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# Photoelectrochemical study on photosynthetic pigments-sensitized nanocrystalline ZnO films☆

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## Abstract

Hetero-structures formed by quantum-sized ZnO nanocrystals and photosynthetic pigments were prepared by adsorbing either chlorophyll *a*, carotenoids or their mixture onto a film of organic-capped ZnO nanoparticles. Photoelectrochemical measurements were comparatively performed on both bulk and nanocrystalline ZnO films after dye-covering in order to probe the photosensitization process occurring at the hetero-junction. The photoconversion process was found to be greatly enhanced at the nanocrystalline electrodes upon sensitization with a dye mixture. The sensitization process is discussed on the basis of the aggregation state of chlorophyll *a*, and of the specific photoprotective action played by carotenoids.

*Keywords:* Dye-sensitized film; Colloidal nanocrystals; ZnO; Chlorophyll *a*; Carotenoids; Photoactivity

## 1. Introduction

In recent years, hetero-structures formed by high band-gap semiconductor materials and suitable organic molecules as sensitizers have been demonstrated to be promising in implementing photovoltaic devices [1]. For example, electrodes based on CdS, ZnO, and $TiO_2$ have been successfully employed as inorganic electron acceptors in dye-sensitized solar cells. As such, semiconductors typically absorb in the UV region of the solar spectrum, a sensitizer able to inject electrons into the conduction band of the semiconductor upon visible light absorption, is required. In most dye-sensitized photoelectrochemical devices, the first excited singlet state of the sensitizer is usually involved in the generation of the photocurrent [2]. However, electron injection can considerably compete with the relaxation of the dye excited states [3], the latter being responsible for the decrease of the photoconversion yield.

As electron transfer processes occurring in photosynthesis have been widely studied as a model for efficient sunlight conversion into electricity, natural pigments can offer an appealing alternative as light absorbers by mimicking the photosynthetic process [4,5]. For example, chlorophyll *a* and carotenoids, which are known to serve as solar radiation harvesting pigments in plants, can absorb in the visible region with a high efficiency ($\varepsilon > 10^5$ $m^{-1}$ $cm^{-1}$). When used as sensitizers, such molecules must show chemical and photochemical stability under operative device conditions, as they must survive upon a large number of photoexcitation and reduction cycles.

Chlorophyll *a* has a polycyclic porphyrinic structure with conjugated double bonds which are responsible for its absorption in the red and in the blue regions of the visible spectrum. Carotenoids serve as light-harvesting accessory pigments in photosynthetic plants by transferring the singlet excitation energy to chlorophyll *a*. Besides being involved in light harvesting and electron transfer, carotenoids can act as photoprotectors both by dissipating the energy of chlorophyll *a* triplets and by scavenging singlet oxygen states which can lead to chlorophyll *a* destruction [6]. The above mentioned properties and the intense light absorption in a wide interval of the visible region make both chlorophyll *a* and carotenoids promising candidates as sensitizers in photovoltaic and photoelectrochemical devices [7].

As a matter of fact, an efficient charge transfer to the inorganic particles can usually occur only through the first

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☆ Dedicated to Prof. Mario Della Monica (January 9th, 1932-September 9th, 2003).

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pigment monolayer, so that the resulting photoconversion efficiency is very low. This limitation can be overcome by depositing the dye molecules onto a porous film composed of nanosized particles. As in nanocrystals the surface-to-volume ratio increases with decreasing the mean particle size, the active area can be extended 1000-fold, thus making light absorption highly efficient even with a dye monolayer on each particle [8]. Moreover, a continuous porous structure can be ensured even after thermal treatments of the inorganic film.

In this paper, hetero-structures formed by ZnO nanocrystalline films and chlorophyll *a*, carotenoids or their mixture are presented and characterized. Surfactant-capped ZnO nanocrystals [9] were used as precursors for the deposition of thin films. Reflectance spectroscopy was performed to characterize the inorganic film surface after deposition of the photosynthetic pigments. Photoelectrochemical experiments showed that the photocurrent response of the sensitized ZnO nanocrystals films was remarkably higher than that obtained in presence of bulk ZnO. Notably, co-sensitization by chlorophyll *a* and carotenoids on nanocrystalline electrodes greatly enhanced the photoactivity of the hetero-junction.

## 2. Experimental section

### 2.1. Materials

Commercial ZnO ($d < 1$ μm), chloroform, anhydrous zinc acetate ($ZnAc_2$), *t*-buthylphosphonic acid (TBPA), and sodium hydroxide (NaOH) were purchased from Aldrich. Hexadecylamine (HDA), methanol, litium perchlorate ($LiClO_4$), and potassium dihydrogen phosphate ($H_2KPO_4$) were from Fluka Biochemika. All aqueous solutions were made by using bidistilled water. The photosynthetic pigments were isolated from *Spirulina geitler* [10] and stored in the dark, in wet *n*-pentane (Aldrich), at − 80 °C under a $N_2$ atmosphere. Purity and concentration were routinely checked using the criteria described elsewhere [11]. ZnO commercial oxide-based electrode prepared as previously reported [12] was also investigated.

### 2.2. Preparation of Q-sized ZnO-based electrodes

Q-sized organic-capped ZnO nanocrystals were prepared by a previously reported non-hydrolytic approach [9]. Briefly, $ZnAc_2$ was thermally decomposed at 220–300 °C in HDA in presence of TBPA as stabilising agent. The $ZnAc_2$/TBPA molar ratio governed the final nanoparticle mean sizes. After extraction from the reaction mixture, the nanocrystals were dissolved in $CHCl_3$ and deposited as thin film. The nanocrystals were characterized by UV–Vis absorption spectroscopy, powder X-ray diffraction (XRD), and transmission electron microscopy (TEM).

ZnO-based electrodes were typically prepared using nanocrystals of about 6.5 nm, immobilised onto a transparent electrode (ITO) by spin-coating or casting.

After thermal treatment at 400 °C for 30 min, the highly porous oxide layer was coated with the sensitizer solution by dipping.

### 2.3. Analysis

Absorption spectra of solutions of the photosynthetic pigments were measured by using a Cary 3 (Varian) spectrophotometer. UV–Vis spectra of the films were recorded by an integration sphere diffuse reflectance accessory (Varian).

Photoelectrochemical measurements were obtained by using an Autolab potentiostat PGSTAT 10. The photoelectrochemical device was a three-electrode cell with Ag/AgCl as reference electrode, ITO as working electrode, and platinum as counter electrode in an electrolyte solution (phospate

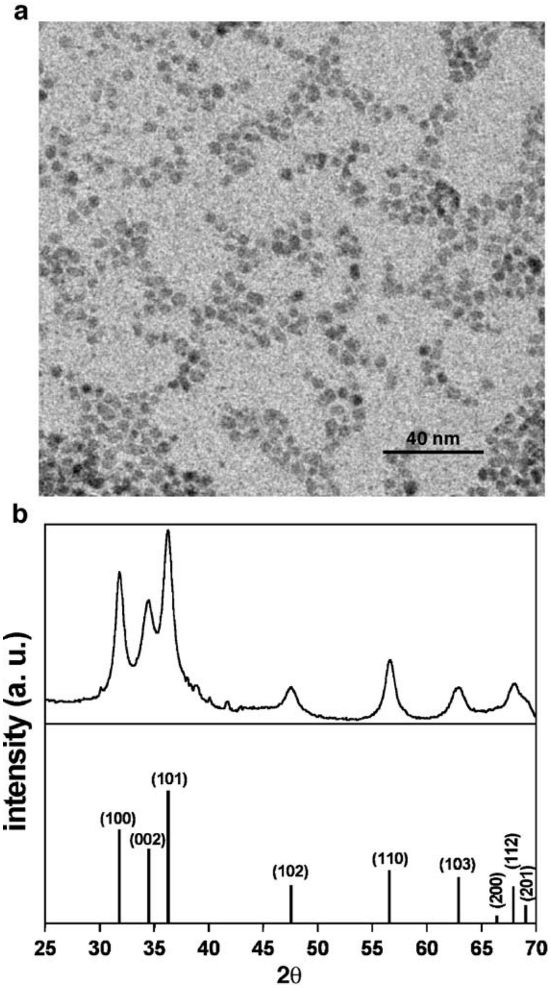

Fig. 1. (a) Low-resolution TEM image of ZnO nanocrystals prepared in HDA at $TBPA/ZnAc_2 = 0.20$ molar ratio. (b) Powder X-ray diffraction pattern of sample (a), along with the standard ZnO wurtzite diffraction lines.

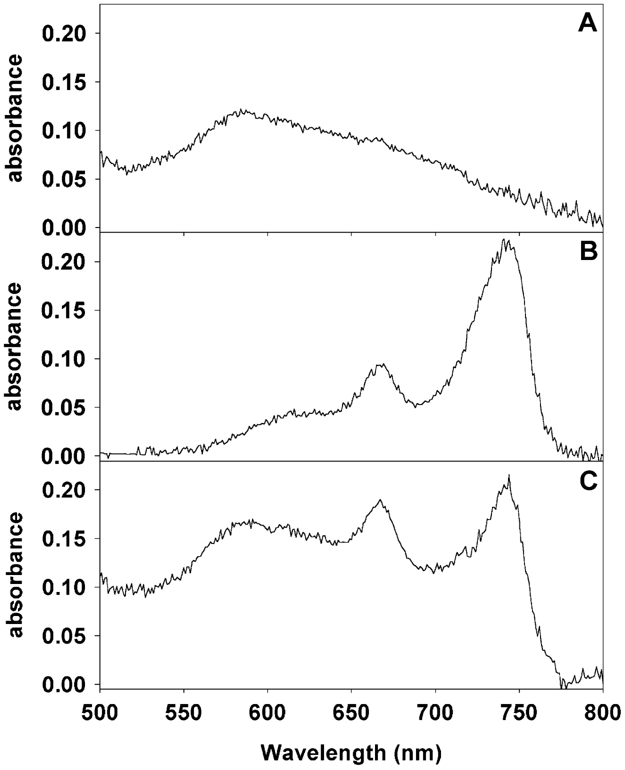

Fig. 2. Reflectance spectra of carotenoids (A), chlorophyll *a* (B) and of a chlorophyll *a*/carotenoids mixture (C) adsorbed onto an ITO/ZnO film.

buffer at pH = 7 or $LiClO_4$ 0.1 M). The cell was subjected to a bias of 0 V. A tungsten lamp (250 W) with an optical fiber was used to illuminate the prepared hetero-junctions.

## 3. Results and discussion

In Fig. 1a, a TEM image of as-prepared ZnO nanocrystals is shown. The sample consists of uniformly sized nanoparticles (mean size 6.5 nm) that are well separated on the grid due to their surface organic coating. The correspondent XRD profile in Fig. 1b matches the standard ZnO wurtzite pattern, while the broadening of the diffraction peaks points to nanosized crystalline domains. The mean particle sizes of the nanocrystals, as estimated by fitting the XRD data with the Debye–Scherrer formula, were in agreement with the values measured by TEM.

In Fig. 2, the reflectance spectra relative to nanocrystalline ZnO films after surface modification with carotenoids (Fig. 2A), chlorophyll *a* (Fig. 2B), or with their mixture (Fig. 2C) are reported. For chlorophyll *a* deposited onto commercial bulk ZnO powders, reflectance measurements show a feature at 662 nm ascribed to the absorbance of sensitizer in the monomer form [13]. By comparison, chlorophyll *a* deposited onto nanocrystalline ZnO (Fig. 2B) exhibits an additional prominent band at longer wavelengths (740 nm). A similar spectral feature is observed in the spectrum of ZnO film covered by the pigment mixture (Fig. 2C), while the large band at about 580 nm (Fig. 2A and C) can be ascribed to the absorption of carotenoids. The absorption at 740 nm may be due to the formation of a hydrate aggregate of the pigment, whose structure and properties have been largely debated in literature [14]. The dye aggregates can act as light harvesting antennae by absorbing in spectral regions different from those of the monomer. Energy transfer between adjacent dye molecules can subsequently occur, then being followed by electron injection into the semiconductor particles. Alternatively,

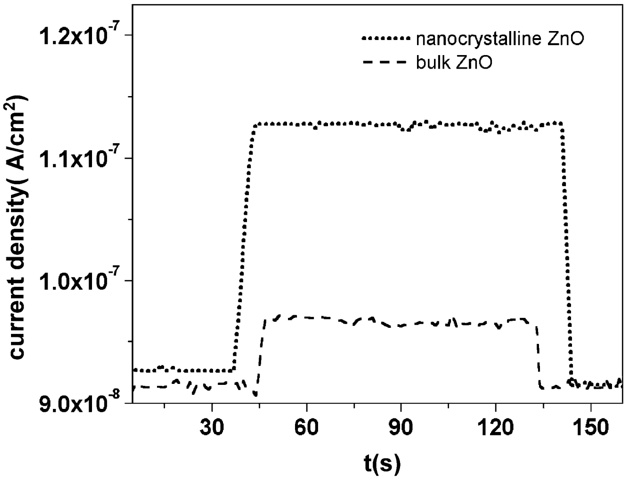

Fig. 3. Photocurrents recorded at 0 V on a ZnO nanocrystalline–ITO electrode (dotted line) and on a bulk ZnO–ITO electrode (dashed line), both sensitized by chlorophyll *a*. The measurements were carried out in a three electrodes cell with Ag/AgCl as reference electrode, ITO as working electrode, and platinum as counter electrode. The solution was a phosphate buffer at pH = 7.

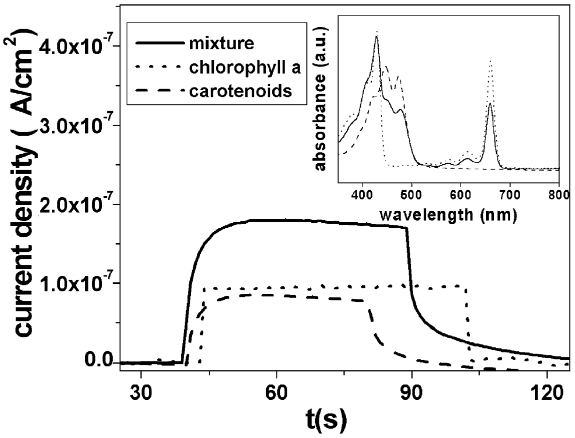

Fig. 4. Photocurrents recorded at 0 V on a nanocrystalline ZnO film–ITO electrode sensitized by chlorophyll *a* (dotted line), carotenoids (dashed line), and chlorophyll *a* and carotenoids mixture (solid line). The measurements were carried out in a three-electrode cell with Ag/AgCl as reference electrode, ITO as working electrode, and platinum as counter electrode. The electrolyte solution was $LiClO_4$ 0.1 M. Inset: Absorption spectra of $10^{-4}$ M chlorophyll *a* solution (dotted line), $10^{-5}$ M carotenoid solution (dashed line), and $10^{-6}$ M chlorophyll *a* and carotenoid mixture (solid line) in diethyl ether.

electrons can be directly transferred from the excited state of the aggregate to the semiconductor nanocrystals [15].

In Fig. 3, the photoelectrochemical behaviour of a nanocrystalline ZnO film is compared with the response of a bulk ZnO-based film. The films were deposited onto ITO and sensitized with chlorophyll *a*. Both chlorophyll *a* films on the different substrate evidenced a very fast response to the light, although a considerably higher photocurrent is detected for the nanostructured film with respect to the bulk oxide electrode. This result can be ascribed to the extremely higher surface density of sites available for chlorophyll *a* adsorption on the film deposited from ZnO nanocrystals, which, in turn, ensures a more efficient light collection. As opposed, the bulk oxide-based film is most likely less porous, as it derives from a suspension of aggregated micrometer-sized crystals. An interconnected particles network may also be favourable for charge carrier percolation through the nanocrystalline film. In addition, as pointed out by reflectance measurements above discussed, the extension of the chlorophyll absorption range when it is adsorbed onto the nanocrystalline particles can also contribute to the enhancement of the photoactivity of the hetero-junction.

Nanostructured ZnO electrodes sensitized by different pigments were photoelectrochemically tested. The hetero-junctions were prepared by sensitizing nanocrystalline ZnO films with chlorophyll *a*, carotenoids, and their mixture, respectively. The measurements were reproducible and no degradation of film was observed within typical observation times.

The observed photocurrent trend shown in Fig. 4 points to a significantly higher photoresponse when the pigment mixture is used, and in particular the blend presents a photoactivity which approximately matches the sum of the intensity recorded for the single dyes. A more detailed observation of the chlorophyll signals reported in Figs. 3 and 4 evidences a difference in the intensity of the photocurrents, reasonably due to the different base electrolytes in solution. The enhancement of the photosensitization process in the presence of mixture can be ascribed to the already mentioned photoprotection role of carotenoids. In addition, the synergic effect of the two dyes in extending the overall absorption (see the inset in Fig. 4) spectrum can play a crucial role.

## 4. Conclusions

Hetero-structures were prepared by sensitizing ZnO nanocrystals-base film with photosynthetic pigments onto an optically transparent electrode (ITO). Photoelectrochemical measurements were comparatively performed on both bulk and nanocrystalline ZnO films after dye-covering in order to probe the photosensitization process occurring at the hetero-junction. The sensitization process is explained by invoking the higher surface area available for light capture on the nanocrystalline film and on the basis of the aggregation state of the adsorbed chlorophyll *a* molecules. The photoconversion process was found to be enhanced at nanocrystalline electrodes upon sensitization with a dye mixture. The photoprotective action played by carotenoids was found to be advantageous in the photoconversion efficiency.

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