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1 A dye sensitized SC incorporating plasmonic nanostructures

On month 24 we have made a no-go decision on dye sensitized solar cell technology, which was summarized in milestone ML11. It explains in detail why DSSC solar cells can't profit efficiently from the plasmonic nanostructures that can be produced within the PRIMA consortium. Below we reiterate the reasoning behind the no-go decision.

1.1 Dye sensitized solar cell go/no-go

In the description of work, we defined the go/no-go decision as follows:

"The target values, defined at the plasmon resonance wavelength, will be $F = 5$ at M24, and $F = 20$ at M36. The M24 target represents a significant step forward compared to our factor 1.6 improvement reported on earlier. The M36 target is on par with the best results achieved experimentally for *any* solar cell technology employing plasmonics."

What follows is our justification of why the dye sensitized solar cell activities within Prima are justified with a "**no-go**" decision.

1.1.1 Planar model systems for 3D dye-sensitized solar cells.

Hole-mask colloidal lithography (HCL) was suggested as a suitable nanofabrication method (i) to produce model planar dye-synthesized solar cell (DSSC) system with embedded nanoplasmonic structures and (ii) to investigate the coupling between a monolayer of dye and plasmonic nanoparticles. Importantly, we were foreseeing that such planar model system would reliably represent the plasmonic effects on the current enhancements in real 3D DSSCs [1]. As we show here, the current enhancements that are predicted with this planar test model are indeed very large (both experimentally and theoretically), largely (orders of magnitude) surpassing similar numbers in any real 3D nanoplasmonics-enhanced DSSCs reported so far. This might already suggest that this simplified planar model might not represent a good approximation of the real up-to-date DSSCs, suggesting that the physical effects in a real DSSC are much more complex than those that could be extracted from the planar model. Having this in mind, we can conclude at this stage that the plasmonic effects on DSSC efficiency should be investigated on 3D structures rather than on planar models in order to account for full physics of the solar cells and to measure their efficiency enhancements.

We fist perform the electromagnetic modeling of the absorption of light in a dye monolayer using a commercially available finite element software, Comsol Multiphysics 3.5a. The schematics of the model under study is shown in Figure 1 (A), where a plane wave illuminates a system composed of a silver nanodisk (with diameter D = 80 nm and thickness t = 20 nm) and 1 nm thick dye layer. The background materials are TiO_2, which refractive index is taken from literature, and electrolyte, with a constant refractive index $n_{elect} = 1.4$. The nanodisk is embedded in TiO_2 at 5 nm distance from the dye layer. The in-plane size of the dye layer is $L_x = L_y = 2D = 160$ nm, which corresponds to a typical area of dye comprised with a single nanodisk in the experimental HCL samples that feature similar nanodisks center-to-center distances. Figure 1(B) shows real and imaginary parts of the refractive index of dye layer used in the calculations. According to this, the maximal absorption of the dye is expected at around 520 nm and it rapidly drops to zero at around 740 nm, which is in close agreement with the experimentally measured dye absorptions reported in the literature. The absorption cross sections of the disk only (red solid line) and dye only (blue dash-dotted line) are shown in Figure 1(C), where we made such a choice so that the plasmon resonance of the disk is close to the maximal absorption in dye layer. In the same figure, we see that the absorption cross section in dye layer (green dashed line), when the nanodisk is present, is enhanced due to the presence of the plasmonic nanoparticles and its enhanced near-fields. Integrating the absorption cross sections, in a way similar to equation (23) in reference [2], we can estimate a spectral photocurrent enhancement as $F = I_{sc} / I_{sc\text{-}ref} = 1.9$ and a peak photocurrent enhancement $F(\lambda = 550\text{ nm}) = I_{sc}(\lambda = 550\text{ nm}) / I_{sc\text{-}ref}(\lambda = 550\text{ nm}) = 2.83$, where λ is the wavelength of the light, I_{sc} is the short circuit photocurrent of the solar cell with a nanodisk present, and $I_{sc\text{-}ref}$ is the reference photocurrent without the nanoparticle present. These values are in a

good agreement with the experimentally reported peak enhancements for plasmonic enhanced solar cells based on a planar array of plasmonic nanostructures and a dye monolayer [3,4]. These studies were reported during the execution of the PRIMA project by other research groups. In these experiments, the current enhancement for a dye monolayer was studied dependent of the distance between dye and plasmonic nanoparticles by changing the thickness of TiO_2 spacer layer. It was found that if the thickness of the spacer layer is too large, the current enhancement gets lower due to a decrease in the near-fields of the particle, and if the thickness was too small then quenching of the dye and particle corrosion due to electrolyte both decreased eventual current enhancement. The optimal thickness of the spacer layer was found to be few nanometers and it differed from 2 nm till 7 nm in different studies. Having in mind that neither in our model nor in the reported experimental studies the optimization of the structure is not done (e.g. size and shape of the particle, density of the particles, distance between the particle and dye layer, etc.), the calculated and measured enhancements for dye monolayers can probably be further enhanced, so potentially even the F=5 (and F=20), stated in the formulation of the go/no-go decision, can be reliably attained both theoretically and experimentally. We show below, however, that this advance does not translate into the actual comparable enhancement due to nanoplasmonics with the realistic 3D DSSC systems.

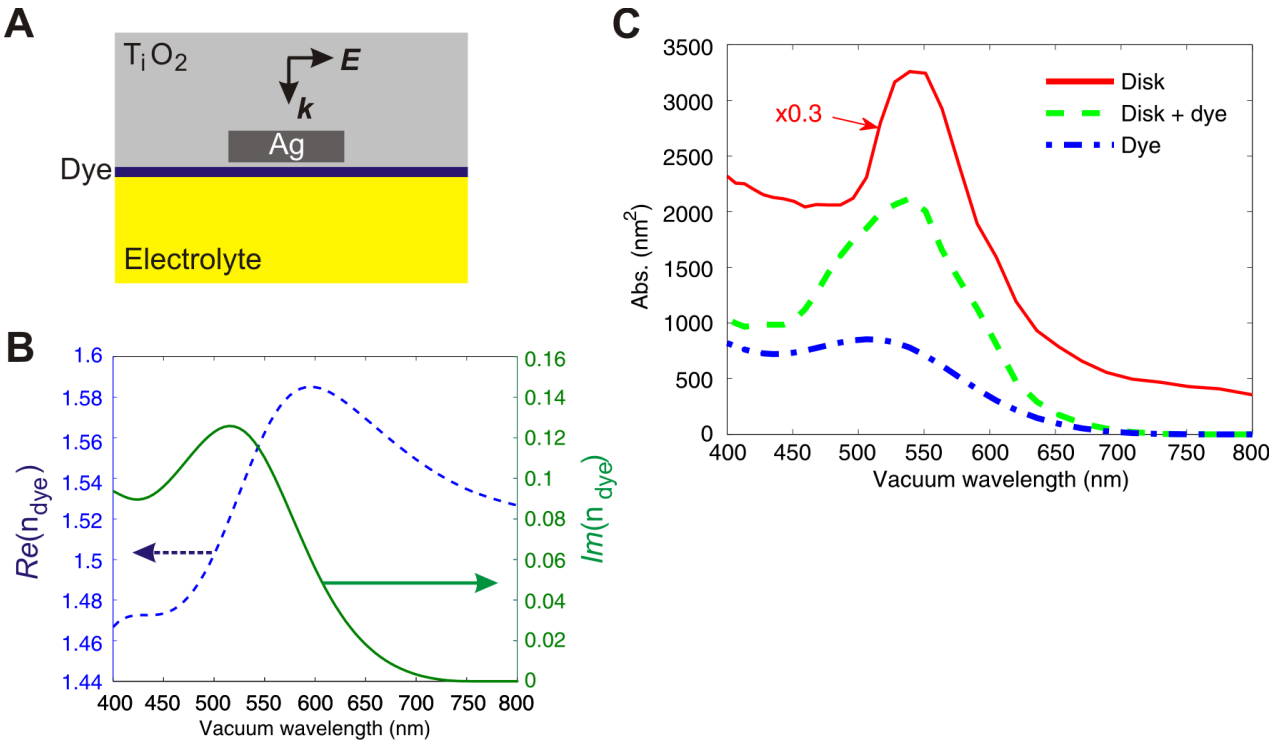

Figure 1. (A) Schematic of the modeled system. (B) Refractive index of the dye layer. (C) Absorption cross section of Ag nanodisk without dye layer present (red solid line), absorption cross section of the dye layer with disk present (green dashed line), and absorption in dye layer without the disk present

During the execution of the project, several plasmon-efficiency enhancement experimental studies in realistic 3D DSSCs have been reported [5,6]. In these experiments, small core-shell nanoparticles were directly embedded into the mesoporous TiO_2 paste before sintering and making a final device. The efficiency enhancements reported in these papers are very promising (about 30-40%), but still obviously much smaller than that reported in the model DSSCs studies with dye monolayers. Interestingly, in addition to the current enhancements the improvements in the open-circuit voltage and fill factor have also been reported in these studies. Strikingly, Qi et al. showed that it is even possible to make thinner plasmonic DSSCs with the same efficiency as conventional DSSCs without any plasmonic nanoparticles. Such a thinning of the solar cell besides saving in the material provides better efficiency due to a better charge separation in a thinner active layer. In the same study the authors investigated how DSSC efficiency depends on the concentration of core-shell particles inside the TiO_2 paste and an optimal concentration, which provided the maximal enhancement was found. Interestingly the optimal

concentration is substantially smaller than the particle concentrations used in the experiments based on dye monolayers. These results prompt the conclusion that in order to get a real estimate of plasmonic enhancements for DSSCs, the fabrication and measurements on 3D solar cells rather than on planar models is needed. Accordingly, *further optimization of model planar DSSCs comprising array of nanoplasmonics structures and a dye monolayer in order to get even higher enhancement seems irrelevant to the real potential realization of plasmon-enhanced DSSCs.* Most importantly, the final step of translating HCL-produced model planar plasmon-enhanced DSSC layers into the 3D architecture also seems unfeasible at this point. So far reported results suggest completely different route of merging DSSC with nanoplasmonic structures – i.e., embedding the latter into the porous (titania) template. Nanostructures for this are chemically synthesized rather than patterned with any kind of lithography due to the low yield of the latter.

1.1.2 Summary of no-go decision

In summary, we revise our initial concept of the potential applicability of the HCL method for the real 3D DSSCs. Importantly, in planar model systems that comprise arrays of nanoplasmonic structures and a dye monolayer, targeted values can be reliably attained. This is confirmed by the independent studies of several other research groups and is verified by us theoretically. At this point we make the main conclusion that the model planar plasmon-enhanced DSSC assemblies, most probably, do not represent the reliable systems to foresee the future plasmon-related enhancements in the real 3D dye+electrolyte-based DSSC systems. This is the background of the **'no-go'** decision on the plasmon-enhanced DSSC technology with PRIMA.

References

[1] C. Hagglund, M. Zach, and B. Kasemo, "Enhanced charge carrier generation in dye sensitized solar cells by nanoparticle plasmons," 92, 013113, Appl. Phys. Lett., 2008.
[2] K. Miettunen, J. Halme, A. Visuri, and P. Lund, "Two-Dimensional Time-Dependent Numerical Modeling of Edge Effects in Dye Solar Cells," 115, 7019-7031, J. Phys. Chem. C, 2010.
[3] S. D. Standridge, G. C. Schatz, and J. T. Hupp, "Distance Dependence of Plasmon-Enhanced Photocurrent in Dye-Sensitized Solar Cells," 131, 8407-8409, JACS, 2009.
[4] T. Kawawaki, Y. Takahashi, and T. Tatsuma, "Enhancement of Dye-Sensitized Photocurrents by Gold Nanoparticles: Effects of Dye-Particle Spacing," 3, 2865, Nanoscale, 2011.
[5] M. D. Brown, T. Suteewong, R. S. S. Kumar, V. D'Innocenzo, A. Petrozza, M. M. Lee, U. Wiesner, and H. J. Snaith, "Plasmonic Dye-Sensitized Solar Cells Using Core-Shell Metal-Insulator Nanoparticles," 11, 438-445, Nano Letters, 2011.
[6] J. Qi, X. Dang, P. T. Hammond, and A. M. Belcher, "Highly Efficient Plasmon-Enhanced Dye-Sensitized Solar Cells through Metal@Oxide Core-Shell Nanostructure," 5, 7108-7116, ACS Nano, 2011.