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Photoelectrochemical Deposition of Metals on TiO_2 Powders in the Presence of Alcohols

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Photodeposition of Pt, Ag and Au was performed on an anodically biassed TiO_2 electrode in a solution containing "current-doubling" alcohols. Indirect reduction of the metal ions by the radical intermediates produced from the alcohol is, thus, suggested to participate in the photocatalytic preparation of metal-loaded TiO_2 powders.

A photoelectrochemical procedure is widely employed as a photocatalytic preparation of metalized semiconductor powders, with a variety of sacrificial electron donors, e.g. methanol, ethanol, formaldehyde and acetic acid. In such a case the sacrificial reagent was considered as a hole scavenger which promotes conduction band electrons to reduce metal ions in the vicinity of the surface of the powdered semiconductors.[1,2] Almost the same scheme has been accepted in the study of photoimaging technique on TiO_2 and in other applicational fields.[3,4]

Even when the Fermi level of the semiconductor powders shifted upward under the band-gap illumination, it seems improbable that the conduction band electrons ($e^-_{C.B.}$) directly flow into metal ions against the electrical barrier of the space charge layer of the semiconductor. In the case of Pt, however, it was assumed that the $PtCl_6^{2-}$ is reduced by the radical intermediates produced from the sacrificial reagents with the photogenerated holes on the semiconductor surface.[5] On the other hand, a flaw or a defect on the semiconductor surface was reported to afford a reduction site to be deposited those metals such as palladium, silver, and platinum.[6]

Considering that a reducing reagent is generally introduced in the preparation of photocatalyst, the active role of the sacrificial reagent, as well as the surface electron traps, in the photodeposition of metals was studied in the present report. In this respect, a potentiostatic photodeposition of metals, using a polycrystalline TiO_2 electrode, was performed, and the results were associated with the photocatalytic preparation of metalized TiO_2 powders.

A conventional PEC cell was employed and the TiO_2 electrode, which showed a photocurrent for an electrode potential more positive than -0.5 V vs. SCE, was anodically biassed at +0.2 V vs. SCE in the aqueous solution containing 0.1 M (mol dm^{-3}) of Na_2SO_4 as supporting electrolyte, 2 mM of a metal salt (H_2PtCl_6, $HAuCl_4$,

$AgNO_3$ or $CuCl_2$) and 10 vol% of a given alcohol (methanol, ethanol, 2-propanol or t-butyl alcohol). Then the TiO_2 electrode was irradiated with a 250 W xenon lamp through a water jacket, while the solution was continuously bubbled with nitrogen gas. After the photoelectrodeposition of the metals, typically for 30 min, the deposited metal on TiO_2 electrode was dissolved in an acid solution such as aqua regia or nitric acid, and was measured quantitatively by means of an induced-coupled plasma emission spectroscopy (ICP; Nihon Jarrell-Ash ICAP-575).

The results are summarized in Table 1. The I-V characteristics of the TiO_2 electrode under illumination in the presence of either an alcohol or a metal salt did not show any significant change in the anodic region, while cathodic waves were newly observed in the presence of metal salts. The photoelectrodeposition was unsuccessful both in the case of copper and in the presence of t-BuOH. And it is quite interesting that no metal deposition was observed for experiments in the dark or in the absence of alcohols, while Au, Ag and Pt were photodeposited in the presence of MeOH, EtOH or 2-PrOH, although the loaded amount in the case of 2-PrOH was somewhat less for all metals. Thus, the photogenerated $e^-_{C.B.}$ of the anodically biassed TiO_2 electrode did not take part in the photodeposition of metals. Hence, these results indicate that the metal ions used were reduced by the particular species which have an electronically higher energy.

Table 1. The amount of the photodeposited metal on n-TiO_2 electrode after 30 min of potentiostatic photoelectrodeposition at the electrode potential of +0.2 V vs. SCE [a)]

Alcohol / Metal Salt	blank	MeOH	EtOH	i-PrOH	t-BuOH
$AgNO_3$	0	700[b)]	750	20	0
H_2PtCl_6	0	210	200	10	0
$HAuCl_4$	0	760	830	10	0
$CuCl_2$	0	0	0	0	0

a) Cell condition: Na_2SO_4 (0.1 M); metal salt (2 mM); alcohol (10 vol%) in aqueous solution (120 ml).

b) In the unit of μg. The surface area of the TiO_2 electrode is 2.3 cm^2.

According to the knowledge of the current doubling effect for illuminated ZnO or TiO_2 electrodes, alcohols, such as MeOH, EtOH, and 2-PrOH, are photoelectrochemically oxidized to produce cation radicals, which have electronically higher energy so as to inject another electron into the conduction band.7) Therefore the species which brought about the metal deposition was assigned to the same radical cations as seen in the current doubling behaviour of alcohols, even though the current doubling was hardly observed for the alcohol concentration (10 vol%) in the present experiment. Consequently, the lower activity of 2-PrOH in the reaction was readily explained because 2-PrOH is too weakly adsorbed on TiO_2 as to be included in surface reactions such as the reduction of metal ions adsorbed on TiO_2 or the current doubling effect.8)

For the purpose of substantiating this mechanism also in the photodeposition of metals on semiconductor particles, an aqueous TiO_2 dispersion (Kishida, anatase), containing a given metal ion ($\simeq 10^{-4}$ M) and alcohol (10 vol%), was illuminated under continuous bubbling with N_2 gas.

Figure 1 shows the time course of the concentration of each metal ion. The

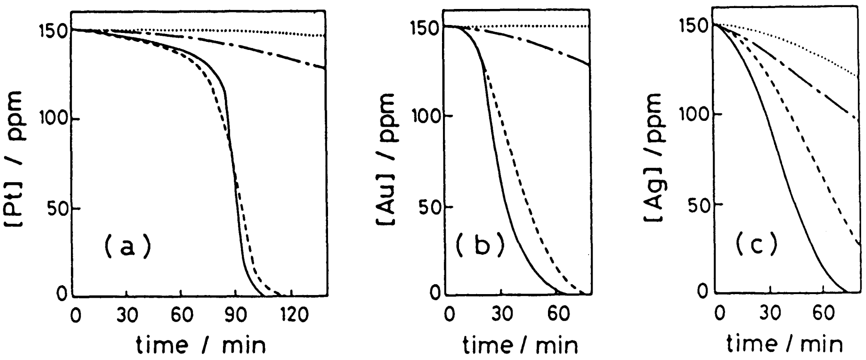

Fig. 1. The time course of the concentration of each metal ion dissolved in the illuminated TiO$_2$ suspension. The aqueous TiO$_2$ dispersion contains alcohol and a given metal ion ($PtCl_6^{2-}$, $AuCl_4^-$, and Ag^+ for (a), (b), and (c), respectively). —— : ethanol, ----- : methanol, —·— : t-butanol and ·········· : without alcohol.

induction period as seen in Fig. 1(a) was supposed to be brought about by a filter effect of the salt solution, because in the PEC experiment with TiO$_2$ electrode an aqueous H_2PtCl_6 solution filter, which was put in between the cell and a light source, almost vanished the photocurrent. In the case of copper, it is noteworthy that the outgassing of the sample suspension, connecting the reaction vessel to a vacuum line instead of bubbling with N$_2$ gas, have shown the photodeposition of copper metal in the presence of MeOH.

Based on these results, the reaction mechanism of the photocatalytic deposition of metals on TiO$_2$ powders in the presence of an alcohol is proposed as follows (Fig. 2). The $\dot{O}H$ radical, which is formed by the photogenerated hole with OH$^-$, initially produces an α-alcohol radical like in the current doubling process.[7] Taking into account the oxidation potentials of the radicals appearing in this study,[9] the direct reduction of metal ions by these radicals (denoted as (1) in Fig. 2) is supposed to proceed rather slowly, since the free energy change of the reaction is rather large ($\geqq$ 1.5 eV).[10] In contrast, once the nuclei of a given metal are formed, they serve as cathodic site to facilitate the reduction of metal ions with the photogenerated or the injected electrons from the alcohol radicals, as long as the energetic situation of the reaction is favorable. The energy diagram depicted in Fig. 2 reasonably explains both the difficulties in depositing copper and the detrimental roles of the residual oxygen or of the adsorbed oxygen, and the fairly low activity of t-BuOH as well.

In connection with the generation and the growth of the deposited metal nuclei, the surface electron traps such as flaws and defects are supposed to play a crucial role as pointed out by Yoneyama et al.[6] On the other hand, Itoh et al. have reported that the deactivating electron back-injection from these surface traps is substantial in the electrochemical dye sensitization process.[11] However, as seen above, the photodeposition of metals hardly occurred on the anodically biassed TiO$_2$ electrode in the absence of alcohols. Then, the surface electron traps are active for the reduction of metal ions only when $e^-_{C.B.}$ accumulates to raise conduction band higher or when electrons are injected from outside of the

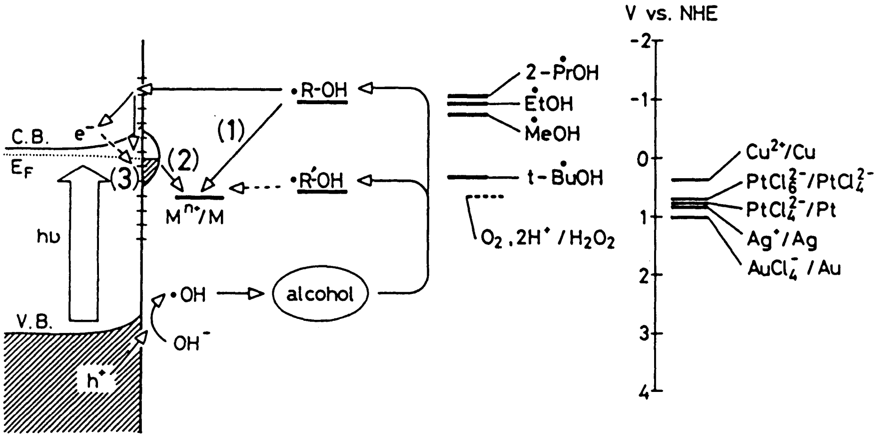

Fig. 2. The schematic diagram for the photocatalytic deposition of metal on TiO_2 particles. The oxidation potentials of alcohol radicals are cited from Ref. 9. The R refers to 2-propyl, ethyl or methyl group, while the R' to t-butyl group. The numbers in brackets correspond to the processes of the metal deposition.

semiconductor surface, i.e. the traps accept those electrons that tunneled a lowered barrier or were injected by radical intermediates ((3) or (2) in Fig. 2). Therefore, alcohols function as an electron source, at the same time as a hole scavenger to promote the accumulation of $e^-_{C.B.}$. The photodeposition of a metal is considered to proceed on the indirect reduction by the sacrificial alcohol via surface electron traps on the semiconductor particles.

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