Photoextraction of silver from aqueous solution using anthracene colloid

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Abstract

Silver from an aqueous solution of Ag^+ ions can be conveniently photodeposited on colloidal anthracene particles using sunlight. This method is advantageous when compared with photoextraction of silver with TiO_{2} , and anthracene can be readily evaporated to obtain pure silver. The sensitivity of anthracene colloid towards sunlight is higher than that of TiO_2 .

1. Introduction

Photodeposition of metals on semiconductor particles (notably TiO₂) has attracted much attention as (1) a method of extracting noble metals from dilute solution [1–7], (2) a potential photographic application, (3) a method of heavy metal decontamination of polluted water [1, 8], and (4) an improvement of the performance of semiconductor catalysts [1, 9–12]. With the depletion of rich metal deposits, the extraction of noble metals from poor ores, ocean and industrial waste waters need serious consideration. Herman *et al.* [1, 4, 10] have perfected methods for extracting noble metals from dilute solutions using TiO₂ as a catalyst and ultraviolet (UV) lamps as the irradiation source.

Metal extraction by photocatalytic deposition on TiO_2 has two distinct disadvantages:

(1) a secondary chemical process (e.g. extraction with nitric acid in the case of Ag and aqua regia or cyanide in the case of Au) or high temperature evaporation is required to separate the deposited metal;

(2) TiO_2 is poorly sensitive to sunlight and artificial light sources are expensive.

In this note we describe a method for photocatalytic extraction of silver (the method is also applicable to Au and other noble metals) from dilute solutions using a colloidal suspension of anthracene particles. Just like TiO_2 and other inorganic semiconductor

photocatalysts, anthracene colloid acts as a sensitizer which absorbs photons to create electron-hole pairs participating in the redox reactions. Silver deposited on anthracene forms a heavy precipitate which readily settles down. Anthracene in the precipitate is easily removed by heating to a temperature of ~150 °C to obtain pure silver powder.

2. Experimental details

Anthracene colloidal suspension was prepared as follows: 100 mg anthracene (Aldrich) was dissolved in 1 ml warm propionic acid (BDH) or glacial acetic acid (BDH). When this solution is poured into water, a milky white colloidal suspension of anthracene is formed. Water (300 ml) containing 3.5×10^{-3} M Ag⁺ (silver nitrate was used) and the anthracene colloid (100 mg anthracene, 1 ml propionic acid) placed in a cylindrical vessel (diameter 11.5 cm), was magnetically stirred and exposed to sunlight (average intensity ~640 W m⁻²). Solar intensity was monitored using an EKO MP-20 pyranometer.

At different intervals of time, aliquots of solution were drawn from the vessel, centrifuged to remove the suspension and Ag⁺ ion concentration was estimated (ammonium thiocyanate-ferric chloride method). In another experiment 300 ml of the solution (Ag⁺ ~ 3.5×10^{-4} M, anthracene ~ 100 mg, propionic acid ~ 1 ml) in a closed vessel exposed to sunlight was kept purged with air or

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nitrogen and the out-going gas analysed chromatographically (Shimadzu GC-9AM gas chromatograph). A similar experiment was also conducted in a quartz walled photochemical reactor (Applied Photophysics) using a 400 W medium pressure mercury lamp provided with a Pyrex filter to cut off light of wavelength <300 nm. The anthracene content in the solution during the progress of each experiment (i.e. to determine the extent of photodegradation of anthracene) was estimated by the following method. Aliquots of solution drawn from the reaction vessels were centrifuged after addition of a little aluminium sulphate (to assist coagulation). Anthracene was extracted with sufficient alcohol, diluted to constant volume and determined by fluorescence spectroscopy (Shimadzu spectrofluorophotometer RF-5000).

3. Results and discussion

Figure 1 (curve a) shows the absorption spectrum of the anthracene colloidal suspension. For comparison, the absorption spectrum of colloidal TiO_2 is also presented (Fig. 1, curve b). In the former spectrum significant absorption is seen even if $\lambda > 400$ nm, whereas in the latter pronounced



Fig. 1. Absorption spectrum of an aqueous suspension of (a) colloidal anthracene and (b) TiO_2 .

absorption occurs only if $\lambda < 380$ nm. As expected from the absorption spectrum, anthracene colloids have better sensitivity in the longer wavelength regions, compared with TiO₂.

Photoconductivity and other semiconductor-like properties of solid anthracene resulting from lightinduced generation of charge carriers are well studied [13, 14]. Photodeposition of silver on anthracene particles could be explained by the following reaction scheme. Photons adsorbed by anthracene particles generate electron-hole pairs, *i.e.*,

$$h\nu + \text{anthracene} \longrightarrow e^- + h^+$$
 (1)

Electrons react with silver ions to generate metallic silver which is deposited on anthracene particles.

$$Ag^+ + e \longrightarrow Ag$$
 (2)

Deposited silver presumably acts as an electron accumulation site (compare Pt deposited on TiO_2) and consequently the silver crystallites grow to form heavy particles. Again silver deposition enhances charge separation; however, light cut-off becomes a limiting factor and the reaction gradually slows down.

Positive holes are captured by hydroxyl ions to yield hydroxyl free radicals that are consumed by the sacrificial agent (propionic acid in the present case) or anthracene (*i.e.* self-scarification of anthracene) in the oxidation reaction,

$$n(OH)$$
 + sacrificial agent $\longrightarrow CO_2 + H_2O$ (3)

Figure 2 illustrates the depletion of silver ion in the solution kept exposed to sunlight (~640 W m⁻²). It is seen that more than 90% of silver is removed from the solution in ~ 3 h. In the experiment with the closed vessel, which is kept purged with N₂, the reaction rate was noted to be faster by a factor ~ 2 . Obviously in the presence of O₂, photogenerated electrons could also be accepted by O_2 to form O_2^- and holes are consumed in oxidation of the sacrificial agent. However, the presence of O_2 does not affect the practicality of the method. Similar observations have been made in photocatalytic deposition of metals on TiO_2 [10]. Figure 3 shows carbon dioxide liberation in the experiment with the UV lamp (cut-off filter $\lambda > 300$ nm) when the solution is purged with N_2 . As the reaction rate is faster with UV light, CO_2 evolution was readily detectable. In the absence of colloidal anthracene (i.e. Ag⁺ ions + propionic acid + water) CO_2 was detectable, but the yield was smaller by a factor of ~ 20 . In



Fig. 2. Depletion of Ag⁺ on exposure to sunlight of an aqueous solution Ag⁺ containing colloidal anthracene (300 ml contained in a cylinder of diameter ~ 11.5 cm, anthracene ~ 100 mg, propionic acid 1 ml).



Fig. 3. Photogeneration of CO₂ from an aqueous solution (300 ml) containing 3.5×10^{-3} M Ag⁺ (initial concentration), 100 mg colloidal anthracene and 1 ml propionic acid (irradiation source 400 W medium pressure mercury lamp with Pyrex filter, purging rate = 12 ml min⁻¹).

all experiments (sunlight or UV presence or absence air) oxidative degradation of anthracene was also noted. This is caused by the reaction of OH⁻ with anthracene instead of the sacrificial agent (propionic acid). Rapid consumption of electrons by Ag^+ is responsible for the oxidation of anthracene. In the absence of Ag^+ , CO_2 was not detected when a colloidal suspension of anthracene is irradiated either with sunlight or a medium pressure mercury lamp using a Pyrex filter. After 3 h exposure to sunlight, the loss of anthracene was ~13\%.

Propionic acid could be replaced with any other water-miscible liquid that dissolves anthracene to some extent (e.g. acetic acid and ethanol). In this investigation we used propionic acid, because here the direct photoreduction of silver ions is negligible. Aqueous solutions of Ag^+ containing acetic acid or ethanol when exposed to sunlight produce a haze colloidal of silver as a result of slow photoreduction. However, in the presence of anthracene colloid and acetic acid or ethanol, non-settling silver colloids are not formed. Thus, for practical applications, acetic acid, ethanol or other organic liquid could be used to dissolve anthracene.

Compared with using TiO₂ in the photoextraction of silver, the above method has an advantage because silver is deposited on a solid which could be easily evaporated by heating to a temperature ~135 °C above room temperature. Again the reaction is more sensitive to sunlight. In the experiment with anthracene colloid (an initial concentration $[Ag^+]$ of 3.5×10^{-4} M) $[Ag^+]$ was reduced to ~ 0.2×10^{-4} M in 3 h. When anthracene colloid was replaced with TiO₂ (TiO₂ concentration adjusted for absorbance at 390 nm comparable to that of anthracene colloid), Ag⁺ concentration was reduced to ~ 0.8×10^{-4} M in 3 h. Furthermore, anthracene is a readily available cheap material.

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