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Non-monotonic dependence of the current density on the thickness of the photoactive layer

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Abstract

We have developed a mathematical model able to predict the dependence of the current density, j_0, in the dc limit, on the thickness of a photoactive semiconductor layer, d, in contact with an electrolyte. The model considers the application of an external bias. The theoretical analysis has been done by means of a diffusive model, where the excess of charges moves by diffusion in the presence of a generation term, due to the incident light, and a recombination term, proportional to the excess of charge carriers. We show that a non-monotonic dependence of j_0 vs. d is expected. For small d, the photocurrent density is proportional to d and the proportionality constant is related to both the attenuation of the light in the photoactive semiconductor layer and to the applied potential. In the opposite limit of large d, the current tends to a constant value that is dependent on both the light intensity and the applied bias. Our theoretical predictions are in qualitative agreement with the experimental data reported in literature for $BiVO_4$ films.

PACS numbers:

INTRODUCTION

The production and storage of energy coming from renewable sources and the reduction of CO_2 emissions to the atmosphere and its re-use are top challenges for humankind. Extensive research and technology development are in progress to exploit the enormous amount of solar energy that falls on our planet (100,000 TW) such as the so-called artificial photosynthesis process. The greatest challenge of this technology leads in the development of efficient photo-catalytic systems able to overcome the high intrinsic over-potential of the water oxidation reaction that, requiring a four-electron transfer process, is responsible for the slow kinetics of photo-electrochemical (PEC) system for both water splitting and solar fuels production [1–3]. The development of n-type semiconductor photo-electrodes is one of the most investigated strategies for that purpose and, in particular, metal oxides have attracted a great deal of interest because of their good cost-effectiveness. For instance, TiO_2 [4], ZnO [5] and $SrTiO_3$ [6], among others, have deeply been investigated for their photo-catalytic activity under UV light irradiation. Nevertheless, visible-light responsive materials (e.g. $BiVO_4$ [7], WO_3 [8], Fe_2O_3 [9], TaON [10]) are currently more promising for an efficient utilization of the solar energy. The most recent exciting developments in water-splitting PEC systems have utilized $BiVO_4$ (band gap, Eg = 2.4 eV) as the photoanode [11–14].

A variety of synthesis techniques have been used to synthesize films of these metal oxides. The most widely used methods, especially for preparing $BiVO_4$ films, are based on wet chemistry combined with spin-coating [15], spray pyrolysis [12] or electrodeposition [16], which are cheap and flexible processes. Recently, physical techniques such as reactive magnetron sputtering [17, 18] have emerged due to the superior purity, uniformity and adhesion of the films that can be attained, which is particularly important for the practical application of such materials at high scale. Several experiments have been performed in order to optimize the thickness (d) of the semiconductor-based films (such as TiO_2 [4], WO_3 [19] and $BiVO_4$ [18, 20]) with respect to light absorption (high d) and separation of the electron-hole pairs (low d), and also to enhance the charge transport in the photo-electrode layer. Nonetheless, the control and tuning of the film thickness require playing with several parameters (e.g. concentration of precursors or kind of target, humidity, temperature, pressure, synthesis atmosphere, applied power, etc) [15, 18, 22], which depend on the chemical or physical process employed. Therefore, in order to improve the photocatalysts performance and fas-

ten the progresses in this field, it is of primary importance to define guidelines that direct the experimental developments. For instance, for undoped $BiVO_4$, without additional films (i.e., blocking layers, catalytic films), current reported photocurrents for water oxidation with AM1.5 illumination are lower than 1 mA/cm^2 [17, 23], which is less than 15 % of the theoretical maximum for a 2.4 eV absorber.

In recent papers devoted to the activity of $BiVO_4$, WO_3 and TiO_2 thin film electrodes for solar-driven water splitting, it has been observed that the electric photo-current density depends non-monotonically on the thickness of the film [18–21]. Thus, the goal of this work is to present a theoretical model able to describe the dependence of the photo-current on the thickness of the active layer. This model represent a useful tool for fastening the progress on the development of photo-anodes materials and for developing an efficient PEC water splitting device.

MATHEMATICAL MODEL FOR ELECTRON TRANSPORT IN BIVO$_4$

We consider a slab of photoactive semiconductor of thickness d in contact at the left with a conducting substrate, and at the right with an electrolyte, as shown in Fig.1. When a light of intensity I_0 is incident on the film, for photoelectric effect are produced electrons and holes. We indicate by n the bulk density of excess of electric charge in the presence of light, and by n_0 the bulk density of electrons in the dark, in the absence of bias. n_0 is determined by the equilibrium exchange at the photoactive semiconductor-electrolyte interface. It is assumed position independent. The cartesian reference frame used for the mathematical description has the x-axis perpendicular to the surfaces of the slab, with the origin on the surface at the left, coinciding with the conducting substrate. In the slab approximation all dynamical variables characterizing the state of the system depend only on the coordinate x and time t. We indicate by D and μ the diffusion coefficient and the electric mobility of the charge carriers in the film, respectively. The dynamics of n is governed by the partial differential equation [24–27]

$$\frac{\partial n}{\partial t} = D\,\frac{\partial^2 n}{\partial x^2} - \mu n E - \frac{n-n_0}{\tau} + \alpha I_0 e^{-\alpha x} \qquad (1)$$

representing the equation of continuity for $n = n(x,t)$. In it the term $D\,\partial^2 n/\partial x^2$ is the diffusion term, $\mu n(x,t)E(x,t)$ the drift term, $(n-n_0)/\tau$ a term accounting for the recom-

bination phenomenon, and $\alpha I_0 \exp(-\alpha x)$ the term charged to describe the generation of charge carriers. In Eq.(1) τ is a characteristic recombination time and α the absorption coefficient of the light in the active layer [28]. The quantity $1/\alpha$ is a length related to the absorption of the light. If $\alpha = 0$ there is not absorption, and hence the generation terms vanishes identically. The electric field $E = E(x,t)$ is related to the excess of electric charge by Poisson's equation

$$\frac{\partial E}{\partial x} = \frac{q}{\varepsilon}\,(n - n_0), \tag{2}$$

where q is the electronic charge and ε the dielectric constant of the active layer. In the limit of small I_0, $n(x,t) - n_0$ is small, and the drift term $\mu n(x,t)E(x,t)$ can be neglected with respect to the diffusion term, as we will do in the following [26, 27]. In this framework, for constant in time intensity $n = n(x)$ and Eq.(1) reduces to an ordinary differential equation of the type

$$D\frac{d^2 n}{dx^2} - \frac{n - n_0}{\tau} + \alpha I_0 e^{-\alpha x} = 0. \tag{3}$$

Equation (3) is valid when the electron transport in the photoactive semiconductor layer occurs via diffusion, and the recombination time τ is position independent in the film [29]. It is more convenient to rewrite Eq.(3) in terms of the relative variation of the bulk density of electrons defined by $v(x) = (n - n_0)/n_0$ and of the dimensionless coordinate $\xi = x/L$, where $L = \sqrt{D\tau}$ is a characteristics length related to the diffusion process [29]. In terms of these quantities Eq.(3) reads

$$v'' - v + \kappa\, e^{-\eta\xi} = 0, \tag{4}$$

where the prime means a derivation with respect to ξ, $g' = dg/d\xi$, $\kappa = \alpha\tau I_0/n_0$ is the dimensionless quantity related to the incident light and $\eta = \alpha L$ is the dimensionless absorption coefficient.

Equation (4) is an ordinary differential equation of second order with constant coefficients. Its solution is of the kind $v(\xi) = v_H(\xi) + v_P(\xi)$ where $v_H(\xi)$ is a solution of the associated homogeneous differential equation

$$v_H'' - v_H = 0, \tag{5}$$

and $v_P(\xi)$ a particular solution of (4). Solution of Eq.(5) is

$$v_H(x) = C_1\, e^{-\xi} + C_2\, e^{\xi}, \tag{6}$$

where C_1 and C_2 are two integration constants to be determined by means of the boundary conditions. The particular solution is of the type $v_P(\xi) = B \exp(-\eta\xi)$, where B is obtained substituting $v_P(x)$ into Eq(3). A simple calculation gives

$$B = \frac{\kappa}{1-\eta^2}. \tag{7}$$

In the dark, since $I_0 = 0$, we have $\kappa = 0$, and hence $B = 0$. From Eq.(7) it is evident that for $\eta \to 1$, B diverges. However, as we will see in the following, the physical quantities of interest remain finite in this limit.

The general solution of Eq.(3) is then

$$v(\xi) = C_1\, e^{-\xi} + C_2\, e^{\xi} + B\, e^{-\eta\xi}. \tag{8}$$

At the back contact the electrons are removed as a photocurrent, and one of the boundary conditions of Eq.(8) is

$$v(0) = v_s = \frac{n(0) - n_0}{n_0} = G(V), \tag{9}$$

where $G(V) = \exp[f(V)] - 1$ is a function of the bias voltage such that $G(0) = 0$ [25]. As discussed in [29]

$$G(V) = \exp\left(\frac{qV}{mk_BT}\right) - 1, \tag{10}$$

where $m \sim 2$ is a correcting factor introduced to take into account the potential drop at the semiconductor-electrolyte interface and in the electrolyte, and k_BT is the thermal energy at the absolute temperature T. In the absence of bias, $V = 0$, boundary condition (9) is simply $v(0) = 0$. Furthermore we assume that the electrons reaching the interface with the electrolyte, at $\xi = b = d/L$, are blocked. Since the diffusion current density is $j = -Ddn/dx = -D(n_0/L)v'$, the remaining boundary condition is

$$v'(b) = 0. \tag{11}$$

Imposing boundary conditions (9,11) the integrations constant C_1 and C_2 have to be solution of the linear system

$$C_1 + C_2 + B \;=\; v_s, \tag{12}$$

$$-C_1 e^{-b} + C_2 e^{b} \;=\; B\eta e^{-\eta b}. \tag{13}$$

Since $v_s(V = 0) = 0$ and $B(\kappa = 0) = 0$ solutions of Eq.s(12,13) can be separated as

$$C_1 \;=\; C_1(\kappa = 0) + C_1(V = 0) \tag{14}$$

$$C_2 \;=\; C_2(\kappa = 0) + C_2(V = 0), \tag{15}$$

where

$$C_1(\kappa = 0) = \frac{e^{2b}}{1+e^{2b}}\, v_s, \tag{16}$$

$$C_2(\kappa = 0) = \frac{1}{1+e^{2b}}\, v_s, \tag{17}$$

are related to the dark state, and

$$C_1(V = 0) = -\kappa\, \frac{e^{2b} + \eta\, e^{(1-\eta)b}}{(1-\eta^2)(1+e^{2b})}, \tag{18}$$

$$C_2(V = 0) = -\kappa\, \frac{1 - \eta e^{(1-\eta)b}}{(1-\eta^2)(1+e^{2b})}, \tag{19}$$

are connected to the situation without bias.

RESULTS

The electric current density entering into the photoactive semiconductor is $j_0 = -qDn'(0) = -Dn_0 v'(0)$. Consequently, taking into account (7) and (14,15) with (16,17), (18,19) we get that the total current density due to the electrons diffusion can also be separated in the unbiased ($V = 0$) and dark ($\kappa = 0$) parts as $j_0 = j_0(V = 0) + j_0(\kappa = 0)$ where

$$j_0(V = 0) = qI_0\eta \frac{1 + \eta - 2\eta e^{(1-\eta)b} - (1-\eta)e^{2b}}{(1-\eta^2)(1+e^{2b})}, \tag{20}$$

is the current density in the light state without bias, and

$$j_0(\kappa = 0) = qn_0 \frac{D}{L} G(V) \tanh b, \tag{21}$$

the current density in the dark, with bias. As expected $j_0(\kappa = 0)$ is independent of the dimensionless attenuation coefficient $\eta = \alpha L$. It is possible to rewrite $j_0(V = 0)$ given by (20) as

$$j_0(V = 0) = -qI_0\eta \frac{\sinh b - \eta \cosh b + \eta e^{-\eta b}}{(1-\eta^2)\cosh b} \tag{22}$$

coinciding with that reported in [29].

Note that in the limit $\eta \to 1$, from Eq.(20) we get

$$\lim_{\eta\to 1} j_0(V = 0) = -\frac{1}{2} qI_0 \left(\tanh b + \frac{e^{2b}}{e^{2b}+1} \right), \tag{23}$$

which is a finite quantity, as stated above.

The current density j_0 depends on b in non linear manner, as it is evident from Eq.s(20,21).

In the limit of $b \to 0$ taking into account that $j_0 = j_0(V=0) + j_0(\kappa=0)$ from Eq.s(20,21) we obtain

$$\lim_{b\to 0} j_0 = q\left\{-\eta I_0 + \frac{n_0 D}{L} G(V)\right\} b + \mathcal{O}(b^2) \tag{24}$$

This means that in the limit of small b, i.e. for thicknesses smaller than L, the current density is proportional to the thickness of the active layer. From Eq.(24) it is clear that the photocurrent and the current due to the bias, for $V > 0$ gives opposite contribution to the total current density j_0.

In the limit of very large b, j_0 tends to

$$\lim_{b\to\infty} j_0 = q\left\{-\frac{\eta}{1+\eta} I_0 + \frac{n_0 D}{L} G(V)\right\}. \tag{25}$$

As before, from (25) it follows that photo-current and bias current have opposite sign. Hence, acting on the bias it is possible the reach the state where $j_0 = 0$.

In the limit of small absorption from Eq.(20) we get that the photocurrent is

$$\lim_{\eta\to 0} j_0(V=0) = -q\, I_0\, \eta\, \tanh b, \tag{26}$$

indicating that in the absence of absorption the current density related to the light state, without bias, vanishes.

In Fig.2 we show the thickness dependence of j_0 in the absence of bias. In this situation $j_0 = j_0(V=0)$ where $j_0(V=0)$ is given by Eq.s(20), and the approximated formulae (24) (25) valid in the limit of small and large b for the present case. As it is evident from Fig.2 $j_0(V=0)$ is a non monotonic function of $b = d/L$. The position of the maximum depends on the dimensionless attenuation coefficient $\eta = \alpha L$, as it is possible to see from Fig.3, drawn for different values of η. In Fig.4 the influence of the bias on the thickness dependence of the total current $j_0 = j_0(V=0) + j_0(\kappa=0)$ is reported for four values of bias. The continuous curve corresponds to $V = 0$. Increasing the bias the position of the maximum of j_0 vs. b moves to the left, indicating that the optimum thickness decreases with V. The curves are drawn assuming $K = n_0 D/(I_0 L) = 4.6\times 10^{-4}$, valid for a film of TiO_2 under a light intensity 1.30 mW, as reported by [29] in Table 1. In Fig. 5 we compare the experimental data reported in [20] with the mathematical expression reported above using for the diffusion length $L \sim 10\mu$m corresponding to a diffusion coefficient $D = 5\times 10^{-9}$ m^2/s and to a life time $\tau = 2\times 10^{-2}$ for the photoelectrons in the photoactive semiconductor, and

for the attenuation coefficient $\alpha \sim 2 \times 10^5$ m^{-1}, reported in [30]. The agreement with the experimental current density is rather poor, indicating that the validation of the presented model requires new measurements. We stress that in literature are reported values for the recombination times ranging from 10^{-2}s [30] to 40 ns [31], and hence a comparison of our model with the experimental data is, at the present, rather difficult. Nevertheless, it is woth to notice that the maximumj_0 values predicted by the proposed model are in the range of $BiVO_4$ film thickness between 160 nm and 200 n, which agree well with previous literature reports [18, 20].

CONCLUSIONS

The photocurrent response of photoactive nanocrystalline $BiVO_4$ thin film was studied as a function of the thickness of the film in the presence of a bias voltage. The theoretical model used for the description is based on the assumption that the charge carrier transport in the photoactive semiconductor occurs via diffusion and that the recombination term in the continuity equation is proportional to the excess of electrons, with respect to the dark state, with a recombination time τ. The diffusion coefficient as well as the recombination time in the presented analysis have been supposed constant across the photoactive film. According to our theoretical predictions, the photocurrent depends on the thickness of the film in a non monotonic manner. It presents a maximum for a well defined thickness, and tends to a saturation value in the limit of large thickness. In the limit of small thickness the photocurrent is proportional to the thickness of the film, and the proportionality constant depends on the absorption coefficient and on the applied voltage. The optimal thickness of the $BiVO_4$, corresponding to the maximum of the photocurrent, depends on the absorption coefficient of the light from the film and on the bias voltage applied to the cell and was estimated between 160 nm and 200 nm. Our predictions are in qualitative agreement with experimental observations reported in literature. Therefore, the proposed model could represents a useful tool for the theoreticl determination of the optimal thickness of semiconductor-based photocatalytic films.

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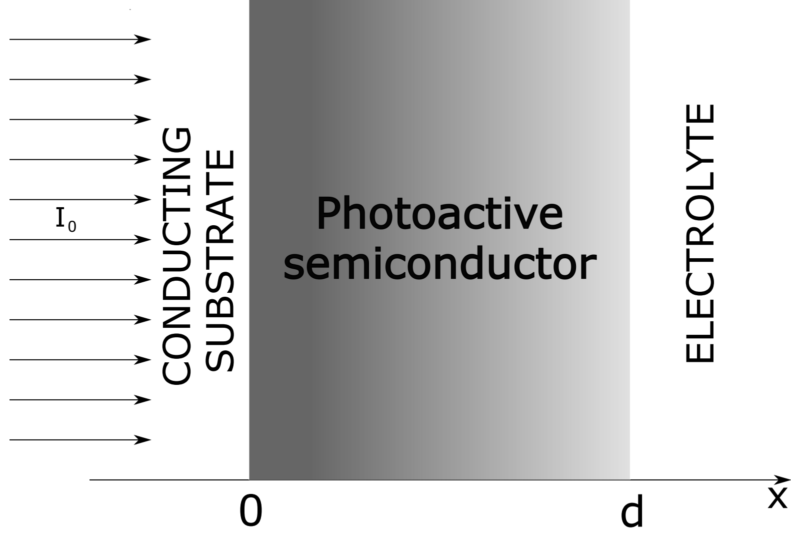

FIG. 1: The photoactive semiconductor layer under investigation, limited by a conducting substrate and an electrolyte. The light is incident on the left side with an intensity I_0.

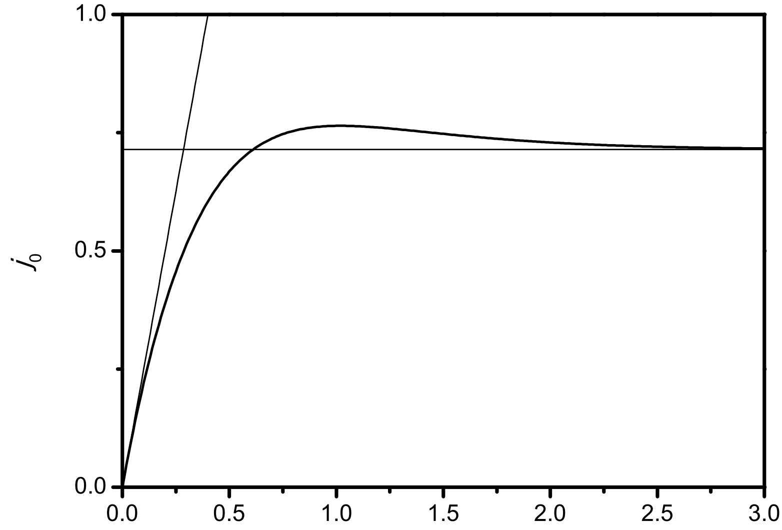

FIG. 2: Current density $j_0(V = 0)$, in units qI_0 versus the dimensionless thickness of the photoactive semiconductor layer $b = d/L$. The straight line passing through the origin is the expression of the current density in the $b \to 0$ limit, Eq.(24), whereas the horizontal line its expression valid in limit of large b, Eq.(25). The curve is drawn for a dimensionless absorption coefficient $\eta = \alpha L = 2.5$.

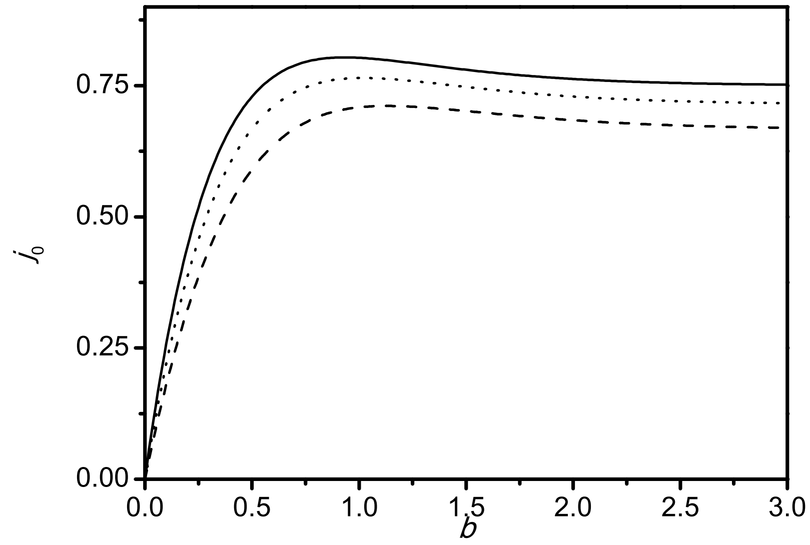

FIG. 3: Current density $j_0(V = 0)$, in units qI_0 versus the dimensionless thickness of the photo-active semiconductor b for a few values of the dimensionless absorption coefficient η. Continuous curve $\eta = 2$, dotted curve $\eta = 2.5$, dashed curve $\eta = 3$.

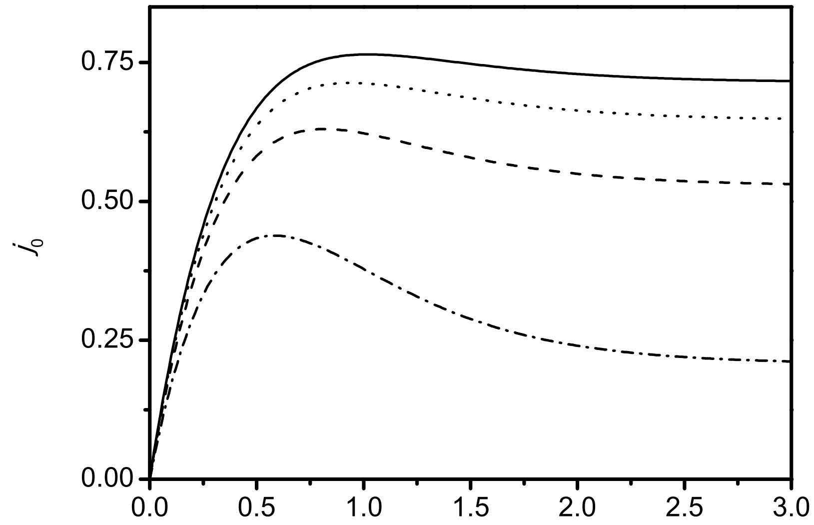

FIG. 4: Current density $j_0(V = 0)$, in units qI_0 versus the dimensionless thickness of the photoactive semiconductor b for a few values of the bias voltage. The curves are drawn for $K = n_0D/(I_0L) = 4.6 \times 10^{-4}$ [29] and $\eta = 2.5$. Continuous curve $V = 0$, dotted curve $V = 2.5$ V, dashed curve $V = 3$ V, dotted-dashed $V = 3.5$ V.

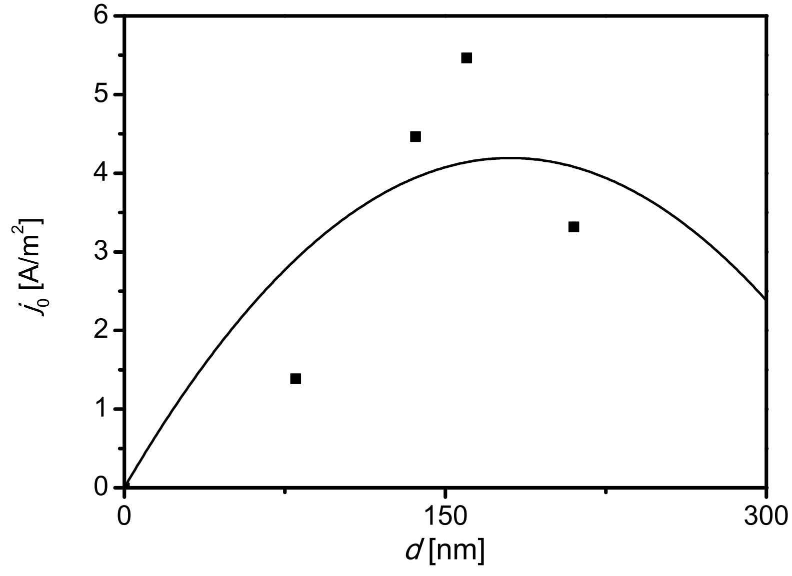

FIG. 5: Comparison of the theoretical predictions of our model with the experimental data reported in [20]. We assume for the diffusion length $L \sim 10\mu$m, and for the attenuation coefficient $\alpha \sim 2\times10^5$ m^{-1} [30].