

Technical Note

Assessing the use of simple dye-sensitized solar cells for drinking water chlorination by communities with limited resources

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ABSTRACT

Dye-sensitized ZnO and TiO₂ photoelectrochemical cells were constructed using recycled waste materials and readily accessible household chemicals to assess whether it would be feasible for low-income communities to utilise solar energy for drinking water chlorination. Prussian Blue sensitized ZnO cells utilising ferro/ferricyanide and iron/copper redox couples for charge transfer produced open circuit potentials of between 0.19 and 0.53 V, and short circuit currents in the range 0.3–1.5 mA cm⁻². Although the power output from these cells was significantly lower than those using the iodide/triiodide redox couple for charge transfer, the significantly lower cost of construction of cells using alternative electrolytes could make these cells accessible to poor communities for producing small amounts of solar electricity for drinking water chlorination.

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1. Introduction

A large amount of the current research and development of new solar technologies is focussed on achieving highly efficient systems that could generate electric power at costs that are competitive with fossil fuels and other energy sources. As a consequence, increasingly sophisticated manufacturing techniques and materials are being used in the development of new solar energy systems that are largely inaccessible in many parts of the world outside of specialised research institutions. This research focus neglects the important role that solar power could play in alleviating health problems caused by unsafe drinking water in rapidly growing urban areas in many parts of the world.

The world is currently experiencing a humanitarian crisis which is largely unrecognised in high-income countries. Currently about 1.1 billion people do not have access to a safe drinking water source within reasonable walking distance of their homes, and this factor combined with poor sanitation and inadequate hygiene practices is causing about 1.6 million deaths each day [1]. For each death, many more people become seriously ill, particularly children who bear much of the burden of diarrhoeal and other water-related diseases throughout the world [2]. These health problems are being exacerbated by squalid and overcrowded living conditions in urban slums as increasing numbers of people move from rural areas to seek a better life in large cities [3]. Currently about half of the

world's population live in urban areas, and this proportion is expected to rise to about 65% in 2015 [3].

The World Health Organisation (WHO) has set the Millennium Development Goal (MDG) target of reducing the proportion of people in the world without sustainable access to safe drinking water and sanitation by half by 2015. If this goal is to be achieved, many communities will need to progressively become more self-reliant and less dependent on external help to manage water sources for potable use, and they will need access to a range of tools and information to help them do this.

The management of many small community or single household water supplies could remain problematic because of the difficulty of disinfecting drinking water using locally available resources. In many regions it may not be possible to obtain enough firewood to boil water because of the effects of deforestation and land degradation. Additionally, many local communities only have limited access to imported chlorination agents for water disinfection which greatly increases the risk of infection by waterborne diseases. Although drinking water can be thermally disinfected using simple solar methods such as the use of cardboard solar box cookers [4] or allowing water to heat in clear plastic bottles [5,6], the treatment rate is limited by the high specific heat of water and the storage of treated water is often problematic.

These problems could be at least partially alleviated if sufficient electricity was made available in regions with unsafe drinking water to generate chlorine for disinfection by the electrolysis of saline water. The amount of energy required to do this would be extremely modest by comparison with typical household usage of electricity in high-income countries, and in many cases could be

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provided by solar power. Brine electrolysis could also enable excess chlorine to be stored in the form of sodium hypochlorite solutions or solid calcium hypochlorite which could either be traded or utilised if adverse weather conditions limited the rate of production of chlorine.

One possible way of increasing the uptake of solar chlorine production would be for communities to be trained in how to construct practicable solar cells themselves using locally available resources. If this were possible, it is likely that (appropriately supported) local enterprises and social networks could distribute the technology far more efficiently than would be possible by external aid agencies acting independently.

This paper outlines the first steps in the process of testing the feasibility of developing and constructing solar cells in a household setting constrained by a limited range of tools and using waste materials and natural products wherever possible. As a result of this work, a number of photoelectrochemical cells were developed using, iodide/triiodide, ferro/ferricyanide and copper/iron redox couples [7] that are capable of producing enough electricity to chlorinate small amounts of drinking water.

2. Constraints and opportunities in low-income communities for constructing solar cells for drinking water chlorination

It will only be viable to construct solar cells in regions with water quality and sanitation problems if the current paradigm of only selecting technologies on the basis of cost, efficiency of energy conversion and the shortness of their “payback” times is reconsidered in these regions. Although low cost will continue to be important, under conditions of poor public health and widespread impoverishment factors such as availability of raw materials and ease of construction are likely to be more important considerations than the overall efficiency of the system. Under these conditions, “payback” could be assessed on the basis of whether the resources and labour invested in constructing solar cells are warranted, and whether more drinking water could be disinfected by utilising the raw materials in other ways (for example, by constructing a short-lived galvanic battery with metallic components for brine electrolysis).

The limited availability of raw materials and lack of access to specialised construction technologies are likely to constrain the range of solar technologies that could be locally constructed in regions with water quality and sanitation problems. These factors would generally make it impractical to construct conventional solid-state solar cells in these regions. Photoelectrochemical cells are likely to be much easier to construct and use under these conditions.

One of the most important sources of construction materials for solar cells in regions with drinking water problems is likely to be

waste streams in large urban centres in these regions. Ironically, the accessibility of materials that could be used for constructing solar cells (Table 1) is likely to be increasing in many regions as the population living in large urban centres progressively grows. This is because the composition of waste streams in many urban centres is changing as an increasing proportion of the population have sufficient disposable income to buy consumer goods that were previously inaccessible. Additionally, many large urban centres are experiencing a large and growing “e-waste” problem as large amounts of obsolete electronic equipment from high-income countries is being dumped in many parts of the world [8]. Obsolete electronic equipment now represents about 8% of most municipal waste streams and this proportion is growing rapidly throughout the world [8].

Natural products in urban areas that have the potential to be raw materials for solar cell construction (Table 1) include fruit, vegetables and other foodstuffs (particularly for dyes); local vegetation (dyes); mangrove mud (a source of sulphides and sulphur); beach sand (generally contains the titanium-bearing minerals ilmenite and rutile for making titanium dioxide); and seaweed (a source of iodine).

3. Methods and materials

3.1. Preliminary testing

Preliminary testing indicated the difficulty of trying to replicate standard solar cell construction techniques without electricity, laboratory equipment and suitable chemical reagents. Although a range of oxide and sulphide heterojunction solar cells including n-ZnO/p-Cu₂O, n-ZnS/p-Cu_xS and n-SnS₂/p-SnS were successfully electroplated onto glass, metal or plastic substrates using aluminium foil as an electron donor, output currents from the devices in sunlight usually were typically less than 10 $\mu\text{A cm}^{-2}$ because of the poor quality and low conductivity of plated films, and the high resistance of unsoldered electrical contacts. Similar problems were encountered when trying to develop films on metal surfaces by heating.

However, the performance of solar cells increased when photoactive oxide semiconductors were deposited on surfaces of partially carbonized wood and on copper wire for use in dye-sensitized metal oxide photoelectrochemical cells [9] using aqueous electrolytes. As solutions containing the iodide/triiodide redox couple are expensive to purchase and have a limited distribution in some parts of the world, additional electrolytes were tested in photoelectrochemical cells including a copper/iron electrolyte [7] using ferrous and cupric phosphates, and; a ferro/ferricyanide electrolyte made with milk, iron, sodium hydroxide (caustic soda) and household cloudy ammonia. Due to the difficulty and

Table 1

Some potential raw materials for solar cell construction from natural products and waste streams and their possible uses.

Material	Products and uses
Galvanised iron fittings (screws, nails, washers etc.); discarded household batteries	Source of zinc for the semiconductors ZnO and ZnS
Copper wire from discarded electrical and electronic equipment	Making electrical connections; source of copper for the semiconductors Cu ₂ O, CuO and Cu _x S; soluble Cu salts for aqueous electrolytes
NiCad rechargeable batteries	Source of cadmium and nickel for the semiconductors CdS, CdO, NiO
Soldered connections from discarded electronic equipment; steel cans	Source of tin for the semiconductors SnO ₂ , SnS and SnS ₂ ; source of lead for PbS (for solder that contains 40% Pb)
Scrap iron	Source of the semiconductors Fe ₂ O ₃ , FeS ₂ ; soluble Fe salts for aqueous electrolytes
Broken light bulbs	Tungsten filaments can be used to make the semiconductors WO ₃ and WS ₂
Scrap aluminium foil	Electron donor for electroplating solar cell electrodes and the chemical reduction of chemicals used in solar cell construction
Soot and pencil “leads”	Carbon for counter electrodes in photoelectrochemical cells
Fruit, vegetables and local vegetation	Natural dyes for sensitizing large band-gap semiconductors
Mud in mangrove areas and coastal salt marshes	Source of sulphur for making sulphide semiconductors
Seaweed	Source of iodine

expense of accessing nanocrystalline TiO_2 , ZnO and Fe_2O_3 made from scrap metal were generally used as the light-harvesting semiconductors in the cells that were tested. Although the resultant cells were far less efficient than conventional Grätzel cells, they have the advantage that it can be easily constructed for little cost from readily available materials without the need for specialised laboratory techniques. The methods used for preparing electrolytes and electrodes used in the photoelectrochemical cells are outlined below together with details of constructing the cells.

3.2. Electrolytes

A solution containing the ferro/ferricyanide (hexacyanoferrate (III/IV)) redox couple was prepared by just covering a quantity of steel wool with fresh or reconstituted powdered milk in a plastic container, and progressively adding pellets of caustic soda (drain cleaner from a supermarket) with stirring until the iron dissolved and the solution developed an orange colour. The solution was filtered through paper towelling and then an equal volume of household cloudy ammonia was added to moderate its pH.

Copper (cupric) and iron (ferrous) sulphates were made by dissolving copper and iron respectively in dilute sulphuric acid (battery acid) and evaporating the solutions to dryness. Powdered copper and iron sulphates were also purchased from a garden supply retailer.

An aqueous solution containing 5% w/v of iodine and 10% w/v of potassium iodide was purchased in a pharmacy to provide the iodide/triiodide redox couple in photoelectrochemical cells that were constructed.

3.3. Electrode construction and cell assembly details

Zinc oxide coated copper wire was used to make the working electrode in photoelectrochemical cells that utilised the copper/iron redox couple for charge transfer. Zinc oxide was deposited on the copper wire by a process of abrasion by firmly rubbing the head of a zinc-plated nail over the surface of copper wire for a few minutes to form a transparent film of ZnO on the copper surface. The coated copper wire was then dipped in a ferro/ferricyanide solution and then in a solution containing ferrous sulphate to form a film of Prussian Blue (ferric ferrocyanide). The treated copper wire was then heated over a candle flame for a few minutes to anneal the ZnO and Prussian Blue films.

The treated copper wire was then placed in one arm of a “U tube” made with transparent plastic tubing (Fig. 1), and another piece of untreated copper wire was placed in the other arm of the U tube to form a counter-electrode. The copper/iron redox electrolyte was made up by half filling each arm of the U tube with copper and iron sulphates respectively. Several pellets of caustic soda were placed in the base of the U tube between the two arms (Fig. 1).

Copper wire could not be used in cells using ferro/ferricyanide or iodide/triiodide electrolytes because of chemical reactions between copper and these solutions. Working electrodes in these cells were made by depositing a film of ZnO on carbonized matchsticks or bamboo slivers. A solution containing colloidal ZnO was prepared by placing several zinc plated nails and a few pellets of caustic soda in a small plastic container containing denatured alcohol. This solution was left for about 3 hours to allow colloidal suspension of ZnO to form. Matchsticks or slivers of bamboo were then gripped with a pair of pliers, immersed in the solution and ignited over a candle flame. The flame was quickly extinguished to ensure that only the surface of the wood was scorched. This process was repeated until the matchsticks or bamboo slivers were uniformly coated with a blue-black film. The ZnO coated wood was then sensitized with Prussian Blue pigment in the manner previously described.

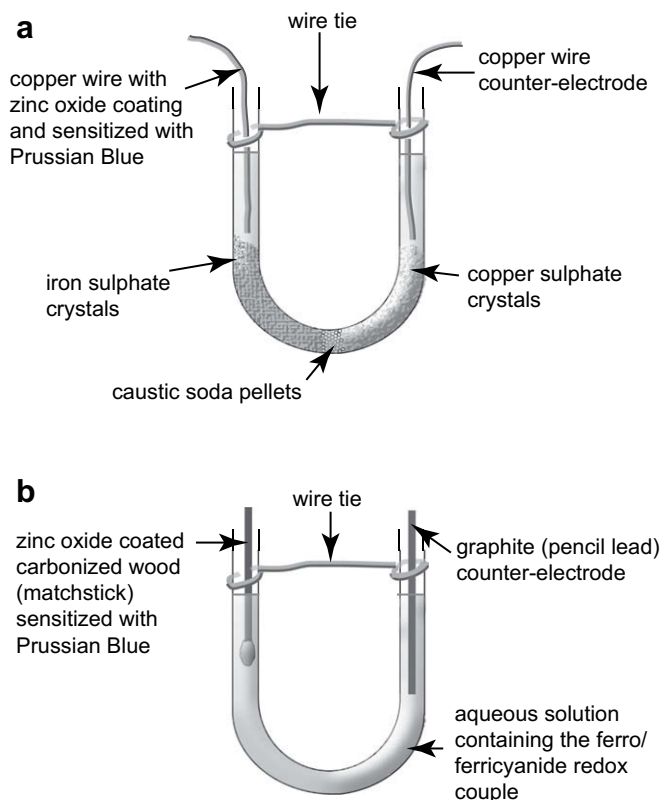


Fig. 1. Construction details for dye-sensitized photoelectrochemical cells using (a) a copper/iron electrolyte; and (b) a ferro/ferricyanide electrolyte. Both cells were constructed within clear plastic tubing.

Counter electrodes for cells using ferro/ferricyanide and iodide/triiodide electrolytes were made using graphite “pencil leads”. These were extracted from wooden pencils by a process of carbonization. Pencils were wrapped tightly in aluminium foil and placed over a small steel can containing a small amount of denatured alcohol. This was ignited, and the pencils were heated until the wood was fully carbonized and could be removed from the graphite core.

ZnO coated carbonized wood working electrodes and pencil lead counter-electrodes were then placed in each arm of a transparent U tube (Fig. 1) with ferro/ferricyanide or iodide/triiodide electrolytes.

Several copper wire and carbonized wood working electrodes were also prepared with a mixed ZnO – TiO_2 coating. These electrodes were initially coated with zinc oxide in the manner previously described, and then covered with a film of sunscreen containing 3% of “microfine” titanium dioxide. The electrodes were then annealed by heating over a candle and sensitized with either Prussian Blue, or with Mercurochrome (Merbromine) which was purchased from a pharmacy.

Table 2

Open circuit potentials (V_{oc}) and short circuit currents (I_{sc}) for photoelectrochemical cells constructed in this study.

Working electrode	Dye	Electrolyte	V_{oc} (V)	I_{sc} (mA cm^{-2})
ZnO on carbonized wood	Prussian Blue	$\text{Fe}(\text{CN})_6^{4-}/^{3-}$	0.19–0.28	0.3–0.8
ZnO on carbonized wood	Prussian Blue	I^-/I_3^-	0.62	0.5–1.0
ZnO on copper	Prussian Blue	Cu/Fe	0.53	1.0–1.5
ZnO on carbonized wood	Mercurochrome	I^-/I_3^-	0.55–0.63	0.5–2.0
ZnO/TiO_2 on carbonized wood	Mercurochrome	I^-/I_3^-	0.63	1.0–2.0
ZnO/TiO_2 on copper	Mercurochrome	Cu/Fe	0.53	1.0–1.5

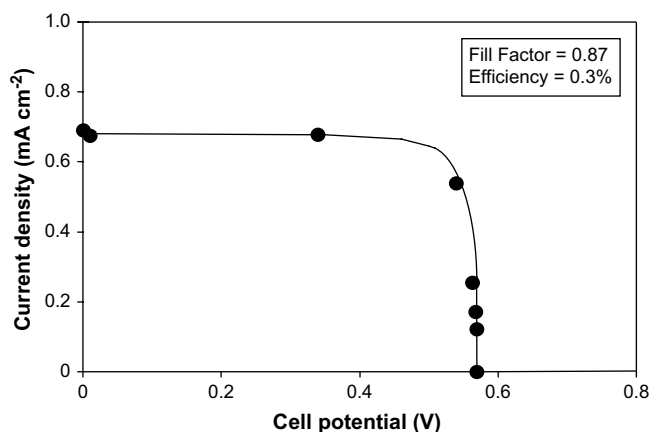


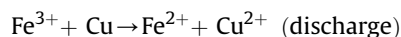
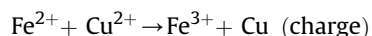
Fig. 2. I - V curve for a Mercurochrome sensitized ZnO photoelectrochemical cell utilising the I^-/I_3^- redox couple.

4. Results and discussion

Measured open circuit potentials and short circuit currents for the cells that were tested are summarised in Table 2. As might be expected, the most efficient cells were those that used the iodide/triiodide redox couple with TiO_2 and ZnO sensitized with Mercurochrome dye, although the performance of these cells was highly variable depending on the quality of the semiconductor film that was deposited on the working electrodes. Testing that was carried out outdoors in full sun conditions with a multimeter and a variable resistive load indicated that the efficiency of solar energy conversion by these cells typically lay in the range of 0.2–0.7% (Fig. 2).

Cells made with Prussian Blue sensitized ZnO and the ferro/ferricyanide redox couple typically produced less than 30% of the power output of cells using the iodide/triiodide redox couple, partly because of the low purity of the electrolyte that was produced by the reaction between milk, iron and caustic soda, and partly because of the lower efficiency of the charge transfer characteristics of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ compared to I^-/I_3^- . However, the ferro/ferricyanide electrolyte can be made from readily accessible materials for about 5% of the cost of purchasing aqueous solutions containing the iodide/triiodide couple (about €10 per 100 mL of solution), indicating that photoelectrochemical cells using the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple could potentially produce electricity more cheaply than those using I^-/I_3^- . Additionally, it is likely that the performance of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ electrolyte could be improved by improving its purity by, for example, recrystallising the solution made from the reaction of milk with iron and caustic soda.

Cells using the copper/iron electrolyte differ from those using ferro/ferricyanide and iodide/triiodide redox couples for charge transfer in being photoelectrochemical storage cells [7] rather than regenerative photoelectrochemical cells where the following electrochemical reactions between iron and copper species take place in separate half cells:



In practice, the cells that were constructed have a very low storage capacity and behaved as regenerative photoelectrochemical cells. The cost per unit output of solar electricity from these cells was comparable with those made using a ferro/ferricyanide electrolyte, as although they produced more power than those utilising the ferro/ferricyanide redox couple for charge transfer, the improved performance would be offset by the increased cost of raw materials for these cells (copper wire and copper sulphate if these materials have to be purchased).

Previous testing of photoelectrochemical cells using the copper/iron redox couple [10] has indicated that an array of these cells with a combined potential of 5 V and a current of 200 mA was capable of producing chlorine at a rate of 4 mg h⁻¹ under full sun conditions from a 1% solution of salt, or enough chlorine to disinfect about 1–2 L of drinking water each hour.

5. Conclusions

Investigations carried out in this study have demonstrated that it is possible to construct viable dye-sensitized solar cells without access to specialised laboratory equipment or iodine solutions and utilising waste materials and readily accessible household chemicals. Although these cells have a much lower efficiency than conventional Grätzel-type dye-sensitized photoelectrochemical cells, their low cost and simplicity of construction means that they are likely to be more accessible to low-income communities.

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