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# Glassy carbon/multi walled carbon nanotube/cadmium sulphide photoanode for light energy storage in vanadium photoelectrochemical cell

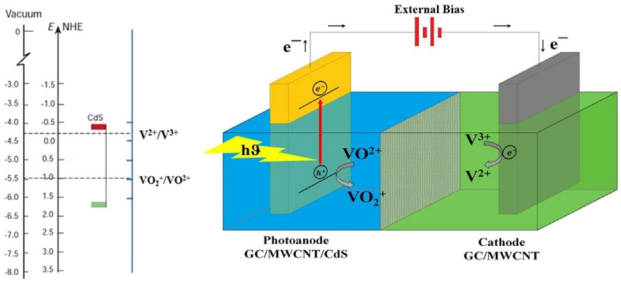
Zahra Peimanifard, Sahar Rashid-Nadimi*

*Department of Renewable Energies Engineering, Faculty of Advanced Science and Technology, University of Isfahan, 81746-73441, Isfahan, Iran*

## HIGHLIGHTS

- Vanadium Photoelectrochemical Cell is a novel system for solar energy storage.
- GC/MWCNT/CdS is used as a photoanode in vanadium photoelectrochemical cell.
- GC/MWCNT/CdS photoanode shows the specific photoresponse toward oxidation of $VO^{2+}$.
- The GC/MWCNT/CdS yields high maximum ABPE of 2.6% in three-electrode setup.
- The GC/MWCNT/CdS yields high maximum ABPE of 2.12% in two-electrode setup.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The aim of this study is utilizing the artificial photosynthesis, which is an attractive and challenging theme in the photoelectrocatalytic water splitting, to charge the vanadium redox flow battery (VRFB). In this work multi walled carbon nanotube/cadmium sulphide hybrid is employed as a photoanode material to oxidize $VO^{2+}$ to$VO_2^+$ for charging the positive vanadium redox flow battery's half-cell. Characterization studies are also described using the scanning electron microscopic-energy-dispersive X-ray spectroscopy (SEM-EDS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and UV −Visible methods. The phtoelectrochemical performance is characterized by cyclic voltammetry and chronoamperometry. Applied bias photon-to-current efficiency (ABPE) is achieved for both two and three-electrode configurations. The glassy carbon/multi walled carbon nanotube/cadmium sulphide yields high maximum ABPE of 2.6% and 2.12% in three and two-electrode setups, respectively. These results provide a useful guideline in designing photoelectrochemical cells for charging the vanadium redox flow batteries by sunlight as a low cost, free and abundant energy source, which does not rely on an external power input.



## 1. Introduction

Current issues such as global warming and declining urban air quality have led to transition from fossil fuels to renewable energy

* Corresponding author.
*E-mail address:* s.rashidnadimi@ast.ui.ac.ir (S. Rashid-Nadimi).

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[1]. Renewable electricity production from sources such as wind and solar power, is sometimes criticized for being variable or intermittent [2]. Therefore, a valid solution to solve this problem would be using electricity energy storage systems (EES), which could provide a temporary medium to store and release electricity as needed. Redox flow batteries are electrochemical storage devices that utilize electrolyte that is stored in a tank separated from the battery stack [3]. They have recently received great attention as one of the most important energy storage technologies as they offer various advantages, such as long cycle life, quick response time, separated battery capacity, high efficiency and low maintenance costs [4–7]. For a number of years now, the NASA-Lewis Research Centre has been involved in the development of redox energy storage systems [8]. Using these batteries for storing electricity produced by intermittently renewable energy sources such as wind or solar power would allow for more efficient operation of power plants and saving energy [9]. The vanadium redox flow battery (VRFB), is a type of rechargeable battery proposed by Skyllas–Kazacos and co-workers [10–13] which uses the same metal on both sides of the cell ($VO_2^+/VO^{2+}$) as the positive electrolyte and ($V^{2+}/V^{3+}$) as the negative one, thus avoiding cross-contamination of the electrolyte [4,7,14]. Charge and discharge reactions are as follows [6,15]:

At the positive electrode:

$$VO_2^+ + 2H^+ + e \underset{charge}{\overset{discharge}{\rightleftharpoons}} VO^{2+} + H_2O \quad E^0 = 1.0\ V$$

At the negative electrode:

$$V^{3+} + e \underset{discharge}{\overset{charge}{\rightleftharpoons}} V^{2+} \quad E^0 = -0.26\ V$$

Generally to charge the battery, electricity is sent to the vanadium battery's stack. Also, the system can be instantly recharged by mechanically exchanging the discharged solution with recharged solution [16]. In this paper, we examine the applicability of photoelectrochemical charging of the VRFB. Photoelectrochemistry provides a promising path for direct conversion of light into chemical fuels, including hydrogen and simple hydrocarbons such as methanol [17,18]. Upon illumination with photons having energy equal or larger than the band gap ($E_g$) of the semiconductor used in electrode configuration, electrons and holes are generated in the conduction and valence bands respectively [19]. The photogenerated electrons and holes are used to promote a redox reaction resulting in storing light energy in the form of chemical energy in the chemical bonds [20]. Honda–Fujishima used $TiO_2$ as the photocatalyst in a photo electrochemical cell (PEC) to decompose water for the first time in the early 1970s [21–24]. Since the finding, a great deal of research has been done on other potentials of PEC based solar cells, such as a solar rechargeable battery or a solar charger. These two points of view have been discussed in more detail in Ref. [25]. A solar rechargeable battery is a kind of battery in which the charging reaction is carried out by light rather than by an external power supply. Sharon et al. developed the cell $BaTiO_3|Ce^{4+/3+}|Fe^{3+/2+}|Pt$ in 1981. In this system, two different types of redox electrolytes with two electrodes (semiconductor electrode and counter electrode) are separated by a suitable membrane. Upon illumination, oxidation of the electrolyte ($Ce^{3+} \rightarrow Ce^{4+}$) would occur near the interface of the n-type semiconductor-electrolyte and the reduction of electrolyte ($Fe^{3+} \rightarrow Fe^{2+}$) would take place near the counter electrode. This way, the battery can be charged by photon energy and discharged in dark condition to generate power [26]. Recently, Liu et al. employed photoelectrochemical path to convert solar energy to chemical energy stored in vanadium redox species [27–30]. They used $FTO/TiO_2$ and $FTO/TiO_2/WO_3$ as the photoanodes and platinum mesh as the counter electrode. Photoelectrochemical water splitting, including oxygen evolution at the photoanode and hydrogen evolution at the cathode, are considerable competitive reactions, which decrease solar energy storage efficiency in vanadium photoelectrochemical cell. Especially when photoelectrodes and counter electrodes are made of materials which show electrocatalytic activity towards oxygen and hydrogen evolution, these competitive reactions intensify. Platinum has an excellent electrocatalytic activity and very low over potential toward oxygen and hydrogen evolution [31]. Thus, it is not a suitable electrode material for vanadium redox species. Therefore, in vanadium photoelectrochemical cell reported by Liu et al, hydrogen evolution at the platinum cathode is more probable than reduction of $V^{3+}$ to $V^{2+}$, and oxygen evolution at the photoanode is not negligible and the photoanodes show photo responses even in the absence of vanadium redox species [28].

The carbon and graphite materials such as carbon felts, graphite felts, graphite powder and carbon black are known as the best electrode material for the VRFBs [4,12] because, at the surface of carbon materials, electrochemical reaction of vanadium species have a faster kinetic rather than competitive gassing reactions (hydrogen and oxygen evolution). Same guide can be used to design vanadium photoelectrochemical cell to increase efficiency of solar energy storage. On the other hand, like the other photoelectrochemical cells, photocatalyst should be employed in combination with suitable electrocatalyst which facilitate charge transfer to vanadium species while inhibiting competitive reactions.

In the present study, glassy carbon/multi walled carbon nanotube/cadmium sulphide (GC/MWCNT/CdS) photoanode performance was evaluated in vanadium photoelectrochemical cell. CdS was used as a photocatalyst which has an appropriate band gap for photoelectrochemical conversion of vanadium species using visible light as shown in Scheme. 1. Also, MWCNT which has an excellent performance and has been known in VRFBs before [4], was employed as a $VO^{2+}$ oxidation electrocatalyst. There was no significant oxygen evolution at the surface of photoanode. A GC/MWCNT was used as a counter electrode in two electrode cell design to avoid hydrogen evolution in cathodic chamber. CNTs not only act as an active material for the VRFB electrodes [4], but also serve as charge separator and charge-transporting highway in the photoactive layer [32].

## 2. Experimental

### 2.1. Materials and reagents

All chemicals were of analytical grade and were used directly without further purification. The pristine MWCNT was retrieved from US Nano Research. The MWCNT was modified via a chemical treatment method to increase surface oxygen content [12]. $VCl_3$ and $VOSO_4$ were used to prepare the anolyte and catholyte solutions and sulfuric acid was used as the supporting electrolyte. Anodic and cathodic solutions employed for efficiency calculation, were the mixture of $VOSO_4/V_2O_5$ and $VCl_3/VCl_2$ which provided $VO^{2+}/VO_2^+$ and $V^{3+}/V^{2+}$ species, respectively. Due to instability of the $VCl_2$ solution, it was prepared freshly via cathodic electrolysis of a $VCl_3$ solution. $CdCl_2$ and $Na_2S$ were used as precursors for preparation of CdS [33].

### 2.2. Preparation of MWCNT/CdS hybrid

MWCNT/CdS hybrid was prepared via the method reported by