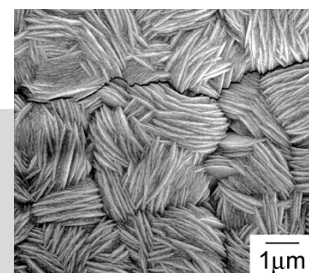


# Electrochemical Self-Assembly of Dye-Modified Zinc Oxide Thin Films

By Tsukasa Yoshida\* and Hideki Minoura

*One-step electrochemical self-assembly is an excellent new method for the construction of hybrid inorganic/organic films for dye-sensitized solar cells (DSSCs). The promising oxide semiconductor zinc oxide can be electrodeposited in the presence of organic dye molecules to give porous thin films with varying morphology suitable for DSSCs (the Figure shows a ZnO film grown in the presence of a tetrasulfophthalocyanine).*



There has been a growing interest in inorganic/organic hybrid materials in recent years, because of the anticipation of new or improved properties, which are not exhibited or reachable by use of inorganic or organic materials alone.<sup>[1]</sup> There can, however, be a broad range of such mixed materials depending on the size scale of the mixture; from composites at the micrometer scale down to inorganic/organic compounds in which new chemical structures at the molecular or atomic level are formed. This can be a consequence of different preparation methods adopted to combine two or more kinds of materials, such as simple mixing of bulk materials, mixing upon sol-gel processing,<sup>[2]</sup> ion-exchange,<sup>[3]</sup> use of Langmuir-Blodgett films<sup>[4]</sup> or surface adsorption of organic molecules on inorganic surfaces.<sup>[5]</sup> The mixture in the atomic regime is of highest interest for us, because such mixtures should behave differently from both of the parent inorganic and organic materials, not just as the sum of them. The usefulness of such special properties exhibited by the inorganic/organic interface has been best manifested in the recent successful development of dye-sensitized solar cells (DSSCs),<sup>[6]</sup> in which very efficient photo-induced charge separation was achieved at the interface between the inorganic semiconductor and the surface-bound organic dye molecules. While formation of ordered assemblies of organic molecules on inorganic surfaces—frequently called self-assembled monolayers (SAMs)—has been actively studied especially for thiols adsorbed on gold single-crystals,<sup>[7]</sup> dye-modified inorganic semiconductors in DSSCs have rarely been regarded as self-assembled inorganic/organic materials. However, the ordered assembly of Ru complexes on a TiO<sub>2</sub> surface has recently been reported.<sup>[5]</sup> This is an ex-

ample of three-dimensional inorganic surfaces modified by SAMs.

The dye-modified porous inorganic semiconductor for DSSCs has been fabricated by stepwise processing in almost all previous studies; i.e., formation of porous film of nanocrystalline TiO<sub>2</sub> by using a colloidal paste of TiO<sub>2</sub> to coat a transparent conductive oxide (TCO) substrate (such as F-doped, SnO<sub>2</sub>-coated glass) and subsequent heat treatment, followed by dye-adsorption by dipping the film into the solution of the sensitizing dyes. It is very important to modify the TiO<sub>2</sub> surface with dye molecules from solution in order to achieve a self-assembled monolayer of the sensitizer and thus creating a photoactive inorganic/organic interface. While dye adsorption from solution allows the dye molecules to choose their structure at the inorganic surface, the colloid processing of the semiconductor film inherently results in random crystallographic structure of the film, because of the random agglomeration of the preformed crystallites. The need for heat treatment also limits the choice of the TCO substrate to being heat resistant. Our motivation was to develop a new method to synthesize the dye-modified semiconductor thin films in a perfectly self-assembled manner, including that for the formation of the inorganic phase. Although deposition of a crystalline TiO<sub>2</sub> film in an aqueous solution has not been realized so far, the oxide semiconductor zinc oxide (ZnO) can be directly crystallized by cathodic electrodeposition from an aqueous solution of zinc nitrate.<sup>[8]</sup> ZnO has been one of the most promising oxide semiconductor materials for the DSSCs.<sup>[9]</sup> We thus asked the question: What will happen if ZnO is electrodeposited in the presence of dye molecules? The answer was the electrochemical self-assembly of dye-modified ZnO thin films in a one-step process without heat treatment.<sup>[10–13]</sup> The deposited thin film electrodes have been found to perform as sensitized photoelectrodes applicable to the DSSCs.<sup>[12–14]</sup>

Surface reactions play a decisive role in crystal growth in chemical and electrochemical deposition of compound thin

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films from solutions.<sup>[15]</sup> When film growth is achieved by atomic layer-by-layer growth of crystallites, and not by piling up small particles, a film made up with single crystalline particles is obtained.<sup>[15]</sup> This situation has been found for the cathodic electrodeposition of ZnO.<sup>[11]</sup> When a cathodic potential of typically  $-0.9$  V (vs. saturated calomel electrode, SCE) is applied to a conductive substrate in an aqueous solution of zinc nitrate (typically  $0.1$  M) maintained at  $70^\circ\text{C}$ , nucleation of ZnO takes place almost instantaneously and further electrolysis promotes further crystal growth, resulting in a film composed of hexagonal faceted crystals. A scanning electron microscopy (SEM) photograph of a ZnO thin film electrodeposited on a basal-plane (van der Waals plane) of oriented pyrolytic graphite (OPG) is shown in Figure 1a. Hexagonal faces of the ZnO crystallites are clearly seen. Correspondingly, the X-ray diffraction (XRD) patterns of the film indicates preferential orientation of the ZnO crystallites with their  $c$ -axis being perpendicular to the substrate, as recognized from the significantly enhanced relative peak intensity for the (002) diffraction (Fig. 2a). Since the anti-bonding  $\pi$ -electronic surface of the OPG basal-plane does not act as a template for ZnO in terms of its crystallographic orientation, it becomes controlled by the anisotropic stability of ZnO crystals in contact with the solution as well as the substrate. The crystallites of ZnO are self-oriented in the observed direction as they expose the most stable, closest packed (002) planes to the solution.

Because chemistry at the solid/solution interface is the determinant factor, adsorption of dye molecules to the growing surface of ZnO has a significant impact on crystal growth. When water-soluble dyes such as metal complexes of 2,9,16,23-tetrakisulfophthalocyanines (TSPcMs;  $M = \text{Zn}^{\text{II}}$  (TSPcZn),  $\text{Al}^{\text{III}}$ [OH] (TSPcAl) or  $\text{Si}^{\text{IV}}$ [OH]<sub>2</sub> (TSPcSi))<sup>[10,11]</sup> and organic dyes such as tetrabromophenol blue (TB)<sup>[12]</sup> or eosin Y (EY)<sup>[13]</sup> were added to the  $\text{Zn}(\text{NO}_3)_2$  bath at low concentration (typically  $50\ \mu\text{M}$ ), colored ZnO thin films with totally different surface morphologies and crystallographic structures from the pure ZnO film were obtained. In many cases, surface adsorption of dye molecules hinders crystal growth, leading to automatic formation of porous thin films composed of nano-sized crystallites of ZnO suitable for the DSSCs.<sup>[10–14]</sup> In some cases, anisotropy in the dye stability of the adsorption results in a preferential growth of ZnO into specific crystallographic direction to create unique textured morphologies.<sup>[11]</sup> In Figure 1b is shown the surface morphology of a ZnO/TSPcSi thin film electrodeposited under the identical conditions as for that of Figure 1a but in the presence of TSPcSi added to the deposition bath. Interconnected fine particles compose flat disk-like deposits with diameter greater than  $1\ \mu\text{m}$ . These disks are assembled almost in parallel to form disk-stacks that are oriented with their disk-plane perpendicular to the OPG surface. Deposits with the identical structure have been observed when deposition has been carried out on a poly-crystalline indium tin oxide (ITO) coated glass.<sup>[11]</sup> The addition of TSPcSi changes the crystallographic orientation by  $90^\circ$  into the (100) planes parallel with the sub-

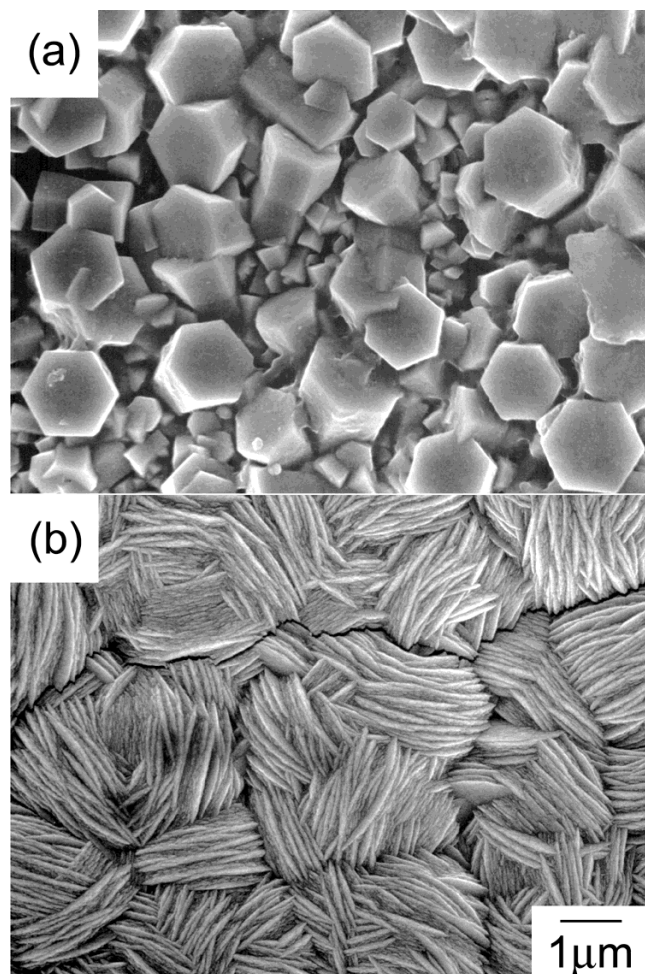


Fig. 1. SEM photographs of thin films of ZnO (a) and ZnO/TSPcSi (b) electrodeposited at  $-0.9$  V (vs. SCE) for 1 h on the basal-plane of oriented pyrolytic graphite substrates from aqueous solutions of  $0.1$  M  $\text{Zn}(\text{NO}_3)_2$  and  $0.1$  M  $\text{Zn}(\text{NO}_3)_2 + 50\ \mu\text{M}$  TSPcSi, respectively. Bath temperature =  $70^\circ\text{C}$ .

strate direction, as found in its XRD pattern with the largely enhanced (100) diffraction peak at the expense of the (002) peak, as compared to the pure ZnO film (Fig. 2). From these observations, it is understood that the edge and the plane of the disk-like deposits correspond to the (100) and (002) crystal faces of ZnO, respectively. Such structure of the film has been further proven by the TEM observation of the deposits.<sup>[11]</sup> Adsorption of TSPcSi molecules takes place preferentially onto the (002) planes of ZnO to hinder the crystal growth along the  $c$ -axis. Consequently, ZnO tends to grow into the (100) direction, thus these crystal faces pointing towards the bulk of the solution to build up the disk-like deposits in the observed alignment (Fig. 3).

While the presence of the dye molecules during the electrodeposition brings about dramatic changes in the crystal growth, ordered surface of inorganic crystals and chemical interaction among the neighboring dye molecules creates ordered assemblies of the dye molecules at the same time.<sup>[10–13]</sup> Because the dye molecules are very much condensed in these electrodeposited films, the absorption spectrum of the film

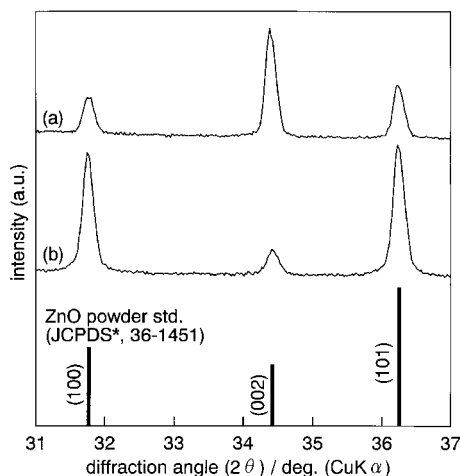


Fig. 2. XRD patterns of the electrodeposited thin films of ZnO (a) and ZnO/TSPcSi (b), corresponding to those shown in Figure 1. The orientation indices calculated for crystal planes with major diffraction,  $X_{100}$ ,  $X_{002}$ ,  $X_{101}$ , using the method described in [11] and taking the powder standard as reference were 0.66, 2.51, 0.53, and 1.62, 0.47, 0.88 for (a) and (b), respectively, showing strong orientation of the  $c$ -axis being perpendicular for (a) and parallel for (b) with the substrate. [\*] Data from Joint Committee on Powder Diffraction Standards.

shows a remarkable difference from that of the dye molecules in solution. This is due to enhanced intermolecular electronic interaction as well as the ZnO/dye interaction. Intermolecular attraction leads to formation of  $\pi$ -stacking aggregates of TSPcZn<sup>[10,11]</sup> or TB<sup>[12]</sup> in the deposited films, while TSPcAl and TSPcSi, with axially coordinated OH<sup>-</sup>, did not permit aggregation in such an arrangement, and were bound to ZnO in their monomeric form.<sup>[11]</sup> An illustration that summarizes electrochemical self-assembly of ZnO/TSPcM thin films is shown in Figure 3. In case of TB and EY, the dye molecules were found to be reduced upon their incorporation to the

film, so that the dye molecules are not passively adsorbed but actively participate in the electrochemical processes.<sup>[12,13]</sup> Varieties of ZnO/dye structures are produced depending upon subtle balance of the interfacial chemical and electrochemical processes.

Visible light irradiation to the electrochemically self-assembled ZnO/dye thin film electrodes in a  $I^-/I_3^-$  redox electrolyte generated photoanodic current, clearly showing photosensitization by incorporated dye molecules, indicating the potentials for their use in the DSSCs.<sup>[12–14]</sup> While  $\pi$ -stacking aggregation of TSPcZn was found to significantly degrade its sensitizing ability,<sup>[14]</sup> aggregates of TB and EY were found to be efficient sensitizers.<sup>[12,13]</sup> Because this process does not require heat treatment at high temperature to crystallize ZnO, it is possible to use TCO-coated plastic substrate to realize fabrication of flexible DSSCs. This technique is very simple and versatile, opening up a way to synthesize thin films of mixed materials of ZnO and various kinds of dyes or other organic molecules. The fact of significant importance is that these materials always have structures chosen by the constituent molecules, ions and atoms, to maximize the synergetic effects for the evolution of new functions from the inorganic/organic interfaces. Such materials are expected to find use not only in the DSSCs but also in applications employing their optical and electrical properties.

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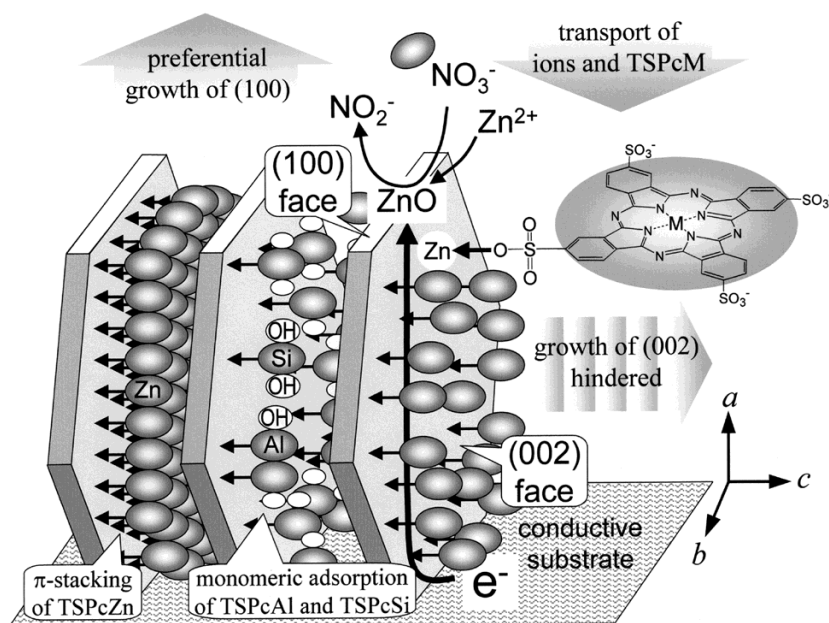


Fig. 3. Illustration summarizing the electrochemical self-assembly of the ZnO/TSPcM thin films, showing the preferential adsorption of TSPcM onto the (002) planes of ZnO and consequent preferential growth of (100) planes to create the stacking "disks" aligned vertical to the substrate. Intermolecular attraction among the TSPcZn molecules leads to surface aggregation in a  $\pi$ -stacking structure, while TSPcAl and TSPcSi are adsorbed in monomeric form due to the steric hindrance by the axial OH<sup>-</sup>.

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