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Selective Photocatalysis by Means of Molecular Recognition

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Heterogeneous photocatalysis, using titanium dioxide as the photocatalyst of choice, is a useful technique for the degradation of many contaminants in air, in water, or on solid surfaces.[1] The process, initiated by the generation of electron−hole pairs following absorption of supra-bandgap photons, continues, in most cases, through oxidation by hydroxyl radicals formed when the photogenerated holes interact with adsorbed water. As such, the process is nonselective, although some selectivity can be obtained by altering the charge on the surface of the photocatalyst, for example by controlling the pH.[2] Since many contaminants can be degraded readily by biological methods, while others are nonbiodegradable, it would be of great advantage if one could use photocatalysis and biological treatment sequentially, such that photocatalysis will be used to degrade nonbiodegradable contaminants to simpler molecules that can be handled biologically. In such a scenario, the need for selectivity is obvious, since contaminated media often contains a large variety of contaminants. Furthermore, since the allowable concentration of a hazardous substance is lower than that of a less hazardous material, it would be beneficial to have a mechanism that would increase the degradation rate of the former, even at the expense of some reduction in the degradation rates of the latter.

In this communication we report on an approach to achieve selectivity, based on molecular recognition sites constructed on inert domains located in the vicinity of titanium dioxide. Although the method is demonstrated hereby for one pair of contaminants, namely benzene and 2-methyl-1,4-naphthoquinone (2MNQ), it can easily be extended to other systems. Likewise, although the samples presented here were prepared on solid films, it should not be too complicated to extend this attitude to powders or the like.

The basic concept is portrayed in Figure 1. Molecular recognition sites (MRS), in this example thiolated, are constructed on inert sites located in the vicinity of titanium dioxide. Due to the affinity between the MRS and the target molecules (here, 2MNQ), the target molecules adsorb on the MRS, from where they surface-diffuse to the photocatalytic sites. Since the molecular recognition sites are organic in nature, care has to be taken to prevent the degradation of the MRS. Constructing the MRS on inert sites is therefore necessary, but is not sufficient, since oxidizing species can travel on inert surfaces, such as silicon, for quite a long distance.[3,4] The observation that self-assembled monolayers on gold and platinum, located near titanium dioxide domains, are not prone to an attack by oxidizing species formed on titanium dioxide[4b] enables one to construct such arrays which serve to "shuttle" contaminants of interest. It should be mentioned that although the surface diffusion of contaminants from adsorptive, inert sites to photocatalytic sites is documented,[5] we are not aware of any attempts to achieve selectivity by combining surface diffusion and molecular recognition.

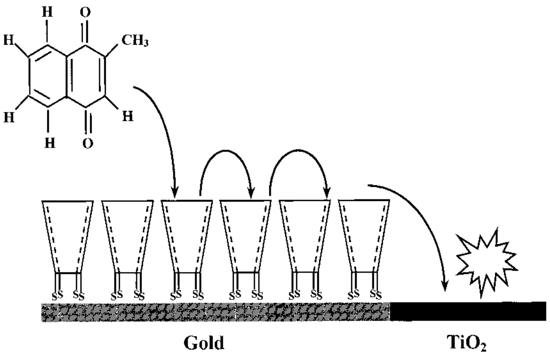

Figure 1. The basic concept.

Thiolated β-cyclodextrin (TCD) was chosen as the molecular recognition site in this work, based on the well-known affinity between this molecule and a variety of hazardous contaminants.[6] This affinity is due to the well-defined cavity found in this cyclic glucose oligomer, which facilitates the hosting of molecules such as 2-methyl-1,4-naphthoquinone or *p*-benzoquinone.[7]

Experiments were performed in three types of substrates. Type A substrates consisted of a thin layer (100 nm in thickness) of titanium dioxide produced by spin-coating an organometallic precursor on 1 in. silicon wafers as described earlier.[8] Type B substrates consisted of type A substrates onto which a repetitive structure made of equal and parallel gold stripes (75 nm in thickness, 5 to 40 μm in width, spacing between adjacent stripes being equal to the width of the stripes) was deposited. For details on the preparation of type B samples see ref 4b. The structures described in Figure 1 (denoted hereby as type C substrates) were prepared by dipping type B wafers in a DMSO/water solution (3:2 v/v) that contained 1 mM per-6-thio-β-cyclodextrin for 12 h. A thorough washing with methanol and water then drying under nitrogen followed this step. The thiolated β-cyclodextrin used for chemisorption on the gold stripes was prepared from β-cyclodextrin (ICN Biomedicals Inc.) following a published scheme[9] and was characterized by NMR and FTIR.

Reflection mode FTIR (Equinox IFS55, Bruker) of type C films revealed spectra which were similar to the one reported by Nelles et al.,[10] where coupled ν(C−C/C−O) vibrations at 1048 and 1069 cm^{-1} and a prominent absorption peak at 1156 cm^{-1} corresponding to the antisymmetric (C−O−C) stretching vibration were observed. Immersion of type C wafers in a 2 mM solution of 2-methyl-1,4-naphthoquinone (2MNQ) in water/propanol (1:1 (v:v)) for 12 h, followed by a thorough washing and drying, yielded typical naphthoquinone peaks at 1666 and 1594 cm^{-1}, together with a slight shifting in the 1157 cm^{-1} cyclodextrin-related peak to 1154 cm^{-1}, probably due to the formation of the cyclodextrin−naphthoquinone inclusion complex. In contrast, no evidence for

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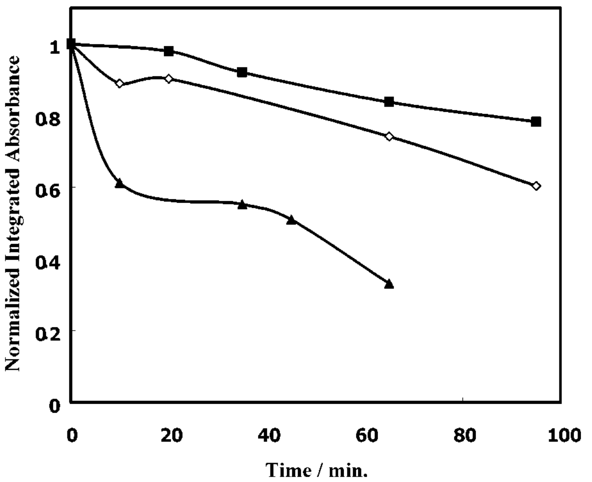

Figure 2. The photodegradation kinetics of 2-methylnaphthoquinone on the type (C) wafers for samples containing Au/TiO_2 stripes of different width. In all samples, the width of the gold stripes was equal to that of the TiO_2 stripes. Filled triangles represent stripes 5 μm in width, empty diamonds represent stripes 20 μm in width, and filled squares represent stripes 40 μm in width.

2MNQ adsorption on gold or on TiO_2 was found for type A and type B substrates.

Photocatalytic measurements were performed in air by exposing the Au/TiO_2 hybrid structures containing the adsorbed 2MNQ on β-cyclodextrin under 365 nm UV radiation (0.07 mW/cm^2) for different periods of time. Following exposure, a decrease in the peaks assigned to the 2MNQ was observed. This decrease was not accompanied by a decrease in the β-cyclodextrin related peaks. Figure 2 presents the kinetics of photocatalytic degradation of 2MNQ, based on the area of the 1666 cm^{-1} peak, for structures having stripes of different sizes. In all wafers, the width of the gold stripes was equal to that of the titanium dioxide, such that the photocatalytic area was equal to 50% for all wafers. As shown in the figure, the smaller the domain width was, the faster the photodegradation of the 2-methyl-1,4-naphthoquinone was. For example, 20% degradation was obtained with the 5 μm width structure after 5 min, whereas the same extent of degradation with the 40 μm width structure required 90 min. This effect of the domain size is in line with the notion that the 2MNQ molecules were adsorbed on the molecular recognition sites, from where they diffused to the photocatalytic titanium dioxide domains. The observation that the degradation of the 2MNQ was not accompanied by a degradation of the molecular recognition sites is in line with the presented mechanism, according to which the photodegradation of 2MNQ in this hybrid structure stemmed from diffusion of contaminants and not from out-diffusion of the oxidizing species. A control experiment where 2MNQ adsorbed on β-cyclodextrin chemisorbed on gold-coated silicon (without titanium dioxide) yielded a negligible decrease in the amount of 2MNQ on the surface even after 1 h of exposure.

The enhanced selectivity of the type C structure was tested in the liquid phase by comparing between the disappearance rate of 2MNQ versus that of benzene. Three types of solutions were prepared and measured: 2MNQ [2.3 mM], benzene [0.25 mM], and a mixture containing the two contaminants [benzene 0.25 mM, 2MNQ 2.3 mM]. As a solvent, 60 mL of a mixture of water−propanol (1:1 v/v) was used. Experiments consisted of exposing sealed Petri dishes containing the solutions and three identical 1 in. wafers to UV light (0.09 mW/cm^2) for 30 min. Aliquots were taken prior to and after exposure and were measured immediately by Circle-Cell Attenuated Total Reflection FTIR. The photodegradation with type C and type B substrates (both having stripes of width 5 μm), as well as with type A wafers, was tested. Table 1 presents the extent of decrease in the concentration of both contaminants following exposure, and the ratio between the relative degradation in 2MNQ to that of benzene, for solutions containing one contaminant at a time and for solutions containing both contaminants. The data in the table were deduced from changes in the height of relevant IR peaks. Although IR peak heights may not be exactly proportional to concentrations, they still can serve as a rough indication for the extent of degradation. A comparison between the three types of wafers reveals that for both types of solutions the type C wafers were significantly more efficient in photodegrading 2MNQ than the type B wafers (60% degradation vs 18.7% degradation, and 32.6% vs 19.8%), demonstrating the enhancement in photodegradation due to the molecular recognition sites. In contrast, the photodegradation rate for benzene with the type C wafers was lower than that with the type B wafers. The overall effect is reflected in the ratio between the degradation rate of 2MNQ to that of benzene, where an increase of more than 10 times (8.1:0.75) was found when comparing solutions containing one contaminant at a time, and an increase of 6 times (4.2:0.71) when solutions containing a mixture of the two contaminants were compared. Hence, the feasibility of obtaining selectivity by constructing molecular recognition sites at the vicinity of titanium dioxide is clearly demonstrated. It is noteworthy that the extent of degradation of both contaminants with the type A wafers was found to be similar to that with the type B wafers, although the photocatalytic area was two times bigger (due to the lack of the gold stripes in the former). Hence, these results may reflect some positive effect of the metal on the degradation rate as was found in many TiO_2/metal systems.[11]

Table 1. The Extent of Decrease in the Concentration of Benzene and of 2-Methylnaphthoquinone following Exposure of Vessels Containing the Various Types of Wafers to 365 nm Light and the Ratio between the Extent of Degradation of 2MNQ to that of Benzene

	one-contaminant solutions[a]			two-contaminant solutions[a]		
	type A	type B	type C	type A	type B	type C
2MNQ	22.3%	18.7%	60%	13%	19.8%	32.6%
benzene	26%	25%	7.4%	26.3%	28%	7.7%
2MNQ/ benzene	0.86	0.75	8.11	0.49	0.71	4.23

[a] Type A (TiO_2); type B (Au/TiO_2); type C (TCD/Au/TiO_2).

Since both adsorption and diffusion are temperature-dependent phenomena, it is likely that changing the temperature may alter the selectivity factor. Hence, it is important to mention that this enhancement in selectivity was obtained at room temperature without any attempt to optimize conditions. Moreover, selectivity is expected to further increase when using smaller domains, such as on powders, where the diffusion length is shorter. Work along these lines with other contaminant−MRS systems is currently under investigation.

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