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Photochemical Synthesis of Nano-Phase Palladium Films on Quartz

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Abstract—Processes of photochemical deposition of palladium films on quartz from solutions of palladium(II) perchlorate and bis(ethylenediamine)palladium(II) tetraphenylborate in dimethyl formamide solutions and dimethyl formamide–ethanol mixtures were studied. The efficiency of the film deposition increases depending on the solvent nature.

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Synthesis of palladium nanostructures is of interest from the viewpoint of their application as catalysts [1, 2]. Palladium colloidal particles are known to be inferior to traditionally used palladium complexes in catalytic activity, being simultaneously highly stable and capable of regenerating. As a rule, metal particles obtained in the synthesis of such catalysts are encapsulated in matrixes of block copolymers [3] or dendrimer structures [4], that considerably reduces their reactivity due to blocking the catalyst surface. The deposition of palladium nanoparticles on the surface of such mesoporous structures as TiO_2 [5], Al_2O_3 [6], and SiO_2 [7] is also widely used.

The aim of this work was to study the kinetics of photochemical deposition of palladium films on quartz depending on a photolyte composition.

EXPERIMENTAL

We used palladium perchlorate $Pd(ClO_4)_2$ and bis(ethylenediamine)palladium(II) tetraphenylborate $[PdEn_2](BPh_4)_2$ (En, ethylenediamine $C_2H_8N_2$; BPh_4^-, tetraphenylborate ion $B(C_6H_5)_4^-$) as initial compounds for the film deposition. To obtain $[PdEn_2](BPh_4)_2$, we used the procedure described in [8] for the synthesis of a $[PdEn_2]Cl_2$ ethylenediamine solution. As a result of the exchange reaction of the obtained $[PdEn_2]Cl_2$ ethylenediamine solution and a solution containing a stoichiometric amount of $NaB(C_6H_5)_4$ (Sigma-Aldrich, 99.5%) a light-beige precipitate was formed. The precipitate was filtered, washed out by water, dried, and stored in darkness in a desiccator. All solutions were prepared on the basis of bidistilled water.

Palladium perchlorate was synthesized from $PdCl_2$ (Aldrich, 99.9%) by the procedure described in [9]. Palladium films were obtained from photolytes by the dissolution of synthesized solid salts $Pd(ClO_4)_2$ and $[PdEn_2](BPh_4)_2$ in *N,N*-dimethyl formamide (DMF) and its mixtures with methanol, ethanol, and propanol-2 in proportions from 20 : 1 up to 1 : 1 (by volume). The solvents were purified according to known procedures [10]. The systems were irradiated by monochromic light of a Philips TUV 4W/G4 05 lamp with the excitation wavelength λ_{exc} of 254 nm. The light quantity was 2.0×10^{15} quant cm^2 s^{-1}. Polished quartz was used as a solid support. The formation of films on a quartz surface was recorded by spectrophotometry (Shimadzu UV-2401). The size of particles, the processes of their formation, growth, and aggregation were recorded with a Hitachi HU-11 electron microscope.

The UV irradiation of DMF solutions of palladium(II) perchlorate $Pd(ClO_4)_2$ in contact with a quartz support leads to a deposition of a grey metalescent film on its surface. According to the X-ray photoelectronic spectroscopy data [11], the film represents pure palladium. Examination of kinetic curves of the formation of palladium films on quartz depending on initial palladium concentration has

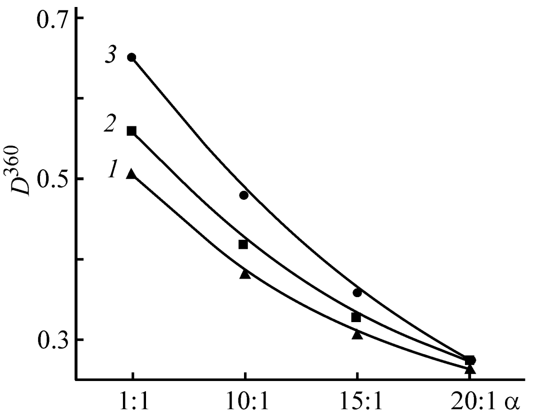

Fig. 1. Dependence of optical density D^{360} measured at λ = 360 nm for colloidal palladium deposited on a quartz surface from 0.01 M $[Pd(En)_2](BPh_4)_2$ solutions on the DMF : alcohol volume ratio α. Wavelength λ_{exc} = 254 nm, τ_{irr} = 5 min. Alcohol: (*1*) propanol-2, (*2*) methanol, (*3*) ethanol.

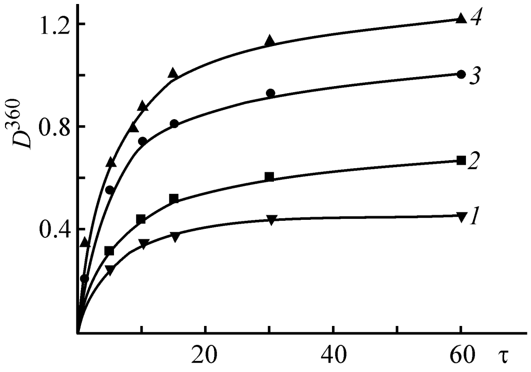

Fig. 2. Kinetic curves of palladium film photodeposition on quartz from 0.01 M $[Pd(En)_2](BPh_4)_2$ solutions within 60 min. Wavelength λ_{exc}=254 nm. D^{360} is optical density measured at λ=360 nm; (τ) irradiation duration (min). Solvent: (*1*) DMF, (*2*) DMF : propanol-2, (*3*) DMF : methanol, (*4*) DMF : ethanol.

shown that the films are deposited without an induction period. After 1 min irradiation kinetic curves flatten out, i.e. the amount of metal precipitated as a film does not change during the further irradiating up to 15 min. The increase in palladium(II) perchlorate concentration in photolyte from 5×10^{-3} up to 5×10^{-2} M allows optical density of a film to be doubled. Nevertheless *D* values do not exceed 0.2 units. According to the electronic microscopy data, the film consists of isolated particles of 5–10 nm in diameter. In the case of a 3 min irradiation the film deposition is accompanied by the formation of agglomerates of particles of 50–70 nm in diameter, their size and number increasing during the further irradiation. Formed agglomerates are sedimentated on the photochemical cell bottom to form black loose deposits.

The use of ethylenediaminepalladium(II) tetraphenylborate $[PdEn_2](BPh_4)_2$ as an initial compound also leads to the deposition of a palladium film on a quartz surface. The intensity of the film coloration increases as the irradiation duration increases. In this case the deposition proceeds more effectively: reached optical densities of films are 1.5-2-fold greater than for films obtained in similar conditions using palladium(II) perchlorate. The film formation occurs without an induction period, kinetic curves flatten for 15 min of the irradiation. No deposits are formed in this case. The size of particles forming a film is 5–10 nm, particles being homogeneously distributed over the quartz surface.

Thus, the efficiency of the metal film deposition is determined by the nature of a palladium initial compound. Metal particles are formed in a near-surface layer of the photolyte. It is essential for the film formation that rates of the diffusion of palladium intermediates to the quartz surface and their sorption on it should be higher than the rate of their growth. Possessing catalytic properties, palladium particles can become larger not only as a result of the photolysis of DMF solutions, but also due to the autocatalytic reduction of Pd(II) ions on their surface. In the case of palladium(II) perchlorate the reduction of ions is rather fast. Agglomerates formed in a near-surface photolyte layer are incapable of sorption and sedimentate on the photochemical cell bottom. Binding of Pd(II) ions in a stable ethylenediamine complex results in slowing down growth processes.

Low values of optical densities of the films are caused by the fact that the rate of nanoparticles growth and agglomeration exceeds the rate of their sorption on a quartz surface. The formation of palladium particles proceeds presumably in bulk photolyte.

Metal deposition can be accelerated if substances capable of regulating sorption and growth processes are added to the photolyte. It is known [12] that alcohols, being secondary reducing agents, can increase the efficiency of the reduction of metal ions to the metal form. In this work we have analyzed the influence of the alcohol nature on the palladium film formation. The addition of alcohols to a DMF solutions of $[PdEn_2](BPh_4)_2$ in the ratio 1:20 (by volume) affects the kinetics of film formation only slightly, whereas the increase in the alcohol content in the system up to the 1:1 ratio results in the 2.5-fold increase in the optical density of the films (Fig. 1).

We have found that the efficiency of film deposition from photolytes containing equal volumes of the components increases in the sequence DMF–propanol-2–methanol–ethanol (Fig. 2).

The obtained results can be explained as follows. The presence of the DMF carbonyl chromophore group with the absorption maximum in the near UV region provides a possibility for occurring sensitized photolysis (λ_{exc}=254 nm) [13] of alcohols with the formation of radicals. Stability of alcohol radicals increases in the sequence $^{\bullet}CH_2OH < {}^{\bullet}CH_2CH_2OH < {}^{\bullet}CH_3COHCH_3$. As secondary alcohol radicals are stable, propanol-2 in comparison with DMF provides a more effective film formation. It should be expected that the efficiency of film deposition increases in the sequence propanol-2–ethanol–methanol. However, a high volatility of methanol leads to a decrease in the rate of film formation under equal irradiation conditions.

The use of $Pd(ClO_4)_2$ as the initial compound in similar systems leads to a 2-3-fold decrease in the film formation rates. It is attributable to the greatest stability of the palladium amine complex compared to the aqua complex.

CONCLUSIONS

(1) Efficiency of the palladium film deposition depends on the solvent nature and increases in the sequence propanol-2 - methanol–ethanol.

(2) The deposition process proceeds without an induction period.

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