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S-layer proteins as possible immobilization matrix for photocatalysts – OH radical scavenging capacity and protein stability

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ABSTRACT

Supported nanostructured photocatalysts were improved by using novel biohybrid materials based on bacterial S-layer proteins. Within the development of advanced photocatalytic materials supported with bacterial S-layer proteins, the OH radical scavenging capacity of suspended S-layer proteins in a photocatalytic system was determined with 2.39×10^5 (mg protein)$^{-1}$ s^{-1} using tertiary butanol OH radical assay. Furthermore, applying the photocatalyst in suspension, S-layer proteins inhibit the photocatalytic process by covering the ZnO nanoparticles. This effect is related to the protein concentration and can be described by a saturation function. S-layer proteins were not conspicuously damaged, such as fragmentation, by photocatalytic treatment. Only a slight cross-linking was visible by gel electrophoresis. For future use, immobilized S-layer proteins will be utilized in significantly lower amounts. Therefore the inhibition by covering particles and the relatively low scavenging capacity will not strongly affect the OH radical yield of the final composite. These findings were also confirmed by degradation experiments with diclofenac. Based on these findings it can be concluded that the implementation of nanoscaled biocomposite materials using S-layer proteins for the preparation of multi-functional coatings for photocatalytic applications is promising.

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1. Introduction

Photocatalysis belongs to the "advanced oxidation processes" (AOPs). These processes are primarily based on the generation and further reaction of hydroxyl radicals (OH radicals or •OH). OH radicals are obviously more reactive than the other oxidative species also used in water and wastewater treatment [1,2]. For photocatalytic water treatment, different nano-scaled semiconductor materials, powdery or variously immobilized, are used as catalyst [3–6]. These materials, for instance TiO_2 or ZnO, are capable to transform the energy of absorbed photons (UVA irradiation or visible light) into charge carriers. The resulting electrons (e^-) and positive holes (h^+) diffuse to the surface of the semiconductor and react with water and oxygen adsorbed on the catalyst surface in aqueous media. This mechanism is shown by the following equations (Eqs. (1)–(4)) [5,7,8] and can be assigned to heterogeneous catalysis reactions.

$$TiO_2 \xrightarrow{h\nu} TiO_2\,(h^+ + e^-) \quad (1)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH_{ad} \quad (2)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

$$e^- + O_2 \rightarrow {}^{\bullet}O_2^- \quad (4)$$

Current investigations on the improvement of photocatalytically active materials are mainly focused on reaching a stable material immobilization. In addition, material modifications were forced to move the active wavelength into the range of visible light.

Once these objectives are accomplished, photocatalysis is a promising alternative technology for the removal of organic pollutants in water or other matrices, particularly at low concentrations [9].

The aim of our work is to develop and to characterize stable photocatalytic active coatings, which can be placed in water

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treatment plants to eliminate different anthropogenic contaminations. These materials should have highly specific surfaces and ordered crystalline lattices without any defects to prevent recombination of the charge carriers and provide enhanced formation of •OH. Nanotechnology in combination with biotechnology can give an important contribution to reach this aim. Nanobiotechnology enables the development of innovative materials using biomolecules. Self-assembling surface layer proteins (S-layer proteins) from bacteria recovered from a uranium mining waste pile are particularly suitable for such an application due to their stability and metal binding properties [10]. These proteins build regular para-crystalline porous networks of high stability covering the bacteria cell to protect it from outer influences [11,12]. Furthermore, it is assumed that S-layer proteins are able to absorb free radicals and are thusly responsible for a higher resistance toward reactive radicals [13,14]. Nevertheless, direct proof of the latter was so far missing.

After isolation, S-layer proteins have the essential property to recrystallize on interfaces and surfaces into highly organized monolayers [15–17]. The special assembly of protein monomers and their biochemical properties allow the production of well-defined and highly ordered nanoparticles or nanostructures supported by S-layers [18–21]. As a result of isolated and non-aggregated immobilization of the semiconductor nanoparticles using S-layer protein acting as templates, the efficiency of the photocatalytic reaction can be enhanced. Furthermore, well-distributed functional groups on the surface of S-layer proteins enable the binding of ionic compounds such as metal ions [19,22] or the coupling of other functional molecules [23,24]. In addition, S-layer proteins are a suitable matrix for mineral formation [25] and possess generally a high application potential in bionanotechnology and for the production of defined nanostructures [26–31].

Based on this, the application of nano-scaled composite materials, which combine biomolecules, inorganic materials, and organic molecules in a simple way, allows preparation of multi-functional coatings for e.g. photocatalytic applications.

Before using biomolecules in advanced oxidation processes, e.g. photocatalysis, it is necessary to investigate the influence of OH radicals on S-layer proteins as well as the influence of S-layer proteins on the photocatalytic active material used. Based on the advisement that these effects occur to a higher extent in suspension in comparison to immobilized materials, nano zinc oxide suspensions spiked with S-layer protein suspensions were used to investigate systematically OH radical formation, scavenging, and protein stability.

To reveal and understand possible influencing parameters/processes, it is essential to explain the physiological behavior of S-layer proteins in suspension. Considering S-layer proteins build monolayers on surfaces, consequently they are also able to envelop zinc oxide nanoparticles. Based on this, a theory was devised that the influence consists primarily of two effects. First, S-layer proteins inhibit the photocatalytic process by covering ZnO nanoparticles. Second, they can act as radical scavenger inactivating the active oxygen species which were generated. The influence of both factors should increase with increasing protein concentration. In this study, these influencing effects were examined. Therewith, to the knowledge of the authors, the OH radical scavenging capacity of S-layer proteins was investigated for the first time. Additionally, the applicability of S-layer proteins as immobilization matrix for photocatalysts for the degradation of environmentally relevant pharmaceuticals such as diclofenac was also confirmed.

2. Theoretical background

In this work, it was necessary to determine OH radical yields in absolute terms. For this purpose, tertiary butanol (*t*BuOH) was added in such large concentrations to the system that the scavenging capacity of the S-layer proteins ($k_1 \times$ [protein]) was suppressed. Since the experiments were conducted in ultrapure water no further scavenging has to be expected. The probe *t*BuOH reacts with OH radicals nearly diffusion controlled ($k_2 = 6 \times 10^8\ M^{-1}\ s^{-1}$). For that reason, practically all OH radicals react with *t*BuOH under such conditions [32]. Even recombination of OH radicals is excluded, because of high excess of *t*BuOH.

$$\bullet OH + \text{protein} \xrightarrow{k_1} \text{protein-}\bullet OH \quad (5)$$

$$\bullet OH + t\text{BuOH} \xrightarrow{k_2} t\text{BuOH-products, e.g. formaldehyde} \quad (6)$$

Under aerobic conditions, formaldehyde is a prominent product. In a radiolytic study, formaldehyde yield was found to be ~25% in relation to the formed OH radicals [33]. Because of using photocatalysis, no further chemicals have to be added and thus there are no special cross reactions expected. Moreover, since *t*BuOH in absolute excess scavenges practically all OH radicals, the formed formaldehyde is protected from further oxidation by OH radicals within the whole experimental period. Therefore, OH radicals formed in the experimental setup can be assayed by determining formaldehyde in absolute terms [33,34]. Furthermore, the OH scavenging capacity of the water matrix can be determined by competition kinetics, as previously employed by Nöthe [32]. For this purpose, the *t*BuOH concentration has to be varied in a wide range. In a competition kinetic experiment, two substrates (here *t*BuOH and S-layer protein) react with one reagent (here OH radicals generated by photocatalysis). While the product of the reaction with *t*BuOH (formaldehyde) can be monitored (reaction (6)) the other reaction (reaction (5)) remains silent [35]. The reaction of various *t*BuOH concentrations with a constant OH radical dose in presence of a certain concentration of S-layer protein was monitored by analysis of the formed formaldehyde. In all investigations *t*BuOH and S-layer proteins are in absolute excess toward the reaction product formaldehyde. A constant OH radical dose was ensured by constant illumination times (radiation dose) and steady amount of photocatalytic active material. The maximum formaldehyde yield $[HCHO]_{max}$ generated through the OH radical dose in this experimental setup was determined by a corresponding reference value without any protein.

In absolute excess of *t*BuOH that overruns any scavenging of S-layer protein and for a given OH radical dose the formaldehyde yield [HCHO] is $[HCHO]_{max}$ (Eq. (7)).

$$[HCHO] = [HCHO]_{max} \quad (7)$$

Based on the reactions (5) and (6), the following equation (8) can be derived applying the approach of competition kinetics [32,35,36].

$$[HCHO] = [HCHO]_{max} \frac{k_2[t\text{BuOH}]}{(k_2[t\text{BuOH}] + k_1[\text{protein}])} \quad (8)$$

Eq. (8) is rearranged to Eq. (9).

$$\frac{[HCHO]_{max}}{[HCHO]} - 1 = \frac{k_1[\text{protein}]}{k_2[t\text{BuOH}]} \quad (9)$$

A plot of $([HCHO]_{max}/[HCHO]) - 1$ versus $[t\text{BuOH}]^{-1}$ leads to a straight line. As the value of k_2 is known, from its slope the OH scavenging capacity of the S-layer protein (k_1[protein]) can be obtained [32,35]. Because of equation (7), usually competition kinetic experiments lead to a straight line crossing the origin of coordinates [35]. Hence, a divergence between [HCHO] in excess of *t*BuOH in presence of S-layer protein and $[HCHO]_{max}$ of the corresponding reference value points to another effect in this system, e.g. the inhibition of the photocatalytic process caused by S-layer proteins covering ZnO nanoparticles. From the gap between formaldehyde

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