

Photochemical oxidation of water on a 1 μm Ag^+ zeolite layer

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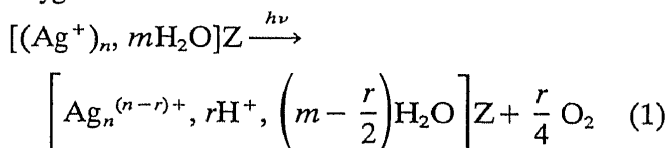
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Abstract

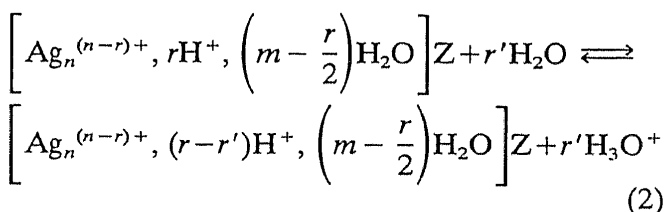
When silver zeolites are illuminated in the presence of water, Ag^+ ions are reduced and molecular oxygen is evolved with a high quantum yield. The lowest energy transition in the previously unilluminated zeolite is a charge transfer which excites an oxygen lone-pair electron to the silver species coordinated by the zeolite and initiates the oxidation of water. Investigation of the spectral sensitivity shows that self-sensitization takes place: as the reaction proceeds, the sensitivity extends initially from the near-UV-visible wavelengths to the red range. We have developed a technique for the preparation of monograin zeolite layers and have been able to demonstrate the self-sensitization of photo-oxygen evolution on these samples. The self-sensitization is a quantum size effect in which, during the photoreaction, new chromophores are produced with bathochromically shifted absorption. The total amount of zeolite irradiated was 70 μg , coated as a thin layer on a quartz window. This is 10^3 times less than in earlier investigations. Therefore a new experimental technique was developed based on a very small reaction volume.

1. Introduction

On illumination of silver zeolites in an aqueous dispersion Ag^+ ions are reduced and molecular oxygen is evolved



Z represents the negatively charged zeolite lattice. The reaction is followed by partial transfer of the zeolitic protons to the solution which results in a decrease in pH



The lowest energy transition in the previously unilluminated zeolite is a charge transfer which excites an oxygen lone-pair electron to the silver species coordinated by the zeolite [1]. This initiates the oxidation of water. An investigation of the spectral sensitivity of this reaction has led to the conclusion that self-sensitization takes place: as

the reaction proceeds, the sensitivity extends initially from near-UV-visible wavelengths to the red range [2]. The self-sensitization is interpreted as a quantum size effect [3] in which, during the process of photoreaction, new chromophores are produced with bathochromically shifted absorption. These chromophores can drive the photo-reaction if they are excited.

Why is photo-oxygen production using visible light an interesting reaction? Water splitting, CO_2 reduction and nitrogen fixation are the main fields of investigation for solar energy conversion and storage systems [4]. A number of approaches have been published, of which only a few are mentioned here [5]. To realize these reactions, oxygen must be evolved. However, in all investigations of molecular photoredox systems, the oxidative half-reaction has been circumvented by the addition of sacrificial donors, as no system is known to produce oxygen from water using visible light; this reaction has led to many controversies in the past. To prevent recombination, the photoreduction and photo-oxidation steps must be separated. We have proposed to do this by means of a membrane [1]. The membrane may have supporting properties for mechanical stability. It must be capable of transporting electrons and protons from one side to the other. The principle of such an arrangement is shown in Fig. 1.

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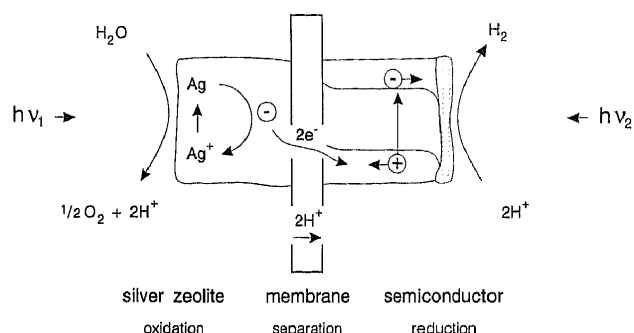


Fig. 1. Schematic diagram of an artificial photosynthesis device. A silver zeolite drives the water oxidation. The water reduction is achieved by a semiconductor, a zeolite loaded with semiconductor particles or a zeolite modified with a transition metal complex such as $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (bpy, 2,2'-bipyridine).

For the oxidative half-reaction a monograin layer of silver zeolite can be used. One of the many known reductive photosystems [5, 6] can be employed to perform the reductive half-reaction on the other side of the membrane. Zeolite-containing semiconductor particles are especially attractive since the zeolite itself may act as the membrane. However, it should be emphasized that zeolites are ion conductors and that particle interphases must be avoided due to their large ohmic resistance.

Interesting methods of preparation of zeolite modified surfaces and electrodes have been proposed [7] but none of them is suited for carrying out the photochemical experiments described. Therefore we have recently developed a technique for the preparation of monograin zeolite layers by covalently linking zeolite particles (0.2–1 μm) as a dense sheet onto a surface [8]. This method allows photochemical, electrochemical, spectroscopic and structural investigations to be carried out on zeolites. We have been able to demonstrate photo-oxygen evolution and self-sensitization in these samples. The total amount of zeolite irradiated was 70 μg silver zeolite, coated as a thin layer on a quartz window. This is 10^3 times less than in our earlier investigations [2]. When working with such small amounts the sensitivity and accuracy of oxygen detection is crucial. Therefore a new experimental technique had to be developed.

2. Experimental details

2.1. Apparatus

The basic idea behind the apparatus shown in Fig. 2 is that a small volume, in which photo-oxygen evolution, oxygen detection and sensor calibration take place, is connected to a large reservoir which enables the solvent to be kept

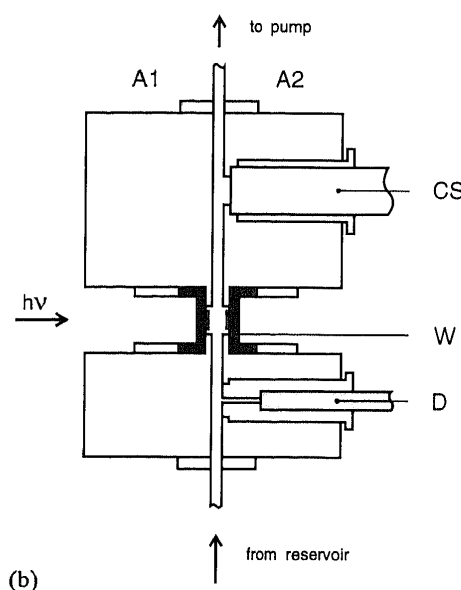
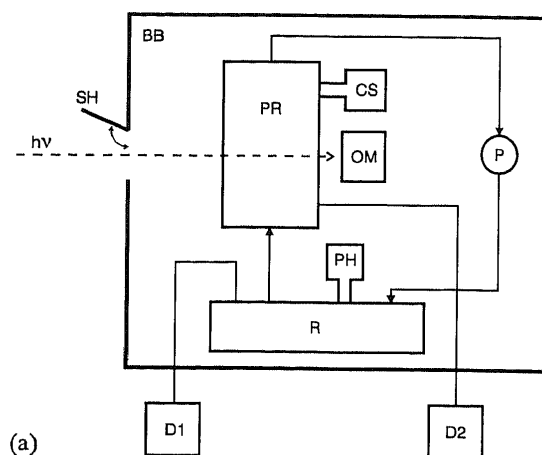


Fig. 2. Flow photoreactor system (see text): (a) overview; (b) cross-section of the photoreactor (PR).

oxygen free by purging with pure nitrogen and the pH to be maintained at the desired value. The water is pumped from the reservoir through the photoreactor, where it passes the zeolite sample coated onto a window, a Clark oxygen sensor and finally returns to the reservoir. Because it is sensitive to light the sensor is placed in the dark and the temperature and water flow are kept constant.

The IR-filtered and intensity-regulated light of a 1000 W high-pressure xenon arc lamp (PTI) is focused onto the sample in the photoreactor. The wavelength band is selected by a set of interference filters that can be exchanged by a home-built filter changer. The light intensity is measured with the photocell of an optometer (OM) after the light has passed through the photoreactor. The complete photoreaction system is placed in a light-sealed

black box (BB) into which light can be admitted by opening a shutter (SH). A personal computer controls the experiment by means of a GPIB communication board. The electrical signals from the oxygen sensor, the light detector and the pH electrode are fed into an analogue scanner which is connected to a Schlumberger digital multimeter 7060. The optical filter change and the shutter position are controlled by the application program.

The flow system consists of a photoreactor (PR), reservoir (R) and peristaltic pump (P). The photoreactor and reservoir are kept at a constant temperature of 23 °C by means of a thermostat. Oxygen-free water is pumped from the reservoir through the photoreactor and back to the reservoir. In the reservoir the water is deoxygenated with a constant nitrogen (99.995%) flux, its pH is controlled using a pH meter (PH) and eventually adjusted by adding 0.1% HClO₄ with a dosimat (D1) from Metrohm. The oxygen is detected in the photoreactor with a Clark sensor (CS) (WTW) connected to a VA-detector 641 from Metrohm. A second dosimat (D2) is used to inject small amounts of oxygen-loaded water to calibrate the Clark sensor.

The photoreactor shown in Fig. 2(b) consists of two blocks A1 and A2 made of stainless steel. The inner surfaces are gold plated. Aligned along the rectangular channel (3 mm × 1 mm) are, from bottom to top, the Clark sensor calibration inlet (D), two quartz windows (W) and the Clark sensor (CS). The parallel windows have a diameter of 20 mm, are O-ring sealed and are held by a polytetrafluoroethylene (PTFE) ring and a hollow screw. The optical aperture is 8 mm. The zeolite samples are deposited on the inner side of the window.

2.2. Sensor calibration

Clark sensors have been described in detail in the literature [9]. We only describe the treatments essential for our experiments. A solution of 5% KCl and 1% NaOH was used as electrolyte in the sensor. In order to obtain maximum sensitivity, the Clark sensor needs to be polarized at -0.5 V (WE (working electrode) vs. Ag/AgCl) for at least 24 h. The constancy of the temperature must be better than 0.1 °C. The calibration of the sensor is performed by injecting oxygen-loaded water. This water is in dynamic equilibrium with air, and therefore its oxygen content follows from Henry's law [10]. Volumes between 0.1 and 3 μl, corresponding to an oxygen content of 1 ng and 25 ng respectively, were typically injected at a speed of 0.1 μl s⁻¹. An example of a calibration run is illustrated in Fig. 3(a). Integration over each peak

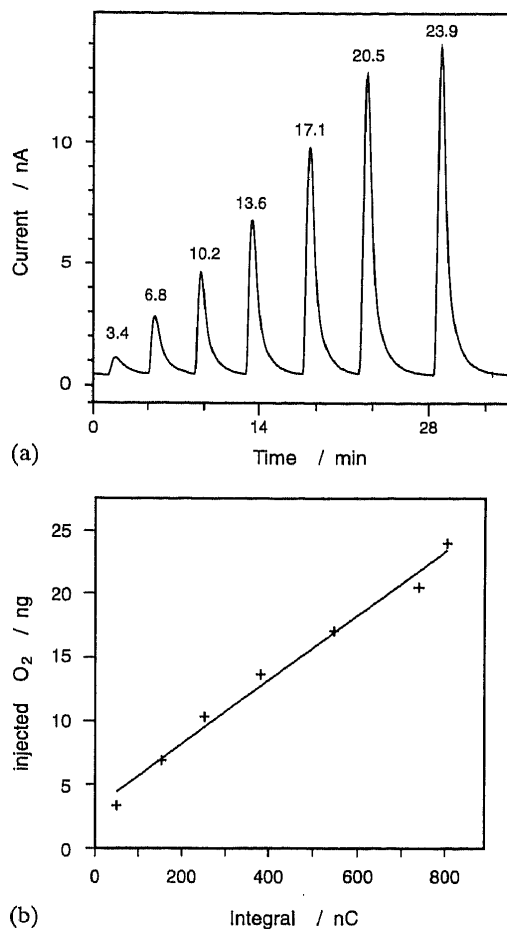


Fig. 3. Detector calibration with air-saturated water: (a) signals of the Clark sensor; the numbers on each peak indicate the number of nanograms of oxygen injected; (b) integrated peak values; the straight line corresponds to a linear regression.

results in the graph shown in Fig. 3(b), in which the number of charges detected vs. the amount of injected oxygen is plotted for each calibration point. A good linear dependence is produced giving a detector sensitivity of 25 pg O₂ nC⁻¹. This means that our apparatus allows very sensitive and accurate oxygen measurements.

2.3. Thin layer preparation of silver zeolites

Sodium zeolite4A (4 g) (Baylith T, Bayer) was dried in vacuum for 1 h at 140 °C. After cooling to room temperature 50 ml of dry ethanol was added and dispersed in an ultrasonic bath for 10 min. While stirring 2 ml of triethoxyvinylsilane was added and the reaction was completed by stirring in the dark for 4 days. This procedure was performed under a nitrogen atmosphere. The modified zeolite was then centrifuged, decanted, washed with ethanol three times and dried in vacuum at room temperature.

To create the monograin layers of zeolite on a quartz window, 20 mg of modified zeolite was

finely dispersed in a mixture of 2 ml of acetonitrile and 1 ml of water. Sellotape containing a hole of 5 mm in diameter was placed on the cleaned quartz window and 10 μl of the above dispersion was placed in the hole. After letting the solvent evaporate very slowly in the dark, the vinyl groups on the zeolite surface were photopolymerized for 20 min by UV irradiation (254 nm, 8 W). The tape was removed and a thin film of 70 μg zeolite (diameter, 5 mm) was obtained on the window. The silver exchange of the zeolite layer was accomplished in the dark by immersing the coated windows for 5 min in a 0.01 M solution of silver nitrate and washing for 3 min in bidistilled water.

2.4. Photoexperiments

Bidistilled water (100 ml) was placed in the reservoir, deoxygenated with nitrogen and adjusted to pH 7. After several hours of degassing, the windows were mounted, one of them covered with a layer of silver zeolite. The oxygen-free water was pumped at a constant speed of 26 ml h^{-1} through the system. The calibration of the Clark sensor was performed as soon as its baseline levelled off.

A photo-oxygen evolution experiment consisted of several cycles. In each cycle the sample was first irradiated with green light (500–540 nm) for 500 s. Then the light shutter was closed for 830 s and the blue filter (430–480 nm) was selected. The sample was then irradiated with blue light for 500 s followed by a dark period of 830 s. The same procedure was repeated in the near-UV region where a 340–390 nm filter was used, and then the next cycle was started. The radiant power on the sample area (2 cm \times 0.2 cm) was about 8 μW for green light, 13 μW for blue light and 4 μW for UV light. Since a cycle lasts for more than 1 h a complete experiment of more than 20 cycles takes a full day. Computer control is useful to collect the data and to control the conditions accurately.

3. Results and discussion

The results of a typical experiment are illustrated in Figs. 4 and 5. In Fig. 4 the oxygen evolution signal is plotted *vs.* time for each irradiation cycle, starting with the first cycle at the front. In each cycle the sample was first irradiated with green light. We omitted UV irradiation in the first cycle. As a result no oxygen evolution could be detected in this cycle. In the second cycle no oxygen was observed during illumination with green and blue

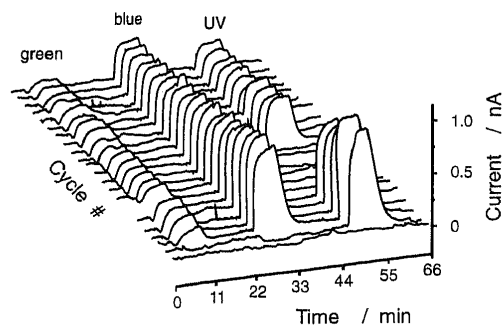


Fig. 4. Self-sensitization of the silver zeolite thin layer in the presence of water. The signals of the oxygen detector are shown as a function of time and the number of cycles, starting with the first cycle at the front. The sample was irradiated consecutively with green light (500–540 nm), blue light (430–480 nm) and UV light (340–390 nm). In the first and seventh to twelfth cycles the UV irradiation has been omitted.

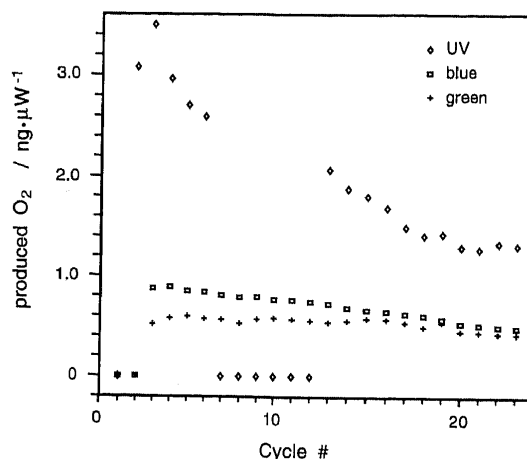


Fig. 5. Oxygen production at various wavelengths *vs.* cycle number. The values correspond to the integrated oxygen signals of Fig. 4. They have been normalized to a radiant power of 1 μW .

light. The first oxygen signal observed was when the sample was irradiated with UV light. The third cycle was started 830 s after the UV exposure with irradiation with green light; a distinct oxygen signal appeared. Oxygen signals were recorded for all the following blue and green illumination periods. This shows that self-sensitization occurs: the system is initially insensitive to visible light but, after it has been irradiated with UV light, it is also photoactive in the visible. Thus the self-sensitization effect first discovered on silver zeolite dispersions [2] can also be observed on 1 μm zeolite layers. It could be argued that no real sensitization takes place but that the energy of the UV photons is somehow stored within the zeolite and released when illuminated in the visible, producing oxygen. This hypothesis can be checked by omitting UV irradiation in some of the cycles. Therefore we kept the light shutter closed during the UV irradiation period for the six cycles 7–12.

Figure 4 shows that, after the system has once been exposed to UV light, the absence of UV illumination does not influence the oxygen production characteristics in the visible region. This proves unequivocally that the observed shift in the spectral response of the system after an initial UV irradiation period is due to self-sensitization. The UV light is only necessary to initiate this process.

Figure 5 shows the total amount of oxygen produced in the different green, blue and UV illumination periods *vs.* the cycle number, normalized to a constant radiant power of $1 \mu\text{W}$ to allow simple representation of the data. The production rate is highest in the UV where it rises steeply and goes through a maximum in the third cycle. After 20 cycles it seems to level off at 40% of the maximum rate. The oxygen production in the blue, initiated by the first UV irradiation, shows a less dramatic time dependence. After the fourth cycle it decays slowly to about 70% of its maximum value. The rate in the green is highest in the fifth cycle and shows an even slower decay than that in the blue. Oxygen production in the green and blue illumination periods reaches the same level after about 20 cycles. Remarkably, these results are very similar to those obtained earlier with silver zeolite dispersions [2]. Additional experiments are needed to determine the quantum yield accurately; it is high, as can be estimated from the incident radiant power and the rate of oxygen production.

The bathochromic shift and the gradual decrease in oxygen evolution of the silver zeolites can be explained by the growth of new chromophores absorbing in the visible spectral region. The chromophores are Ag_n^{m+} clusters with a maximum cluster size which is determined by the size of the zeolite cavity. Clusters of this type have been described by a number of workers. Hermerschmidt and Haul [11] identified Ag_6^{m+} ($m < 6$) in dehydrated Ag-A zeolite by electron paramagnetic resonance (EPR) spectroscopy. Their result was duplicated by Grobet and Schoonheydt [12] and by Morton and Preston [13]. Kim and Seff [14] reported that Ag^+ reduced by hydrogen can be reoxidized to Ag^+ by oxygen and they identified Ag_6^{3+} clusters crystallographically in the large cavity of partially exchanged zeolite A. Very recently, hexasilver clusters stabilized by Rb^+ cations have been identified [15].

We conclude that small silver clusters are present in the zeolites and that their formation, initiated by near-UV irradiation, is responsible for the self-sensitization. The process is controlled by the size

of these particles and therefore can be regarded as a quantum size effect [3]. Further investigations will show to what extent the well-known size dependence of the electrochemical potential of silver clusters [1, 16] is accessible by the $1 \mu\text{m}$ silver zeolite layers. Potential applications in the field of artificial photosynthesis have been mentioned in Section 1. Other fields that may possibly be influenced by our findings are optical data storage, photoelectrochemistry and photographic processes [17].

Acknowledgments

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