CHEMISTRY LETTERS, pp. 157-160, 1981. © The Chemical Society of Japan 1981

ACTIVE SITES OF TiO_2 SINGLE CRYSTAL SURFACE FOR PHOTODEPOSITION OF PALLADIUM

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The photodeposition of palladium onto illuminated surfaces of TiO_2 single crystals was found to occur selectively onto flaws of the crystal surface, indicating that the photosensitized oxidation of water which takes place as the counterpart process of the metal deposition occurs selectively on flaw-free surfaces.

Light-induced heterogeneous reactions on semiconductor catalysts often occur with electrochemical mechanisms. In these cases, a heterogeneous reaction consists of a photosensitized electrochemical process consuming minority charge carriers and a counter process consuming majority charge carriers which is little influenced by illumination.1,2) It is usually believed in reaction systems using powder catalysts, therefore, that the former process occurs on illuminated surfaces of the catalysts but the latter occurs on non-illuminated surfaces, as demonstrated by the photodeposition of Cu onto TiO_2 and WO_3 powders.3) The validity of this view was also confirmed for the photodeposition of Pd onto TiO_2 single crystals4) which consists of the photosensitized oxidation of water and the electrodeposition of Pd.5)

However, it was also found in this reaction system that the deposition of Pd occurred even when the entire surface of the TiO_2 single crystal was illuminated in plating baths by covering the back face with epoxy resin.4) This result gave a strong suggestion that there are any sites on the illuminated surface which work selectively for the individual reaction processes of the heterogeneous reaction. This communication reports the nature of the selective reaction sites.

Figure 1 shows current-potential curves for the individual processes of the photodeposition reaction of Pd. The curve 1 was taken for an electrode polished with 0.05 μm alumina, and the curve 2 for the same electrode but ground with SiC abrasives No. 500. As shown in the figure, the anodic photocurrent markedly decreased with an increase in the particle size of abrasives. The same phenomena have already been reported for ZnO6) and n-GaAs7) single crystals, and crystal defects produced by the abrasion are believed to be responsible for the observed phenomena by acting as hole traps for photo-generated positive holes.6,7) It follows then that the crystal defects cannot act as active sites for the photosensitized reaction process.

As for the cathodic process in the dark which consumes electrons as majority charge carriers, however, a different situation can be seen in Fig. 1. The electrodeposition of Pd became easy to occur by the surface abrasion, indicating that produced flaws provide effective reaction sites for the cathodic process, probably by acting as electron traps. The results shown in Fig. 1 were obtained in the dark, but almost the same results must be obtained for the case where the entire surface of TiO_2 is illuminated, because the amount of electrons in the TiO_2 used, which had the donor concentration of *c.a.*$10^{19}/cm^3$, was so high as to shadow any contribution of photogenerated electrons.

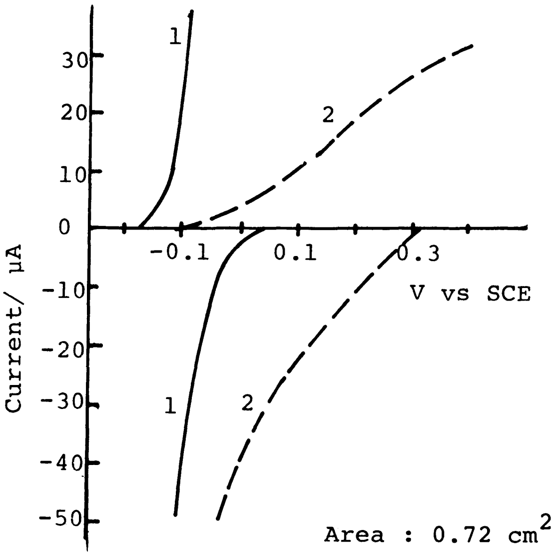

Fig. 1. *i/v* curves of TiO_2 electrodes. Anodic curve: under illumination in a HCl solution at pH=1.7. Cathodic cure: in the dark in $1x10^{-3}$ mol·dm^{-3} $PdCl_2$ at pH 1.7. Curve 1: TiO_2 polished with 0.05 μm alumina. Curve 2: TiO_2 ground with SiC abrasives No. 500. Light source:500W xenon lamp.

As stated above, the introduction of flaws into the surface caused a drastic change in current-potential curves for both photoanodic and cathodic processes. Such changes in the individual processes will lead to a change in the rate of the overall process, since its rate must be quivalent to a current value at a specified potential where the magnitude of the cathodic current is equal to that of the anodic photocurrent.[1] In the present case, the suppression of the photoanodic process was greater than the enhancement of the cathodic process, as shown in Fig. 1, suggesting that the rate of the photodeposition of Pd will be decreased by introducing flaws into the TiO_2 surface.

Table 1 shows that the amount of deposited Pd on TiO_2 for the above-mentioned two kinds of surfaces. The experiments were carried out by immersing the crystals in $PdCl_2$ solutions, and then by illuminating the front surface with the xenon lamp under N_2 atmosphers. The details of the procedures will be described in a separate paper.[4] The followings are noticed from the results given in Table 1. (1) The total amount of deposited Pd was much larger in the alumina-polished TiO_2 than in the SiC-ground one. (2) The photodeposition occurred preferentially on the back non-illuminated surface for the former TiO_2, but for the latter it took place selectively on the front illuminated surface.

Table 1. The amount of deposited Pd on TiO_2 single crystal surface[a]

	TiO_2 polished with 0.05 μm alumina[4]		TiO_2 ground with SiC abrasive #500	
	Illuminated surface	Non-illuminated surface	Illuminated surface	Non-illuminated surface
Amount(μg/cm^2)	83.2	1150	210	0 (negligible)

a) The experiments were carried out in $2x10^{-3}$ mol·dm^{-3} $PdCl_2$ for the alumina-polished TiO_2, but in $1x10^{-3}$ mol·dm^{-3} $PdCl_2$ for the SiC-ground TiO_2. The illumination time chosen was 3 h. Light source : 500 W xenon lamp.

As for the finding (1), it may be suspected that the difference in the solution concentration by a factor of two is responsible. However, this factor is not enough to explain the observed difference in the total amount of deposited Pd. It was found that the photodeposition reaction follows to first order kinetics with respect to Pd^{2+} for both crystals. Therefore, the difference in the deposited amount by this factor should be expectable, but the obtained results showed a much grater difference, suggesting that the introduction of flaws into the crystal surface leads to a decrease in the rate of the photodeposition reaction.

A tentative explanation for the obtained results is given here on the basis of information obtained mainly on ZnO electrodes. By lapping the surface with the SiC abrasives, crystal defects which work as traps for both electrons and positive holes are produced.[8,9] The hole- and electron traps are probably associated with incompletely coordinated oxygen and titanium ions, respectively, and usually have different energy levels,[9] as shown in Fig. 2, which is illustrated after the model given to ZnO.[10] In usual cases, some bandbending is expectable under a condition where the photocatalytic reaction is occurring, but for simplicity the energy band structure is given here for the flat-band condition. Furthermore, the participation of surface states, which is expected for anodic reactions on TiO_2,[11] is also omitted.

Electron traps will be filled with electrons in the dark if their energy levels are deep, and may provide a channel for electron flow to the electrolyte, *i.e.*, Pd^{2+}, by constituting an impurity band if their density is high, enhancing the cathodic reaction.[9] In this case, the electron flow to the electrolyte will mainly occur *via* electron traps. When TiO_2 is illuminated, positive holes are photo-generated, and some fraction of them will be trapped at hole traps. The trapped holes will then be annihilated by recombining with electrons.

It has already been found for the alumina-polished TiO_2 that the rate of the Pd photodeposition depended strongly on electrical conductivity of TiO_2.[4] Such a result will not be expectable, however, for the SiC-ground TiO_2, because the non-illuminated surface showed no contribution to the deposition reaction, suggesting that there is no electron flow from the illuminated surface, where electrons are photo-generated, to the back non-illuminated surface. For the SiC-ground sample, there will be at least two reasons for the back surface not to participate in the photodeposition reaction. (1) An increase in the probability for the carrier recombination process will make a decrease in electron flow toward the crystal bulk. (2) A large fraction of photo-generated electrons will fall into electron traps, as stated above, and the trapped electrons cannot find their ways in the crystal bulk, because the electron traps produced by the abrasion are limited to

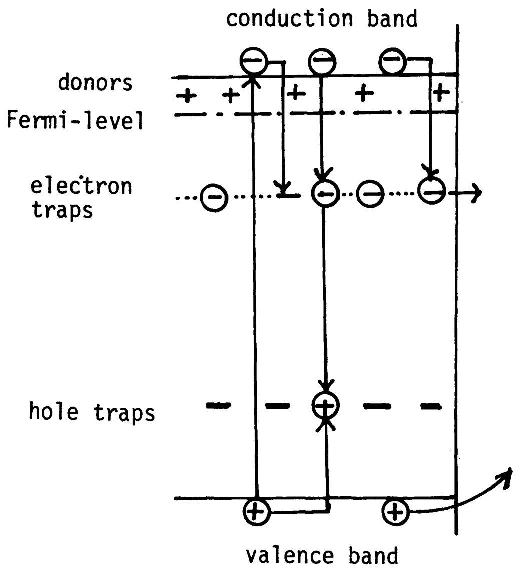

Fig. 2. Schematic illustration of the energy diagrams of TiO_2 having hole- and electron traps.

a surface region in a depth comparable to the grain size of the abrasives.[8]

Figure 3 shows a SEM photograph taken after a photodeposition experiment for 30 min with illumination of the entire surface. It is observed that the deposition of Pd took place preferentially on flaws produced in the course of surface grinding. This result is in good agreement with the above-mentioned view on working mechanisms of flaws in the photodeposition reaction.

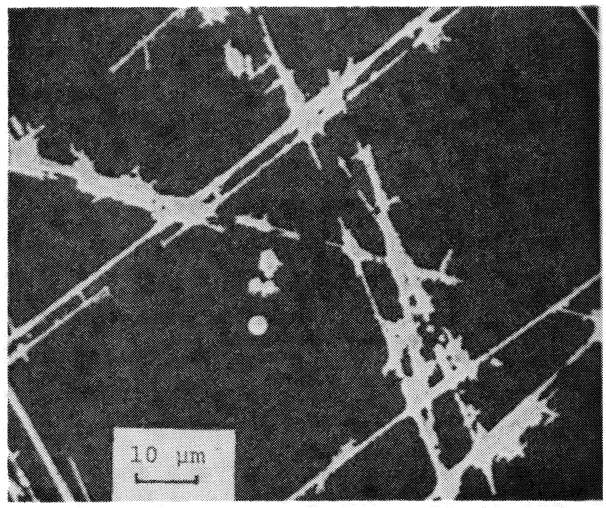

Fig. 3. A SEM photograph showing the selective deposition of Pd onto flaws of illuminated surface of TiO_2. Solution: $2x10^{-3}$ $mol \cdot dm^{-3}$ $PdCl_2$.

All the results reported here give information on active sites for the individual processes constituting the light-induced photodeposition reaction, and almost the same situation is believed to be applicable to other heterogeneous reactions on semiconductor photocatalysts. In this sense, there is a possibility that electrochemical mechanisms prevail in the photolysis of water on $SrTiO_3$ single crystals which occurred only on the illuminated surface of the crystal,[12] though a different classification was given to this reaction system by Wagner and Somorjai. A principal reason leading to this speculation is that their best crystals were prepared by lapping with 1 μm diamond pastes the particle size of which would still be large enough to produce a fairly large amount of crystal defects in the single crystal surface, as judged from results obtained on GaAs.[7]

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(Received November 7, 1980)