the 1-substituted methyl protons of β-carotene (1.03 ppm) is 65 ± 5 ms for the β-carotene$-$AG complex, whereas the characteristic T_2 values for homogeneous solutions are $500-1000$ ms. Because the echo signal decay is well approximated by a monoexponential function, it can be suggested that the equilibrium between the complex and free carotenoid is completely shifted to the complex.

EPR Study of the Free Radicals Generated by Photoirradiation of β-Carotene-Modified TiO_2 in Solution. The electron paramagnetic resonance (EPR) spin-trapping technique with α-phenyl-*N-tert*-butyl nitrone (PBN) as the spin-trap was

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used to detect the free radical intermediates formed during the photoirradiation of the photocatalytic system, β-carotene-modified TiO$_2$ and its complexes with AG.

PBN   spin-adduct
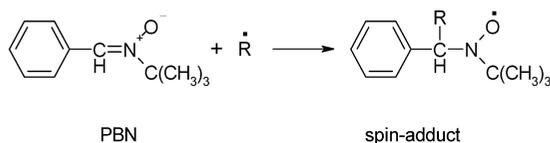
It is known from EPR spin-trapping measurements that UV irradiation of titanium dioxide in a water solution leads to the formation of hydroxyl and superoxide radicals[6,7,29] according to the reactions given below.

$$TiO_2 \overset{h\nu}{\rightleftarrows} TiO_2(h^+ + e^-) \tag{1}$$

$$TiO_2 + Car \overset{h\nu}{\rightleftarrows} TiO_2(+e^-) + Car^{\bullet+} \tag{2}$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \tag{3}$$

$$2O_2^{\bullet-} + 2H_2O \rightarrow 2\dot{O}H + 2OH^- + O_2 \tag{4}$$
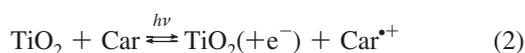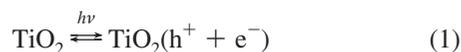
In reactions 1 and 2, Ti(IV) is converted to Ti(III) by electron capture, and in the presence of carotenoid, the holes are trapped by the carotenoid, producing the corresponding radical cation. Another pathway might be light absorption by carotenoids following electron transfer to TiO$_2$. Due to the short lifetime of excited states of carotenoids, this process might be effective only in the case of strong binding of the arabinogalactan complex with the surface. At this moment, we do not have additional evidence of carotenoid binding to the TiO$_2$ surface. The quantum yield of the hydroxyl radical (reactions 3 and 4) formed during the photoirradiation of the TiO$_2$ surface was measured[30] as 7×10^{-5}. It was suggested that the low quantum yield of radical production is due to the high probability of back electron transfer.

In our study, we added a small amount of DMSO to the solution since DMSO is widely used as a trap for the rapidly reacting $\bullet$OH radical to generate more stable methyl radical according to the equation

$$\bullet OH + DMSO \rightarrow \bullet CH_3 + CH_3(OH)SO \tag{5}$$
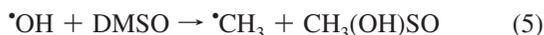
The role of dissolved oxygen on the efficiency of our photocatalytic system was first investigated.

In Figure 3 is given the EPR spectra of the spin adducts formed during irradiation of a water suspension of TiO$_2$ nanoparticles covered by pure β-carotene in air-saturated (top), oxygen-saturated, and nitrogen-saturated (bottom) solutions. The EPR hyperfine couplings deduced from spectral simulation of the spin adduct EPR spectra and compared to the Spin-Trap Data Base [http://tools.niehs.nih.gov/stdb/index.cfm] confirmed the generation of methyl radicals in the air-saturated solution ($a_N = 1.65$ mT, $a_H = 0.36$ mT) and both $\bullet$CH$_3$ and $\bullet$OCH$_3$ radicals ($a_N = 1.50$ mT, $a_H = 0.30$ mT) in the oxygen-saturated solution. No radicals were detected in the oxygen-free solution. This observation confirms that no free holes (h$^+$) are present in solution in our experimental conditions, and the main reaction route for free radicals generated in this system is the reaction of a solvated electron with oxygen (reactions 3 and 4).

The carotenoid radical cations are not stable enough in aqueous solution to form a steady stable radical concentration
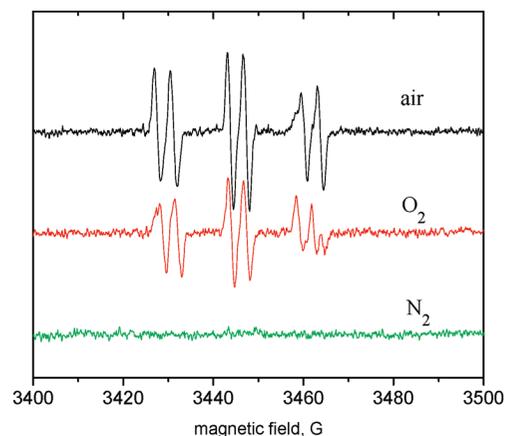
Figure 3. EPR spectra of the spin adducts formed during irradiation of a water suspension of TiO$_2$ nanoparticles covered by pure β-carotene, 20:1 (by weight), irradiated 1 min with visible light in a 10% DMSO aqueous solution in the presence of 25 mM PBN.
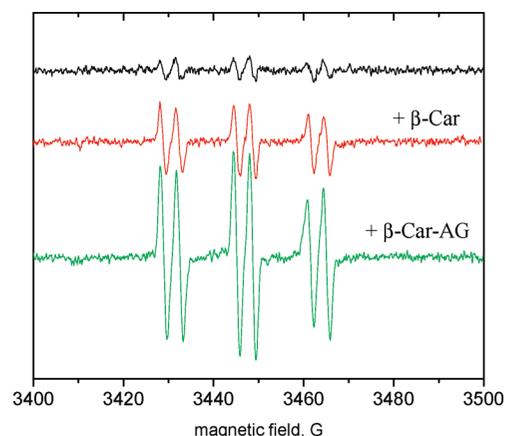
Figure 4. EPR spectra of PBN−CH$_3$ spin adducts formed during irradiation of a water suspension of TiO$_2$ nanoparticles in the absence (upper) and in the presence of β-carotene or a β-carotene−AG complex (lower) with $\lambda > 350$ nm in a 10% DMSO aqueous solution in the presence of 25 mM PBN.

detectable by EPR methods (lifetime < ms). However, both the carotenoid radical cation and Ti(III) are observed in a solid-state complex.[23] The production of the PBN−OCH$_3$ adduct in oxygen-saturated solution is most likely initiated by the reaction of methyl radicals with the dissolved oxygen.[29]

$$\bullet CH_3 + O_2 \rightarrow \bullet OOCH_3 \tag{6}$$

$$2\bullet OOCH_3 \rightarrow 2\bullet OCH_3 + O_2 \tag{7}$$
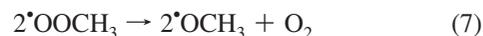
A comparison is made in Figure 4 regarding the EPR spectra of the PPN−CH$_3$ spin adducts detected during irradiation of a water suspension of TiO$_2$ nanoparticles in the absence of β-carotene (Figure 4a) and in the presence of pure β-carotene (Figure 4b) and the β-carotene−AG complex (Figure 4c) in an air-saturated aqueous solution. In all three samples, the same concentration of TiO$_2$ was used. The most intense EPR signal occurred for the water suspension of TiO$_2$ nanoparticle containing a complex of β-carotene and AG. This demonstrates that the carotenoid−AG complex provides the maximum photocatalytic efficiency during visible light irradiation with $\lambda > 380$ nm. Here, photocatalytic efficiency means the quantum yield of the desired spin adducts. This occurs because the AG complex of β-carotene has prevented the back electron transfer to β-carotene, resulting in electron transfer to oxygen (reaction 3). The

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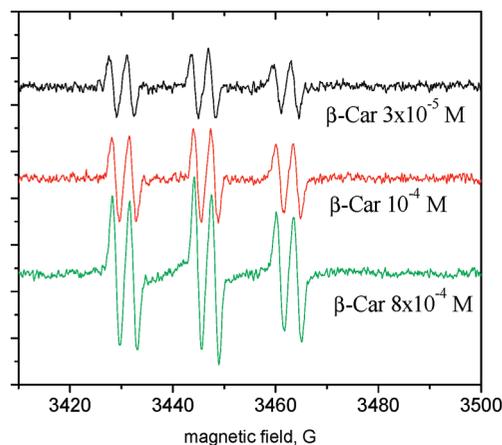
Figure 5. EPR spectra of PBN−CH₃ spin adducts formed during irradiation of a water suspension of TiO₂ nanoparticles (2.5 mg/mL) at various concentrations of a β-carotene−AG complex in a 20% ethanol aqueous solution in the presence of 25 mM PBN.

increased presence of $O_2^{\bullet-}$ results in further $^\bullet CH_3$ production via the reaction of $O_2^{\bullet-}$ with water (reaction 4) producing the $^\bullet OH$ radical. Subsequently, the $^\bullet OH$ radical reacts with DMSO to form $^\bullet CH_3$ according to reaction 5.

As was mentioned above, the use of a pure carotenoid in photocatalytic devices is restricted by their ability to scavenge free radicals. It was demonstrated earlier that radical production in the TiO₂−carotenoid system decreases with increasing carotenoid concentration.[21] On the other hand, the β-carotene−AG complex tends not to scavenge free radicals in aqueous solution.[23] It was demonstrated[23] that the carotenoid−AG complexes are stable for at least 10 min in the presence of free radicals generated by the photo-Fenton reaction 8.[31,32]

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \dot{O}H$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + \dot{O}H \qquad (8)$$
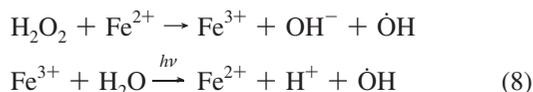
To confirm this advantage of the complex, an experiment was carried out over a carotenoid concentration range from 0.03 to 0.8 mM (Figure 5). In this experiment, a 20% ethanol aqueous solution was used instead of a DMSO solution. As one can see, the increase in carotenoid concentration does not reduce the photocatalytically produced radicals.

The advantage of using carotenoids as sensitizers is not only their high extinction coefficients in the visible area but also the stability of their radical cations due to the presence of a long unsaturated chain. This structural feature significantly reduces the rate of back electron transfer. On the other hand, the disadvantages of using pure carotenoids for photodynamic therapy are their ability to scavenge free radicals and the tendency of the carotenoid radical cations to deprotonate in the presence of water. This tendency reduces the efficiency and lifetime of the carotenoid−TiO₂ system as a photocatalyst. The ability of carotenoids to scavenge free radicals ($^\bullet OH$, $^\bullet OOH$, $^\bullet OR$, $^\bullet CH_3$, $^\bullet CH_2OH$, $^\bullet NO_2$, and others) by electron transfer [Car + ROO$^\bullet$ → Car$^{\bullet+}$ + ROO$^-$], by hydrogen abstraction [Car + ROO$^\bullet$ → Car$^\bullet$ + ROOH], or by addition [Car + ROO$^\bullet$ → ROOCar$^\bullet$] is a subject of several reviews and research papers.[33-35] The interest in this ability is stimulated by epidemiological evidence that dietary carotenoids, which are constituents of fruits and vegetables, can reduce the risk of cardiovascular disease and certain types of cancer. It was suggested that carotenoids act as chain-breaking antioxidants which reduce oxidative stress

in organisms by scavenging damaging oxygen-centered hydroxyl, peroxyl, or alkoxyl radicals. Characterization of the free radical scavenging properties of carotenoids and the properties of the carotenoid radicals arising from such reactions was performed using EPR spin-trapping, laser flash photolysis, and pulse radiolysis techniques.[33-35] As a result of this reaction, less reactive resonance-stabilized carotenoid adducts or radical cations were formed.

Another important question is the stability of the photocatalyst. Usually, carotenoids exhibit a high photodegradation rate in the presence of water. Using β-carotene and canthaxanthin as the examples, it was demonstrated that electrochemically generated radical cations can undergo reversible deprotonation in organic solution.[36] This reversible process can be disrupted by the formation of neutral carotenoid radicals in the presence of water molecules which act as an proton acceptor. Here, it has been shown that supramolecular complexes of carotenoids with AG exhibit a significant increase in photostability in aqueous solutions as compared with pure carotenoids.[23] This may be due to inhibition of subsequent reactions of the neutral radical.[37]

In conclusion, the water suspension of TiO₂ nanoparticles in the presence of the β-carotene−AG complex gives rise to a more efficient photocatalyst when compared to that for a sample with pure β-carotene adsorbed on TiO₂ as well as with pure TiO₂ nanoparticles. It is to be noted that the efficiency of electron transfer from dye molecules to TiO₂ is possible only in the case of effective binding with the surface.[18-20] A previous photocurrent study[18,20,22] showed that in homogeneous organic solvents, efficient electron transfer occurred only for carotenoic-acid-sensitized TiO₂, where the carboxylic acid group binds to the TiO₂ surface. The lack of a binding carboxylic acid reduces the photocurrent generated by several orders of magnitude.[18] We suggest that the presence of hydroxyl and carboxyl groups in the matrix of arabinogalactan can provide such effective binding of the carotene−AG complex with the TiO₂ surface. However, these linkages are not stable in water. Probably, a chelating mode is involved in the binding process.[38]

Supporting Information Available: The crystal structure and DSC measurement of β-carotene (Figure S1) and canthanxathin (Figure S2) and the polymer, arabinogalactan, before and after mechanical treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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