# Modeling the Activity and Selectivity of Semiconductor Photocatalysts in Heterogeneous Photocatalyzed Processes. Inclusion of Subsurface Electric Fields in the Space Charge Region.

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In this study we consider modeling a photochemical reaction on the surface of a solid photocatalyst, which involves photogenerated charge carriers affected by a sub-surface electric field. Two major properties of photocatalysts, namely their activity and selectivity, are examined. The analysis of factors that govern the activity and selectivity of photocatalysts is based on the solution to the continuity equation found using the quasi steady-state approach.

$$-\frac{dj(x)}{dx}-\frac{n(x)}{\tau}=-g(x) \tag{1}$$

where $n(x)$ is the concentration of the charge carriers with lifetime $\tau$, $g(x)$ denotes the spatial distribution of carrier photogeneration, and the current $j(x)$ represents the migration of charge carriers caused by diffusion and drift:

$$j=-D\left(\frac{dn}{dx}+n\frac{E}{kT}\right) \tag{2}$$

To simplify the solution of the problem and its analysis, we consider a one-dimensional model of either an infinite plate or a semi-infinite crystal with a constant subsurface electric field effective at a distance $\delta$ from the surface. The solution to the continuity equation in the proposed model affords the surface concentration of carriers, $n_s$, which is a function of the absorption coefficient $\alpha$, the diffusion length $L$, and the length of drift $l$ of the charge carriers, the distance $\delta$ of the electric field in the space charge layer, the rate of surface recombination $s$, the thickness of the plate $d$, and the photon flow $\rho$. The corresponding correlation between these parameters is

$$n_s=\boldsymbol{fn}(\alpha, L, l, \delta, s, d, \rho) \tag{3}$$

In our model, the activity of photocatalysts is characterized by the quantum yield $\Phi$ of a surface photochemical process as given by equation 4.

$$\Phi=\frac{dN_S/dt}{dN_{h\nu}/dt}=\frac{k_r n_s S}{A\rho} \tag{4}$$

The numerator represents the rate of the surface photochemical reaction and the denominator denotes the rate of photon absorption. Here $k_r$ is the reaction rate constant, $S$ is the concentration of either the surface active centers or pre-adsorbed molecules, $\rho$ is the photon flow of the actinic light, and the dimensionless coefficient $A$ represents the fraction of light absorbed by the photocatalyst. We consider the light absorption obeys the Lambert-Beer law. Substitution of the expression for the surface concentration of carriers $n_s$ (eqn 3) into equation 4 yields a quantum yield as a function of the absorption coefficient $\alpha$, the diffusion length $L$, and the length of drift $l$ of the charge carriers, the distance $\delta$ of the electric field, the rate of surface recombination $s$, and the thickness of the plate $d$. Accordingly,

$$\Phi=\boldsymbol{fn}(\alpha, L, l, \delta, s, d) \tag{5}$$

Clearly, the quantum yield does not depend on light intensity, but does depend on the spectral variation of the adsorption coefficient $\alpha$. That is, the quantum yield of the surface photochemical reaction that characterizes the activity of photocatalysts is spectrally variable. The key parameters that govern the spectral dependence of the quantum yield are $\alpha L$ and $\alpha l$. These determine which fraction of the photogenerated carriers reach the surface either by diffusion or drift to participate in surface photochemical reactions. The product $\alpha\delta$ defines which fraction of the photocarriers is subject to the subsurface electric field, and $\alpha d$ reflects the spatial non-uniformity of photocarrier generation. The subsurface electric field in the space charge region can increase or decrease the surface concentration of photocarriers, and thus increase or decrease the activity of photocatalysts that is dictated by the strength and direction of the electric field. Consequently, this might cause the apparent spectral shift of the curve of the spectral dependence of the quantum yield in a corresponding direction relative to the absorption curve. Detailed analysis of the results obtained using our model and some consideration of the experimental data will be given during the presentation.

Another important feature of photocatalysts is their selectivity $S_i$, that is the ability of photocatalysts to turn the reaction pathway toward a certain product. It is defined as

$$S_i=\frac{dN_i/dt}{dN_r/dt}=\frac{\Phi_i}{\Phi_r} \tag{6}$$

where $S_i$ is the selectivity of the photocatalyst toward the ith-reaction product, $dN_i/dt$ and $dN_r/dt$ are the rates of formation of the ith-product and destruction of the reagent respectively, whereas $\Phi_i$ and $\Phi_r$ are the quantum yields of the corresponding processes. In our previous studies {1}, we demonstrated that the variation of selectivity of a photocatalyst is governed by the ratio between the surface concentrations of electrons and holes, $\gamma = [e_s]/[h_s]$. In particular, if $\gamma >> 1$, the reaction favors a reductive pathway, whereas if $\gamma << 1$ the oxidative pathway is preferred. Consequently, the selectivity can be described by:

$$S_i=\boldsymbol{fn}(\gamma)=\boldsymbol{fn}(\alpha, L_{e,h}, l_{e,h}, \delta, s_{e,h}, d) \tag{7}$$

that is, the selectivity of a photocatalyst is spectrally variable and its value is determined essentially by the strength and direction of the subsurface electric field in the space charge region, which affects the value of the length of drift of both electrons and holes. Some important cases of variation of selectivity of photocatalysts and their consequences will be considered and compared with experimental results {2} during the presentation.

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## References.

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