

# The Photogeneration of Hydrogen

## EFFECTIVE PLATINUM-GOLD COLLOIDAL CATALYSTS

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*Bimetallic colloidal particles, comprising variable mol fractions of platinum and gold, function as effective catalysts for the photochemical production of hydrogen under sacrificial conditions. With increasing mol fraction of gold there is a significant decrease in the rate of hydrogenation of the reactants such that higher yields of hydrogen are attainable.*

Colloidal dispersions of platinum, stabilised with various surfactants, have been used as catalysts for the photoreduction of water to hydrogen as a means of storing solar energy in the form of chemical potential (1, 2). Hydrogen evolution can be extremely efficient over short irradiation periods but, unfortunately, the colloids catalyse hydrogenation of unsaturated bonds as the reaction proceeds (3). The total yield of hydrogen is limited, therefore, by the susceptibility of the reactants towards hydrogenation. Often, the performance of a catalyst can be improved markedly by forming an alloy with a compatible metal and it is known that adding small amounts of gold to macroscopic platinum catalysts inhibits alkane hydrogenolysis while increasing the rate of dehydrogenation (4). Preliminary studies have suggested that this approach may be applied to highly dispersed catalysts supported on graphite (5), and we have shown recently that bimetallic platinum-gold colloids can function as efficient hydrogen-evolving catalysts in solar energy storage devices operated under ambient conditions (6).

### Results and Discussion

Colloidal dispersions of platinum and gold were prepared by  $\gamma$ -radiolysis of mixtures of  $\text{Na}_2\text{PtCl}_6$  and  $\text{NaAuCl}_4$  in nitrogen-saturated water at pH7 containing Carbowax 20M ( $1 \times 10^{-3}$  mol/dm<sup>3</sup>) (1, 2). The total metal concentration was fixed at  $5 \times 10^{-4}$  mol/dm<sup>3</sup> and the mol fraction of each metal was varied from

0 to 1. The actual composition of each colloidal dispersion, after treatment with ion-exchange resins, was determined by atomic absorption and the average particle sizes were established by high resolution transmission electron microscopy. X-ray emission spectroscopy carried out in conjunction with scanning transmission electron microscopy confirmed that individual particles contained both platinum and gold but their relative intensities, compared to the atomic absorption results, suggested segregation with surface enrichment of gold.

The platinum-gold colloids were used to catalyse hydrogen-evolution from a well-established sacrificial photosystem using zinc tetrakis(N-methyl-4-pyridinium)porphyrin as photosensitiser, methyl viologen ( $\text{MV}^{2+}$ ) as electron relay, and dihydronicotinamide adenine dinucleotide (reduced form) as sacrificial electron donor in nitrogen-saturated water at pH4 (7). Upon illumination of this photosystem with visible light, the reducing radical  $\text{MV}^{\cdot+}$  is formed in high yield and it persists for many hours in the absence of oxygen. Photolysis in the presence of a colloid ( $[\text{metal}] = 2 \times 10^{-4}$  mol/dm<sup>3</sup>) resulted in evolution of hydrogen. As the mol fraction of gold increases, there is an increase in the rate of evolution of hydrogen ( $R_{\text{H}_2}$ ) until an optimum value is reached at about 20 to 30 per cent gold after which  $R_{\text{H}_2}$  decreases. There is also a progressive increase in the total yield of hydrogen on exhaustive photolysis ( $[\text{H}_2]$ ) as the mol

fraction of gold increases. Overall, the optimum composition for the catalyst appears to be about Pt<sub>0.7</sub>Au<sub>0.3</sub>.

The increased yields of hydrogen obtained with increasing mol fraction of gold are attributed to inhibition of hydrogenation of the reactants by surface gold atoms. With mol fractions of gold exceeding 20 per cent, hydrogen is not consumed upon prolonged irradiation although this is a serious problem for colloids containing little or no gold. Many of the platinum atoms on the colloid surface are prevented from functioning as active catalytic hydrogen evolving sites because of specific adsorption. The adsorbate may be H<sup>•</sup> atoms, MV<sup>2+</sup>, MV<sup>+•</sup> or surfactant used to protect the colloid against flocculation. Incorporating gold atoms into the colloid surface dilutes platinum-platinum co-ordination sites where specific adsorption occurs, allowing surface platinum atoms to operate as active hydrogen sites.

In hydrogen-saturated aqueous solution at pH4 containing colloidal platinum ( $2 \times 10^{-4}$  mol/dm<sup>3</sup>), hydrogenation of MV<sup>2+</sup> occurs very slowly. The reducing radical MV<sup>+•</sup>, however, is hydrogenated readily under ambient conditions and it is apparent that this reaction is responsible for consumption of hydrogen during photolysis. The rate of hydrogenation of MV<sup>+•</sup> ( $R_{MV}$ ), as catalysed by the various colloids, was measured by electrochemical methods. It was found that  $R_{MV}$  decreased significantly with increasing mol fraction of gold. The inhibition of hydrogenation of MV<sup>+•</sup> on the bimetallic particles is a consequence of the decreased mobility of H<sup>•</sup> atoms (8) and the increased energy of adsorption of H<sub>2</sub> (9, 10).

This study has shown that the use of bimetallic platinum-gold colloids can improve the rates and yields of hydrogen evolution from photosystems in which one or more of the reactants is susceptible towards hydrogenation. This arises because gold atoms at the surface of the colloidal particle inhibit specific adsorption and hydrogenation of the reactants. This behaviour, which is well known for macroscopic catalysts (11, 12), shows the

advantages that may be gained by using alloys in place of pure metals.

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### Cleavage in Iridium Crystals

As the only metal with good mechanical properties in air at temperatures above 1600°C, iridium is used for the crucibles in which presintered mixed oxides are melted during the growing of high purity single crystals for electronic applications. Fabrication techniques have been developed to enable these crucibles to be manufactured to the required high standard, none-the-less the factors that govern the deformation of iridium are not yet fully established.

A recent letter from the Department of Physics of the Urals State University, U.S.S.R., where the deformation and fracture of metals is a traditional subject of research, contributes to the topic with a discussion of the possible cause of cleavage in iridium single crystals (P. Panfilov, A. Yermakov and G. Baturin, *J. Mater. Sci., Lett.*, 1990, **9**, (10), 1162-1164).