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Understanding the role of nanostructuring in photoelectrode performance for light-driven water splitting

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ABSTRACT

The analysis of capacitance data for regular nanostructured photoelectrodes is revisited using a hematite nanorod array as an example. The effects of the cylindrical nanorod geometry on the capacitance-voltage behaviour are outlined, and the limiting case of complete depletion is discussed in terms of the residual geometric capacity at the base of the nanorods. Since nanorod arrays generally leave areas of the substrate exposed, it is necessary to consider the parallel capacitance associated with the fraction of uncovered surface. The sensitivity of the capacitance fitting to parameter variation is explored. The enhancement of external quantum efficiency (EQE) by nanostructuring is also discussed using hematite nanorod arrays as experimental examples. It is shown that, although very substantial EQE enhancement should be achieved by simple geometric effects, the performance of nanostructured hematite electrodes in the visible region of the spectrum is considerably lower than predicted if all charge carriers generated in the space charge region (SCR) were collected. Further analysis reveals that the internal quantum efficiency increases with photon energy, suggesting that the probability of generating free, rather than bound, electron-hole pairs in hematite depends on the excess energy $h\nu - E_{\text{gap}}$.

1. Introduction

Against a background of increasing deployment of photovoltaics for electricity generation, light-driven water splitting to generate hydrogen as a fuel and feedstock remains an important goal of energy research since it addresses the key problem of energy storage. The search for stable photoelectrodes with suitable optoelectronic and chemical properties has occupied electrochemists for decades. Since light-driven water splitting reactions involve minority carriers (holes for oxidation at n-type photoanodes and electrons for reduction at p-type photocathodes), we would like ideally to use semiconductors that have long minority carrier lifetimes, high carrier mobilities and suitable light harvesting properties. Unfortunately, while the best materials from an optoelectronic point of view (for example, silicon, III-V and II-VI semiconductors and, more recently, the lead halide perovskites) can be used to fabricate efficient solar cells, as photoelectrodes, they are prone to photo-corrosion and must therefore be protected by a stable impervious layer such as TiO₂. This configuration corresponds to a ‘buried’ junction in which the generated photovoltage is used to drive electrolysis at metallic or pseudo-metallic electrodes [1,2]. By contrast, photoelectrolysis systems in which the light harvesting semiconductor is in

direct contact with the electrolyte are more demanding in terms of stability as well as band alignment with the oxygen and hydrogen redox Fermi levels. For this reason, oxide materials such as hematite (α -Fe₂O₃) [3–6] and bismuth vanadate (BiVO₄) [7–9] have been studied widely, despite their rather poor optoelectronic properties (hematite, for example, is an indirect n-type bandgap semiconductor with a very short hole lifetime and low hole mobility).

An often-cited figure of merit in this context is the minority carrier diffusion length, which in the neutral bulk of a semiconductor is defined as $L_{\text{min}} = (D_{\text{min}}\tau_{\text{min}})^{1/2}$, where τ_{min} is the minority carrier lifetime and D_{min} is the minority carrier diffusion coefficient, which is related to the mobility μ_{min} by $D_{\text{min}} = \left(\frac{k_B T}{q}\right)\mu_{\text{min}}$. Based on early studies, hole diffusion lengths for hematite are believed to be in the range of a few nm [10,11], many orders of magnitude smaller than minority carrier diffusion lengths in III-V semiconductors such as GaAs, for example, which can be several microns [12]. A low hole diffusion length means that the separation and collection of photogenerated electron-hole pairs that is essential for any photovoltaic or photoelectrochemical device to function only takes place in regions that are strongly depleted of majority carriers. In the case of a conventional planar hematite

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photoelectrode, this means that only photons absorbed in the space charge region (SCR) of the semiconductor/electrolyte contact contribute to the photocurrent. Nearly all holes generated in the quasi-neutral region (QNR) recombine very rapidly with electrons, which are present in large excess. Only holes generated very close (i.e. within one ca. diffusion length) to the edge of the SCR have any chance of being collected at the semiconductor/electrolyte interface. Since the penetration depth of the incident illumination (typically close to $1\mu\text{m}$) is generally much greater than the width of the space SCR (a few tens of nm for a typical hematite electrode), the external quantum efficiency (EQE) of the photocurrent is much less than 100%. However, as we shall see below, even the assumption that all carriers generated in the SCR are collected is open to doubt in the case of hematite.

A popular approach aimed at tackling this problem of mismatched characteristic lengths is to nanostructure the water-splitting photoelectrode. The often-repeated argument is that if the scale of the nanostructure is comparable with the minority carrier diffusion length, this will enhance the chance of photogenerated minority carriers reaching the semiconductor/electrolyte interface, increasing the EQE. We show here that this interpretation of the beneficial effects of nanostructuring does not stand up to scrutiny. For highly doped materials like hematite (here we take highly doped to mean a doping density $> 10^{18}\text{ cm}^{-3}$), we show that it is the collection of holes in the SCR and not the hole diffusion length in QNR that explains why nanostructuring can enhance the EQE.

To be able to model the EQE of regular nanostructured systems such as nanorod arrays with cylindrical geometry, we need to have reliable estimates of the doping density. Reliable determination of the doping density, N_d , is important since it allows us to distinguish between cases where the space charge layer thickness is either smaller than or larger than the characteristic lengths of the nanostructures. However, the conventional Mott Schottky analysis used to determine N_d for planar electrodes cannot be applied to non-planar electrodes. Instead, the geometry (spherical, cylindrical etc.) of the nanostructure needs to be considered. In addition, we need to have some idea of how rapidly minority carriers are consumed at the interface with the electrolyte, either by reaction with electrolyte species or by recombination with majority carriers. The well-known analysis of the external photocurrent quantum efficiency by Gärtner [13] assumes that the interface acts as a perfect sink for minority carriers. However, water splitting involves multiple electron/proton transfer steps, and the reaction of holes in the photooxidation of water, for example, is remarkably slow. It follows that the rate of the water splitting reaction cannot be controlled by the rate of hole transport to the interface (except as insofar as this affects recombination in the SCR: see below). Consequently, arguments about the benefits of nanostructuring that are based on matching the feature sizes of the electrode to the diffusion length of holes in the QNR are unconvincing. In this paper, we explore some of the difficulties encountered in the determination of doping densities for a hematite nanorod array and discuss an alternative explanation for the superior performance of nanostructured oxide electrodes. We also examine the performance of hematite nanorod electrodes by comparing it with the performance predicted by assuming that all electron-hole pairs generated in the SCR are collected. We show that recombination in the SCR is a likely to be a major limiting factor in the performance of hematite electrodes.

2. Capacitance measurements of nanostructured semiconductor electrodes

2.1. The planar case

We begin by revisiting the classical theory of the semiconductor electrolyte interface before moving on to discuss the case of an array of cylindrical nanorods. For simplicity, we initially ignore the effects of inversion, which are discussed later. Instead we assume that deep

depletion is possible because the rate of thermal generation of minority carriers is smaller than the rate of their removal at the electrolyte contact. Furthermore, we omit consideration of surface states and Fermi level pinning.

The width of the SCR, W_{SCR} , formed at a planar semiconductor-electrode junction depends on the doping density (N_d), the relative permittivity (ϵ) of the material and the potential drop, $\Delta\phi_{SCR}$, across the space charge region.

$$W_{SCR} = \left(\frac{2\Delta\phi_{SCR}\epsilon\epsilon_0}{qN_d} \right)^{1/2} \quad (1)$$

For low-doped semiconductors, this potential drop is equal to the difference between the applied potential E and the flat band potential E_{fb} , but in the cases that we consider here, the doping is sufficiently high that a significant part of the change in potential difference with applied voltage appears across the Helmholtz double layer. Following the approach of De Gryse et al. [14], we therefore separate the overall potential drop into two terms.

$$E - E_{fb} = \Delta\phi_{SCR} + \Delta\phi_H \quad (2)$$

Treating the Helmholtz capacitance C_H as constant (capacitance and charge are expressed per unit area), the potential drop, $\Delta\phi_H$, across the Helmholtz layer is given by

$$\Delta\phi_H = \frac{Q_{SCR}}{C_H} \quad (3)$$

where Q_{SCR} , the charge in the SCR, is given in the Mott Schottky approximation by

$$Q_{SCR} = (2q\epsilon\epsilon_0N_d)^{1/2} \left(\Delta\phi_{SCR} - \frac{k_B T}{q} \right)^{1/2} \quad (4)$$

The potential drop across the Helmholtz layer therefore changes according to the expression [14]

$$\Delta\phi_H = \left(\frac{2q\epsilon\epsilon_0N_d}{C_H^2} \right)^{1/2} \left(\Delta\phi_{SCR} - \frac{k_B T}{2} \right)^{1/2} \quad (5)$$

From Eq. (2) and Eq. (5) we obtain a more general form of the Mott Schottky equation that is applicable to highly-doped electrodes in the deep depletion approximation (i.e. ignoring the effects of inversion) [14]. Eq. (5) must be replaced by the more general form

$$\frac{1}{C^2} = \frac{1}{C_H^2} + \frac{2}{q\epsilon\epsilon_0N_d} \left(E - E_{fb} - \frac{k_B T}{q} \right) \quad (6)$$

where C is the measured total capacitance [14]. It can be seen from eq. 6 that the Mott Schottky plot passes through the point $1/C_H^2$ on the y-axis when $E - E_{fb} - k_B T/q = 0$ and intercepts the voltage axis at an electrode potential E_0 given by

$$E_0 = E_{fb} + \frac{k_B T}{q} - \frac{q\epsilon\epsilon_0N_d}{2C_H^2} \quad (7)$$

Eq. (6) was derived for deep depletion conditions. However, for the case of hematite under water splitting conditions, the deep depletion condition cannot be achieved, as demonstrated by the fact that water oxidation occurs in the dark. This process must involve holes generated at the surface by thermal excitation of electrons from the valence band or by tunnelling of electrons through a narrow space charge region from the valence band at the surface. The latter process could be assisted by thermal excitation of electrons to surface states located in the band gap. The presence of mobile holes gives rise to a very narrow charge region and a correspondingly high capacitance, as shown below in Fig. 1. Under these conditions most of the potential drop will occur in the Helmholtz layer, and the electrode will behave more like a metal.

The general expressions for the space charge capacitance including accumulation depletion and inversion conditions can be found in textbooks, for example Sato [15]. Fig. 1 illustrates the three regions in the

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