

# Single Particle Photoelectrochemistry

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Literature Seminar

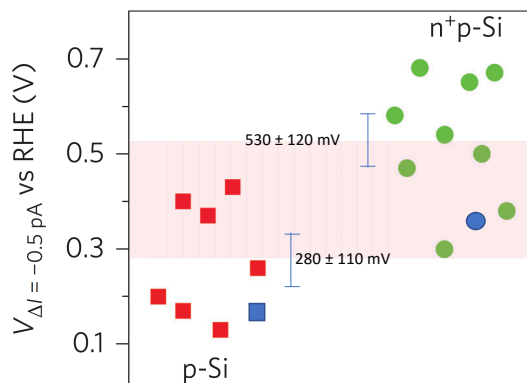
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Following 1973 oil crisis, the whole world has been searching for alternative sustainable energy sources.<sup>1</sup> Scientists started working on solar energy conversion and storage since the sun is a sustainable, abundant and inexpensive energy source.<sup>2</sup> A type of the solar cells developed during this period is semiconductor-liquid junction cells.<sup>3</sup> When photon of energy equal to greater than the energy band gap is absorbed by the semiconductor material, electron(e<sup>-</sup>)-hole(h<sup>+</sup>) pair is created. If the e<sup>-</sup>h<sup>+</sup> pair can be separated so that the e<sup>-</sup> flows to a suitable acceptor species, or an electron from a suitable donor fills h<sup>+</sup> then the light energy has been stored as redox chemical energy. But the lifetime of the excited state is very, the excited electron can immediately recombine with its hole to release energy in various forms such as heat or emission of photon. To utilize the light in a form other than heat, one must achieve separation of the e<sup>-</sup>h<sup>+</sup> pair before recombination. In case of natural photosynthesis reaction, this recombination is prevented by spatially separating the electron-hole pair, electron hops through series of electron acceptors and therefore spatially separated from the hole which prevents its recombination kinetically even though thermodynamically recombination is possible since electron is at higher energy than the hole. In case of semiconductor-electrolyte junction, it uses an electric field which prevents the charge recombination. Electric field is created spontaneously at the surface of the semiconductor when it is immersed into the electrolyte solution as a result of the equilibration process of electrochemical potential.<sup>4</sup> The excited electron senses this electric field and either attracted or repelled by the field based on its direction, which creates a directional flow of charge carriers and hence spatial separation.

Nanostructured semiconductors are preferred over bulk semiconductor materials since they encompass features like high surface-to-volume ratios,<sup>5</sup> tunable bandgaps through quantum confinement<sup>5</sup>, reduced charge migration distance and less expensive solvent based synthesis methods. The difference in the space charge region is one of the main contributing factors which leads to the difference in efficiency of nanoparticle and bulk semiconductor electrode behavior. Since the space charge region exceed the dimension of the nanoparticle, potential drop occurs across the nanoparticle and Helmholtz double layer at the solid-liquid interface.<sup>5,6,7</sup> Most of the findings regarding the nanoparticle photoelectrochemistry is based on ensemble averaged approaches. Single particle level approach is necessary to elucidate the structure/function correlation between particle size, shape, composition and photoelectrochemical properties which are masked in ensemble averaged approaches. The rise of single particle photoelectrochemistry(SPP) began in the year 2016.

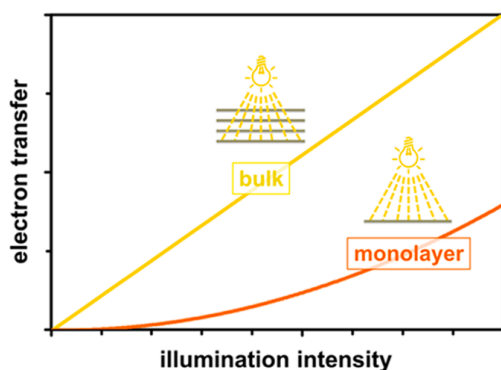
There are two different approaches to study SPP, one being spatially controlled charge carrier collection (photocurrent is collected only from a single particle even though all the nanoparticles are excited by the photon beam) and another being spatially controlled charge carrier generation(laser beam is confined

so that electron-hole pairs are generated only in a single particle). These two approaches are presented below.



**Figure 1.** Statistical distribution of onset potential for seven p-Si and nine n<sup>+</sup>p-Si devices.  $\Delta I$  is the difference between photocurrent and dark current. The top and bottom of pink band represents the average onset potential between n<sup>+</sup>p-Si and p-Si respectively. The data points with blue color represents the onset potential of vertically aligned nanowire array electrodes.

measurements revealed that there is a significant difference between the photovoltage output of large area nanowire array electrode and that of single wires



**Figure 2.** Dependence of monolayer and bulk MoS<sub>2</sub> electron kinetics on irradiance

monolayer system (Figure 2). Findings of this work will be useful to tune the electrochemical performance of this transition metal dichalcogenide nanosheet by of its structure external environment and illumination.

One of the main disadvantages of spatially controlled charge carrier collection experiment is, in single nanoparticle cell approach, sub particle resolution cannot be achieved because the whole nanoparticle is immersed in electrolyte from which photocurrent is measured. The second approach to study single particle photoelectrochemistry is by spatially controlling charge carrier generation instead of charge carrier collection.<sup>10,11</sup> Velciky *et al.* delivered 25  $\mu\text{m}$  electrolyte droplet on the surface of nanoflake and the droplet only had contact with basal planes and didn't take into account for the perimeter and interior edge site

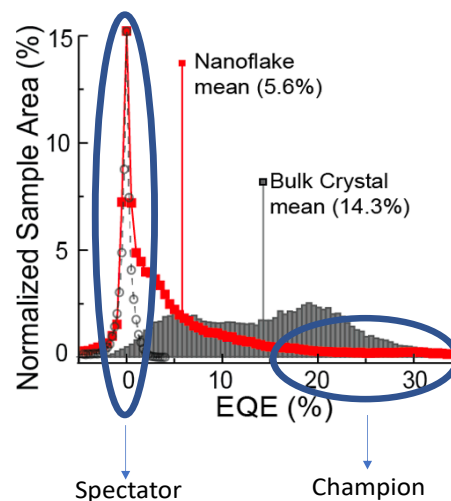
One way of spatially controlling the carrier collection is by creating appropriate electrochemical cell which could restrict the photocurrent measurement from a single particle.<sup>8,9</sup> In 2016, Yang and coworkers developed a single semiconductor nanowire electrochemical cell to study the hydrogen evolution reaction (HER).<sup>8</sup> Pt nanoparticles which act as proton reduction catalyst were coated over the semiconducting extrinsic Si nanowire which serves to absorb light. Single nanowire

measurements revealed that there is a significant difference between the photovoltage output of large area nanowire array electrode and that of single wires (Figure 1). Another method is to spatially control charge carrier collection across the electrolyte/nanoparticle interface. In 2016, Velciky *et al.* used microdroplet electrochemical approach to study the photoelectrochemical properties such as electron transfer kinetics and electrical double layer capacitance of pristine monolayer and few-layer basal plane MoS<sub>2</sub>.<sup>9</sup> Bulk MoS<sub>2</sub> exhibited faster electron transfer kinetics compared to monolayer system and was attributed to the difference in light absorption and diffusion of charge carriers in bulk and

effects.<sup>9</sup> It is already reported the edge sites for transition metal dichalcogenide(TMD) can have impact on photocurrent efficiency in case of bulk semiconductor electrode.<sup>12</sup> In 2018, Sambur *et al.* developed a method to elucidate why semiconducting TMD bulk electrodes have more efficiency compared to the nanoflakes focusing on the perimeter and interior edge effects. The photocurrent response as a function carrier excitation location was measured; hence the photocurrent collection efficiency at interior steps and perimeter edges can be studied. The external quantum efficiency(EQE) map shows that the mean EQE nanoflakes is 5.6% and for bulk crystal is 14.3%. But

there is a champion population in the nanoflakes that have EQE, exceeding the mean EQE of bulk crystals. But the effect of these champion nanoflakes are masked by the spectator nanoflake which have very low efficiency(Figure 3). The photocurrent mapping also revealed that charge carrier recombination is greater near perimeter edges than interior steps. The results here can be used to improve the design of 2D semiconducting TMD electrodes for higher efficiency.

In summary, conventional measurement tools are insufficient to study the photoelectrochemistry of nanoparticles. Ensemble averaged photochemical response may be dominated by a small population of highly active “champion” or inactive “spectator” particles. Single particle-level studies can predict new designs to improve ensemble level- performance.



**Figure 3.** Normalized distributions of all illuminated bulk crystal (gray bars) and nanoflake areas (red squares) vs EQE values that they produce. The vertical bars represent the mean value for each sample.

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