Organic-inorganic hybrid nanostructured materials for photovoltaics and solar fuels
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In this chapter, the importance of low-dimensional and solution processable materials for solar energy to fuel conversion as well as the possible impact to society is discussed. Furthermore, a forecast of the utilization possibilities of the result presented in this thesis is attempted.
7.1 Solution processable photocathode

This research was part of the BioSolar Cells program, co-financed by the Dutch Ministry of Economic Affairs, aiming to discover new low-cost artificial photosynthetic systems that can efficiently convert the solar energy into chemical fuels. Hydrogen is an ideal chemical fuel because: (i) the raw starting material (water) is abundant; (ii) it can be converted into electricity by using fuel cells without producing pollutants; (iii) H₂ storage has progressed rapidly in the last decade.

Figure 7.1 shows that the efficiency of the photoelectrodes that convert the solar energy into the hydrogen decreases as the inverse of the fabrication cost. The champion photoelectrodes are made from the epitaxial growth of III-V semiconductors which are very expensive, including high vacuum, high temperatures, and time-consuming processes. On the contrary, the low-cost dye sensitized photoelectrodes made by ruthenium dye bridging TiO₂ and IrO₂.nH₂O nanoparticles shows extremely low quantum efficiency (0.9%). To date, most researchers delved non-solution processed methods to growth active materials by using chemical vapour deposition (CVD) and epitaxial growth, which are inherently high-cost.

In photovoltaic technology, the third generation solar cells, aiming to have low cost and high efficiency by discarding high vacuum/temperature processes and embracing solution deposition methods such as doctor blading, have seen gigantic progress in the past decade. However, until now, examples of solution processable photoelectrode for solar energy to fuel conversion are still rare. The main difficulty, which has refrain researchers to pursue this challenge, is the lack of knowledge of the phenomena occurring in these solution processable materials when inserted into electrolytes. In addition, many solution processable materials are sensitive to ambient conditions.

In this thesis, we have demonstrated solution processable materials, which can harvest light from the visible to near infrared spectral region and are stable in electrolyte under illumination. We discover that QDs/polymer hybrids are a very good candidates for solar energy to fuel conversion. The optical and electronic properties of the QDs can be easily adjusted by simply tuning their size. While in this thesis CdSe QDs were used, more environmental friendly nanocrystals, such as FeS₂ (Pyrite), Ag₂S, InP, and CuInS (CIS) are other potential candidates for this application. In Figure 7.2 we demonstrate that the open circuit voltage of this type of hybrid photoelectrode can reach more than 0.8 V_RHE, which is the record value for solution processed photoelectrodes. A photon to hydrogen efficiency as
high as 15% was achieved in the visible. This work demonstrates that low fabrication cost and high performance photoelectrode can be achieved utilizing solution processable hybrid organic-inorganic semiconductors.

Figure 7.1. Different types of photoelectrodes presented in literature ordered in terms of their efficiency and expected cost trend.\(^{[3-5]}\)

Figure 7.2. Benchmark of open circuit voltages and band gap of the most important materials for H\(_2\) evolving photocathodes, the deposition technique and eventual special treatments are indicated by the symbols.\(^{[6]}\)
7.2 Tandem photoelectrode

The thermodynamic potential required for the water electrolysis \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \) is \( E_{\text{H}_2\text{O}}^0 = 1.229 \text{ V} \). Therefore the photovoltage produced from a single junction photoelectrode is not enough to drive the whole reaction. A tandem type photoelectrode is proposed as strategy to achieve this goal.

By employing the concept of the natural photosynthetic reaction center by using a bio-inspired photoinduced electron transfer (type II heterojuincton) between the hybrid organic-inorganic donor and acceptor to create the required chemical potential from solar light. The active layers comprise donor-acceptor mixtures that give rise to the formation of charges upon illumination. In Figure 7.3(a) the blue and red represent two different photoactive layers that are separated by a recombination layer that consists of electron and hole transporting materials. These two photoactive layers are composed by a donor-acceptors designed to absorb and convert complementary (e.g. visible and near infrared) parts of the solar spectrum, respectively, in this way adding the respective generated photovoltages. The transparent and conductive inter-layer serves to connect the two active layers with minimal energy loss. Figure 7.3(b) shows the external quantum efficiency of the top and bottom layers that harvest long and short wavelength of the solar spectrum, respectively. This idea is expected to realize easily by low-temperature solution processed technique. This low-cost monolithic tandem cell is expected to complete the whole water splitting reaction without additional supply of electrical power under solar irradiation.

Figure 7.3. (a) Schematic drawing of an hybrid tandem photoelectrode. (b) The corresponding external monochromatic photon to electron conversion quantum efficiency of the two separate layers.
7.3 Photoelectrochemical CO₂ reduction

The CO₂ is a greenhouse gas that absorbs and emits radiation within the thermal infrared range. In this thesis, we demonstrate that the hybrid nanostructured materials can convert the solar energy into hydrogen by splitting the water. This photoreduction requires two electrons to generate one H₂ molecular. From the thermodynamics point of view, this hybrid photocathode can also be used for CO₂ reduction since the energy level for CO₂ reduction (CO₂/CH₄) makes this reaction more favorable than H₂ reduction. However, the CO₂ reduction requires more than two electrons e.g. CO₂ + 8H⁺ + 8e⁻ → CH₄ + 2 H₂O. Therefore, from the kinetics point of view, this reaction is more sluggish. It has been demonstrated by many researcher that it is possible to convert the CO₂ to other low carbon fuels such as methanol and methane by photoelectrochemical reduction.[7] The energy required for CO₂ reduction is lower than that of proton reduction.

\[
\begin{align*}
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} & \Delta G_{\text{f}} &= -114 \text{kJ mol}^{-1} \\
\text{H}_2\text{O} & \rightarrow \text{H}_2 + 1/2 \text{O}_2 & \Delta G_{\text{f}} &= 237 \text{kJ mol}^{-1}
\end{align*}
\]

Once the CO₂ catalysts, such as Cu nanocrystals, are well installed, it is very possible to convert the CO₂ to low carbon fuels.[8] The low-cost and solution processable photocathodes developed in this thesis are potential candidates for PEC CO₂ reduction.

7.4 Outlook of utilization

The low cost hybrid photocathode is expected to gain more efficiency and stability by employing (1) nanorod, (2) low band gap polymer, (3) tandem structure and (4) TiO₂ coating upon the active layer.[9, 10] We expect that these strategies may significantly improve the photocathode performance. The optimized photocathode efficiency should be close to the NCs/polymer hybrid solar cell, which has a record around 5% to date.[10] We believe once the solar energy to H₂ conversion efficiency reaches 5%, it may draw substantial attention and may have big impacts to its future commercialization.

7.5 References

Utilization and outlook


