

Optically transparent metallic catalysts on semiconductors

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Abstract

Optically transparent films of metals are obtained if the particles constituting these are made much smaller than the wavelength of the transmitted light. Films consisting of 5 nm platinum particles, that are substantially transparent, have been prepared by photoelectrodeposition of platinum onto p-InP under mass transport limited conditions. The resulting hydrogen-evolving photocathodes convert sunlight to stored chemical energy at a 13% Gibbs free-energy efficiency.

Photoelectrodeposition of similar platinum microcrystallites onto spinach chloroplast membranes, followed by transmission electron microscopy, opens the way to the mapping of photopotentials in these membranes.

Incorporation of metallic catalysts in surfaces of semiconducting photoelectrodes, or in photosynthesizing chloroplast membranes, reduces the overvoltages for certain reactions. Reduction in overvoltage translates to an increase in the efficiency of conversion of solar energy to stored chemical energy, or to a change in the nature of the products of the photosynthetic reaction, or to both. Thus, for example, the incorporation of hydrogen evolution catalysts such as platinum, rhodium or ruthenium in surfaces of p-InP photocathodes increases the Gibbs free energy efficiency of the conversion of sunlight to chemical energy, stored as hydrogen and an oxidant, by a factor of 10^4 , to 13% (ref. 1). Similarly, the incorporation of platinum in spinach chloroplasts switches the photosynthetic path to the production of hydrogen and oxygen (ref. 2).

In order to avoid losses in quantum yield, the metals must not absorb or reflect light and the junctions between the metallic catalysts and the semiconductors must allow high photovoltages.

In photosynthesizing membranes, hydrogen is evolved only at sites that are platinized and that reach sufficiently reducing photopotentials to allow the reduction of water. Platinum can be selectively photoprecipitated from potassium hexachloroplatinate containing solutions at reducing sites. If the precipitated platinum crystallites are small, it becomes possible to resolve, by transmission electron microscopy, such sites in chloroplast membranes. We shall see in this lecture that transparency and resolution of the reducing sites in photosynthesizing membranes both require that the metallic particles be small (~ 5 nm diameter). Such metal particles can be formed by photoreduction of the PtCl_6^{2-} anion under mass transport limited conditions. These exist in unstirred solutions at concentrations below 10^{-3}M .

THEORY OF TRANSPARENCY OF METALS

The theory of the optical properties of microstructurally engineered metallic films has been presented elsewhere (ref. 3). The essence of the theory is as follows: A metal film of thickness x and coefficient of extinction k_{met} absorbs a fraction f_{abs} of the photon flux at a wavelength λ . These variables are related through the Beer-Lambert equation (Eq. 1).

$$f_{\text{abs}} = 1 - e^{-\frac{4\pi k_{\text{abs}} x}{\lambda}} = 1 - e^{-\alpha x} \quad (1)$$

The fraction of photons reflected, f_{refl} , for a normally incident beam is given by Eq. 2

$$f_{\text{refl}} = \frac{(n_{\text{met}} - n_a)^2 + k_{\text{abs}}^2}{(n_{\text{met}} + n_a)^2 + k_{\text{abs}}^2} \quad (2)$$

where n_{met} is the index of refraction of the metal film and n_a is the index of refraction of the ambient phase.

To minimize the absorption and reflection losses, k_{met} and n_{met} must be as low as possible. The two are connected through the complex dielectric function $\tilde{\epsilon}_{\text{met}}$ (Eq. 3).

$$\tilde{\epsilon}_{\text{met}} = \epsilon_1 + i\epsilon_2 = \tilde{n}_{\text{met}}^2 = (n_{\text{met}} + ik_{\text{met}})^2 \quad (3)$$

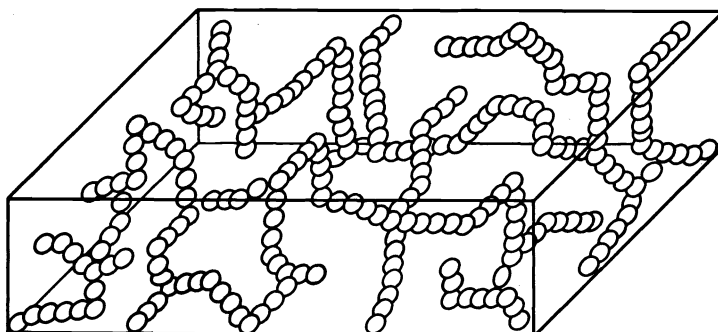


Figure 1. Schematic diagram of the microstructure of a three-dimensionally isotropic assembly of platinum particles.

In this equation ϵ_1 is the real part of the wavelength dependent dielectric function, ϵ_2 is its imaginary part, and \tilde{n}_{met} is the complex refractive index. From Eq. 3 we find that

$$\epsilon_1 = n_{\text{met}}^2 - k_{\text{met}}^2 \quad (4)$$

and that

$$\epsilon_2 = 2n_{\text{met}}k_{\text{met}}. \quad (5)$$

Thus, to maximize transparency, it is sufficient and necessary that $\tilde{\epsilon}_{\text{met}}$ be minimized. $\tilde{\epsilon}_{\text{met}}$ can be reduced to approach the dielectric function of the ambient, $\tilde{\epsilon}_a$, by making the metal particles of which the film consists much smaller than the wavelength of the transmitted light, and by reducing the electrical connectedness of the particles as much as possible in a self-supporting film (Fig. 1). When these two conditions are met, the Bruggeman Effective Medium Theory (ref. 4) applies, and the actual dielectric function $\tilde{\epsilon}$ is obtained by solving Eq. 6,

$$f_{\text{met}} \frac{\tilde{\epsilon}_{\text{met}} - \tilde{\epsilon}}{\tilde{\epsilon}_{\text{met}} + 2\tilde{\epsilon}} + f_a \frac{\tilde{\epsilon}_a - \tilde{\epsilon}}{\tilde{\epsilon}_a + 2\tilde{\epsilon}} = 0 \quad (6)$$

where f_{met} and f_a are, respectively, the volume fractions occupied by the metal and by the ambient fluid (air, water, solution etc.) in the volume between the metal particles. Eq. 6 applies whenever the metal-containing phase is 3-dimensionally isotropic. Examination of the equation reveals that $\tilde{\epsilon}$ does not increase linearly with $\tilde{\epsilon}_{\text{met}}$. Indeed, when f_{met} is much less than unity

$$\tilde{\epsilon} \approx \epsilon_a (1 + 2f_{\text{met}}) \quad (7)$$

becoming altogether independent of $\tilde{\epsilon}_{\text{met}}$. The reason for this independence is screening: The photon field is excluded from the metal particles, so that their optical properties become irrelevant. The photons are squeezed into the ambient fluid surrounding the particles, thereby increasing the effective field strength within the voids and the apparent refractive index of the filling fluid. As a consequence, both the absorption and the reflection losses vanish.

MICROSTRUCTURE

The structure of porous platinum films that are substantially transparent to light is seen in Figs. 2 and 3. The naked eye cannot see these films, nor can their structure be resolved by optical microscopy. Scanning electron microscopy reveals a structure that resembles an array of tightly packed "cotton-balls," with an average diameter of 70 nm (Fig. 2). Each of these "balls" consists of a secondary array of 5 nm particles (Fig. 3). Both the 70 nm units and the 5 nm particles contact each other only at a few points. This accounts for the low electrical connectedness within the films, and thus for their transparency.

OPTICAL PROPERTIES

By measuring the Faradaic current of photoelectrodes under photon-flux limited conditions it is possible to directly measure the sum of the light absorption and reflection losses introduced by metallic catalyst films. Thus, for example, one can follow the increase in such losses during the photoelectrodeposition of platinum onto p-InP photocathodes: The hydrogen-evolution current, at sufficient reducing potentials, where it is light limited, is measured first. Subsequently, one measures the hydrogen-evolution current at increasing platinum-film thicknesses. We have found that losses in controlled-microstructure platinum films are $\sim 10^2$ times lower than in dense platinum films at equal platinum-mass per unit area.

The actual film thickness, its absorption, reflection, and the volume fraction the metal occupies, can be simultaneously monitored by spectroscopic ellipsometry during the photoelectrodeposition of the metal. Such measurements independently confirm their substantial transparency. Furthermore, in hydrogen-evolving p-InP photocathodes it is possible to cover the entire surface with such films, without reducing their current (i.e. quantum) efficiency.

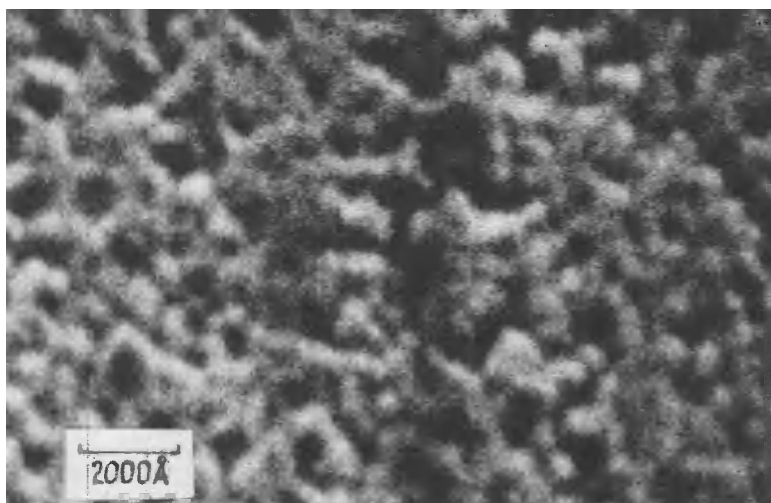


Figure 2. Scanning electron micrograph of a transparent Pt films.

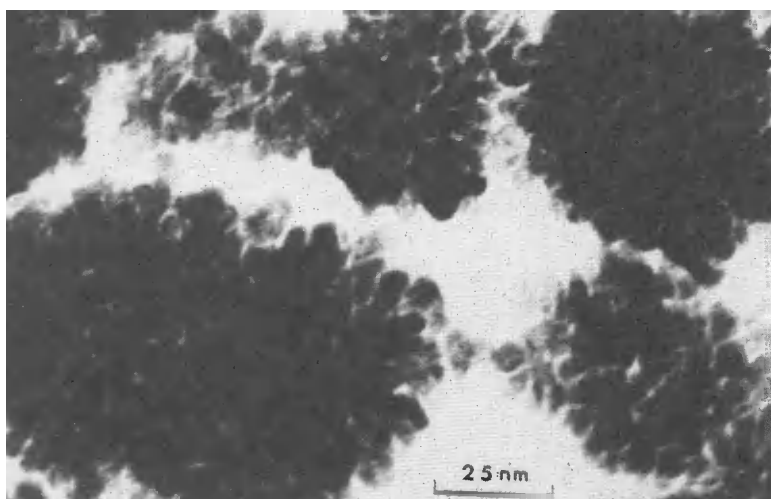


Figure 3. Transmission electron micrograph of a lifted portion of the film in Fig. 2.

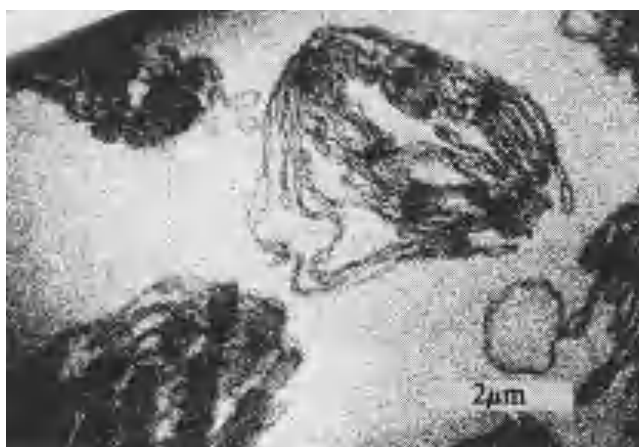


Figure 4. Transmission electron micrograph of photoplatinized chloroplast membranes.

APPLICATION TO THE STUDY OF PHOTOSYNTHESIS IN CHLOROPLASTS

Mass-transport limited photot electrodeposition of small heavy-metal crystallites onto photosynthesizing membranes opens a route to the mapping of the membrane photopotentials, because the pattern of deposition can readily be distinguished by transmission electron microscopy. Fig. 4 shows the pattern obtained upon photot electrodeposition of platinum from a 10^{-3}M PtCl_6^{2-} containing medium onto a spinach chloroplast membrane. Such a membrane produces hydrogen following the photodeposition of the metal. One sees that the stroma and lamellae reach the platinum deposition potential, negative of 0.4V (SHE) (ref. 5).

REFERENCES

1. A. Heller, *Science*, **223**, 1141 (1984).
2. E. Greenbaum, *Science*, **230**, 4732 (1985).
3. A. Heller, D. E. Aspnes, J. D. Porter, T. T. Sheng and R. G. Vadimsky, *J. Phys. Chem.* **89**, 4444 (1985).
4. D. E. Aspnes, *Thin Solid Films* **89**, 249 (1982).
5. E. Greenbaum, J. Woodward, D. P. Allison, C. S. MacDougall, J. M. Brown, T. T. Sheng and A. Heller, *Proc. 10th DOE Solar Photochemistry Research Conference*, 1986.