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Photovoltaic photographs

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ABSTRACT

In the field of photovoltaics (PV), an important trend is to increase the aesthetic and creative design aspects of solar cells towards more attractive and customized devices for integration in for instance architecture, *e.g.* building integrated photovoltaics (BIPV). Here we introduce the concept of "photovoltaic photographs", defined as semi-transparent solar cells (STSC) that are treated with a light-induced process to integrate an image in the photoactive layer, allowing creative applications such as photovoltaic photographs, paintings, posters, etc. Contrary to previously reported patterning processes used in emerging photovoltaics such as inkjet printing or methods where patterned transparent foils are assembled on top of the solar cells, the approach proposed here to obtain a patterned 2D-photoactive layer, is by using a direct photo-induced patterning process based on photobleaching of chromophores. Proof-of-principle demonstrators have been realized using dye-sensitized solar cells and the obtained insights can open the way to the exploration of combining this concept with other PV technologies.

1. Introduction

In the field of photovoltaics (PV), an important trend is to increase the aesthetic and creative design aspects of solar cells towards more attractive and customized devices for integration in for instance architecture (*e.g.* building integrated photovoltaics BIPV) and cars (*i.e.* automobile integrated photovoltaics AIPV) [1]. Recent evolutions in this domain are situated in all classes of PV, from conventional silicon technology to emerging PV such as organic solar cells (OPV), dye-sensitized solar cells (DSSC) and perovskite solar cells (PSC). The latter technologies provide additional degrees of design freedom, as they can be processed by wet deposition techniques and allow the realization of semi-transparent solar cells (STSC) and the use of various colors. In the following paragraphs, a brief overview is provided of the current state-of-the-art in relation to colored and patterned solar cells.

In STSCs, patterns correspond to a controlled spatial variation of device transparency and color, both of which are primarily related to compositional and structural properties of the active layer and the electrodes. Since photovoltaic power generation requires the absorption of light, STSCs are burdened with an intrinsic trade-off between efficiency and transparency.

General strategies to build STSCs include the use of ultrathin active layers – which is applicable to both hydrogenated amorphous Si (a-Si:H) solar cells [2] and emerging technologies such as OPVs, PSCs and DSSCs [3,4] – and the use of active materials with low absorption in the visible range [5,6]. Alternatively, transparency can be achieved by creating gaps between the active material, *e.g.* by laser scribing patterns [7], mesh-assisted self-assembly [8], or by replacement of uniform films by micro-holes [2] or "islands" of active material—as has been demonstrated with neutral-color semi-transparent perovskite solar cells [9]. Color-tuning often involves the use of colored electrodes [7,10] or the introduction of additional reflecting layers such as one-dimensional photonic crystals and light coupling layers [3,10]. Of course, the chemical composition of the active material influences the color of OPVs and PSCs [2,10–12], and "color-tinting" has been realized by adding a dye to the hole transporting medium of initially neutral-colored PSCs [9]. In DSSCs, the light absorbing dye is the vital component regarding color [13] – and optical properties can be tuned with quantum dot size in so-called quantum-dot-sensitized solar cells [14,15] – but the color and transparency of the electrolyte also influences the appearance of the final device [16].

Much research has been dedicated to the development of top electrodes that are both highly conductive and semi-transparent. Conventional metal film top electrodes are usually reflective, but trans-

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parency can be achieved by making the films ultrathin [17,18]—however, the trade-off in conductivity is generally considered non-profitable [10]. Therefore, conventional metal films are routinely replaced by silver nanowires in OPVs and PSCs, except in DSSCs where the liquid electrolyte causes poor stability of the nanowires [3,10]. Non-metal high performance transparent electrodes have been developed – ranging from transparent conductive oxides [19,20] to conducting polymers [21,22] and carbon materials [23–26] – with a focus on stability and processability [2,10]. When considering aesthetic and BIPV applications, additional aspects such as color-neutrality become important.

One way to achieve colored solar cells is by the application of color coatings. This method is used on black solar cells, *e.g.* a-Si, to raise their aesthetic value [27]. Besides covering PVs with semi-transparent foils or printing a pixelated pattern on the outer glass [28], the most straightforward way of displaying patterns with PVs is by connecting conventional solar cells in an arrangement, which is exemplified by the mosaic module concept based on metal-wrap-though cells [29]; however, with this approach, the sub-cells are opaque and their size limits the resolution. More flexible single-cell patterning methods are searched for in the fields of semi-transparent dye-sensitized, organic and perovskite solar cells. A recent study regarding DSSC anodes stained by inkjet printing demonstrated multi-colored solar cells with tailored transparency [30], and monochrome logos and images have been inkjet-printed using perovskite precursor ink [31]. Moreover, precise removal of materials by computer-controlled non-thermal laser ablation allowed for manipulation of transparency and aesthetic pattern design in PSCs [32].

Although research on DSSCs has grown significantly over the last two decades, performance – lab record efficiency of 12.25% [33] – and stability restrictions are at present the main obstacles to compete with conventional silicon solar cells, which dominate the PV market [34,35]. However, DSSCs offer differentiating intrinsic properties, which could lead to creative niche applications beyond the reach of silicon solar cells. As with OPVs and PSCs [36,37], DSSCs can be fabricated into flexible, semi-transparent modules available in wide color ranges at low production costs [34,38], which are appealing features for aesthetic purposes. The colored sensitizers used in DSSCs are mainly synthetic dyes, usually transition metal complex based compounds or organic dyes [39,40]. Alternatives are natural dyes (*e.g.* chlorophylls, anthocyanins, carotenoids,..) whose popularity originates from their relative abundance, large absorption in the visible spectrum, ease of preparation, cost effectiveness and eco-friendliness [40,41], but in general suffer from low efficiency and stability issues compared to their synthetic substitutes.

The semi-transparent character and ease of color implementation place DSSCs on the forefront of BIPV and AIPV [1]. One such example is the development of smart windows in zero energy buildings [38,42], with large-scale installations having been introduced over a decade ago [43] and successful long-term outdoor testing supporting the concept [44]. Recent works discussing the use of semi-transparent DSSCs as PV windows are reviewed elsewhere [45,46]. These PV glass modules do not only produce electricity, but also provide a wide variety of solar shading, which is made possible through the color tuning ability of these devices [47]. BIPVs also affect the image of our cities by providing buildings with an attractive and environmentally-friendly appearance. Specifically, when applied in large quantities, they contribute to the reduction of carbon emissions, while at the same time servicing an aesthetic or shading purpose.

It is clear that significant progress has been made in the realization of uniform colored photovoltaic films, with however only limited attention to patterned devices, *e.g.* through inkjet-printing or add-on transparent printed patterns. In the evolution towards more aesthetical solar cells, here the proposed innovation consists of integrating an image (photographs, paintings, geometric and graphical patterns, text,..) with photo-active functionality into the STSC using a direct photo-induced patterning process. Key advantages of this approach include: (1) preparation time is independent of size, (2) patterning process is compatible with the traditional production process, (3) no external, fragile foil is needed, (4) high-resolution patterning is possible, and (5) this methodology could possibly be applied to various classes of solar cells, specifically technology based on photosensitive absorbing layers that are prone to bleaching (*e.g.* OPV and PSC [48–50]).

As a proof-of-principle for the concept of photovoltaic photographs, demonstrators (up to 9×9 cm^2) have been realized using DSSCs, due to ease of fabrication and broad variety of available colors. In the following sections the photo-induced patterning process and the preparation and results of photovoltaic photographs will be presented. The ultimate goal of this endeavor is the introduction of photovoltaic photographs as a potential novel route to enhance the aesthetical and design possibilities for a variety of PV technologies.

2. Materials and methods

2.1. Direct photo-induced patterning of 2D-photoactive layer

The approach proposed here to obtain a patterned 2D-photoactive layer is by using a direct photo-induced patterning process, *i.e.* one-step photolithography in the presence of oxygen to induce selective photobleaching in the photoactive layer of organic-based solar cells. The method differs from traditional photolithography as employed in for instance semiconductor industry, as here no sacrificial resist film is needed, and no additional etching steps or chemical removal steps are required.

The approach to pattern the photoactive layer of organic-based solar cells to realize photovoltaic photographs is inspired by the anthotype photographic process; an ancient photographic method of transferring images from a transparency film to a sheet of paper (see Fig. 1). This invention can be attributed to Sir John Herschel (1792–1871) [51,52]. An anthotype photograph starts out as a sheet of paper dyed with a pigment extracted from mostly natural sources, such as berries, leaves, petals, …A mask containing the desired image is placed over the dyed sheet, whereafter the assembly is left exposed to sunlight. This process will cause the underlying sheet to bleach in areas that are exposed to the light, while covered areas remain dark. The result is a monochromatic photograph of the image from the mask. Depending on the type of dye, the anthotype process can take from a couple of hours to a few days to develop. Recently, the anthotype technique has been rediscovered in several domains; for instance, for producing motifs on textile [53] and in the artistic work of experimental photographers such as co-author K. Vrancken [54].

2.2. Preparation of proof-of-principle photovoltaic photographs using DSSCs

The proposed procedure towards DSSC-based photovoltaic photographs using light-induced processes consists of the following general steps: first, the TiO_2 anode is dyed with a synthetic or natural dye. A transparent sheet (mask) containing the desired image is placed over the dyed electrode, and the assembly is exposed to a light source (see Fig. 2). The result is a monochromatic photograph that looks like the original image. For this process, the underlying photoanode will bleach in areas that are exposed to light, while covered areas remain dark.

By following this procedure we realized several proof-of-principle photovoltaic photographs based on different colors, offering a renewable energy source while servicing an aesthetic purpose. A detailed description of the fabrication process is discussed in the following paragraphs.

2.3. Materials

Experiments were done using two different types and sizes of anode material. Both types of DSSCs were built using pre-sintered titania