Lithiated nanoparticle diamond energy converter for Concentrated Solar Thermal Power Generation

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Thermionic cathodes are required that can operate at temperatures lower than 700°C and produce current densities in excess of 10A/cm². The application for such technology would be terrestrial thermionic energy conversion devices that can generate electrical power from concentrated sunlight, with a power output of 1-2W/cm². Research is being carried out at the University of Bristol into the synthesis and characterisation of lithiated nanoparticle diamond for use as the cathode and collector coating material. Electron emission tests of lithiated material have demonstrated that it can be made to exhibit a low work-function surface and that this surface is stable at elevated working temperatures. Theoretical modelling has identified that a lithium-doped diamond surface can induce a very large negative electron affinity, which should help to mitigate space charge in prototype vacuum diode energy converters employing lithiated nanoparticle diamond.

Introduction

A novel nano-material that creates electricity using the sun is being investigated in E.ON's International Research Initiative. The material absorbs solar radiation to produce electricity in devices called thermionic energy converters (TECs). Special electrodes using nano-particles of diamond powder. The project aims to achieve operation below 'red heat' level, possibly as low as 320˚ Celsius. Conventional TECs with metal electrodes require temperatures well above 1,500˚ Celsius to produce sufficient electrical current.

Further parts of the project will look at other factors including those affecting the density of the current.

Final stages will be field tests of a prototype TEC with a target efficiency above 25 percent compared to a maximum of about 15 percent in current devices.

The trials, in south-west England and southern France, will use parabolic dishes to concentrate the sun's rays to provide heat energy for the cathode. The UK locations are the highest latitudes at which a domestic-sized TEC using solar power could meet most of a property's annual generation needs.

This project aims for a solar-based technology that may be an alternative to photovoltaic cells, requiring less space and having potential along the sunnier coastlines of the UK and Europe.

The wider market would be to link the new TECs with plant that is already available to concentrate solar power for utility, commercial and domestic use via other technologies. In the longer term, TECs raise the prospect of developing a cost-effective renewable resource, whose supply is virtually unlimited, if the electricity is transported from the world's solar belts.

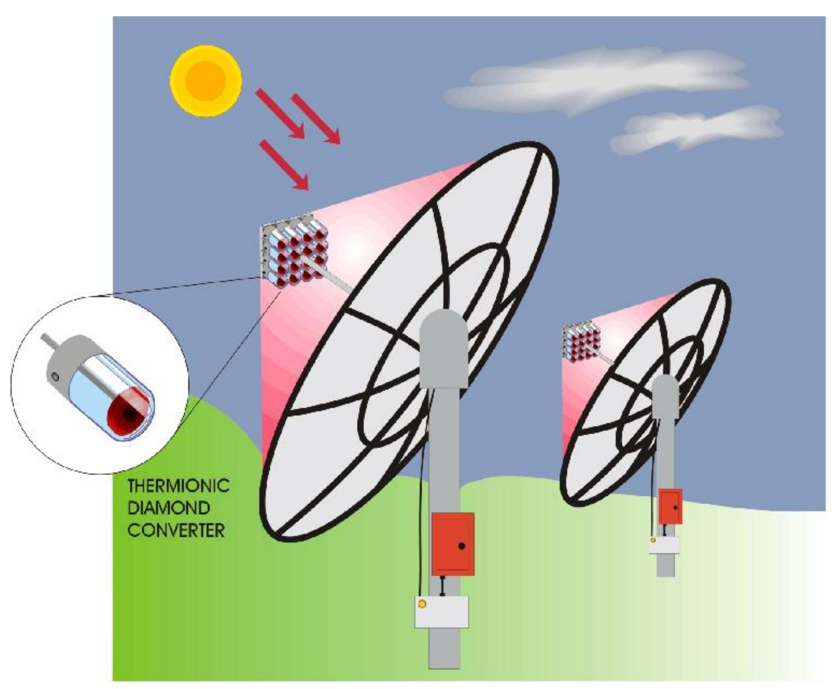
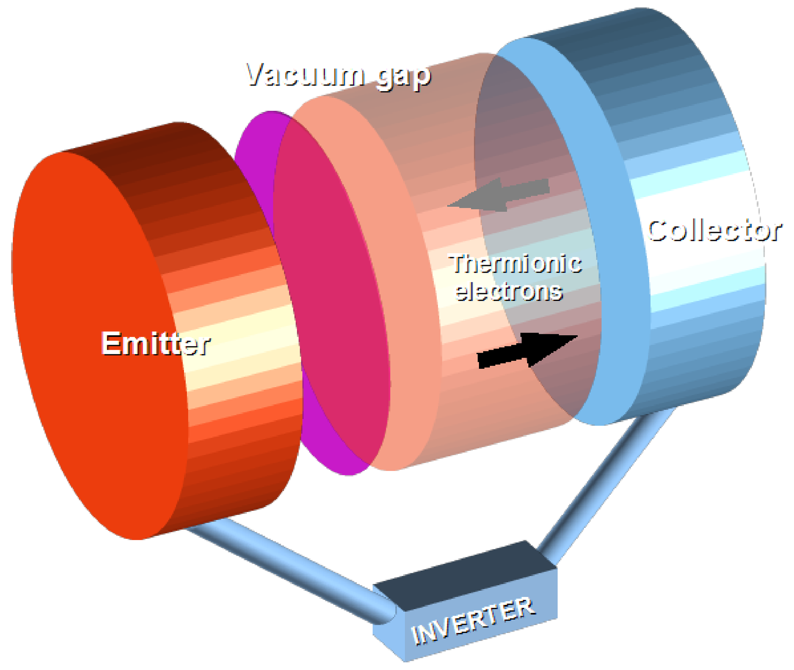


FIG. 1. Prototype Thermionic Diamond Converters fitted to parabolic dish concentrators .

Thermionics & Energy Converters



Thermionic emission current density (*J*) depends on two key factors that determine the current that can be output from a thermionic device; the emitter work-function (φ_E) and the temperature (T) of the emitter, as described by equation (1),

$$J = A_G T^2 e^{\frac{-\varphi_E}{kT}} \quad (1)$$

where the constant $A_G = \lambda_B(1 - r_{av})A_0$,
r_{av} is an average reflection coefficient,
A_0 is Richardson's coefficient,
λ_B is related to the band-structure of the emitting material, after Modinos.

In a thermionic diode energy converter heat is converted into thermionic electrons. The electrons are given additional kinetic and potential energy which enables them to leave the emitter and move ballistically across a vacuum gap to the collector. At the collector the electron's kinetic energy is absorbed as heat and its potential energy may be used to do work in an electrical load thereby generating useful electrical power. The power (P) generated by such a converter may be expressed by equation (2).

$$P = A_G T^2 e^{\frac{-\varphi_E}{kT}} \cdot (\varphi_E - \varphi_C) \quad (2)$$

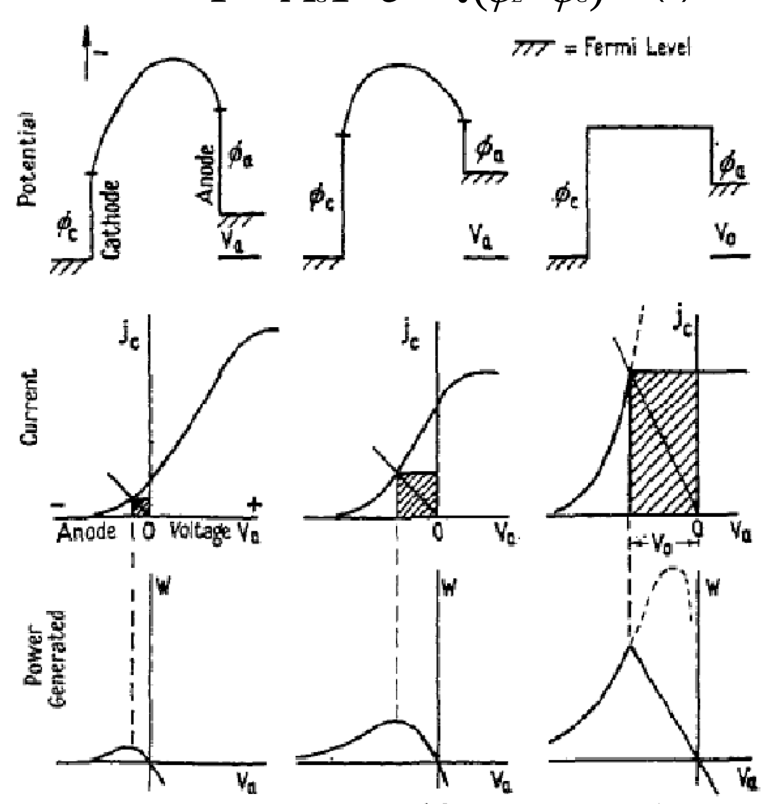


FIG.2.Potential distributions and electrical characteristics for a vacuum diode (left), diode converter (centre), and space charge-free converter (right).

Lithiated Nanoparticle Diamond

Diamond is a promising photocathode, field emitter and thermionic emitter due to its chemical stability, high thermal conductivity and the relative ease of inducing a negative electron affinity. A negative electron affinity, where the conduction band minimum is at a higher energy than the vacuum level, is invariably induced by a surface treatment leading to an adsorbate on the diamond surface.

During the last decade, advances in doping of artificial diamond have led to a number of promising materials for low work-function thermionic devices. In addition to successful p-type doping using Boron, researchers have created n-type diamond using Phosphorous, Nitrogen and Sodium.

Potentially, Lithium dopants sit closer to the conduction band than any other n-type dopant. Lithium's mobility at high temperatures means that its incorporation into diamond films during CVD growth is problematic. The Bristol project uses a different approach. Commercial High Pressure High Temperature (HPHT) nano-crystalline powders are thermally treated with a lithium-containing compound to introduce lithium by diffusion into the nanoparticle surfaces. *FIG 3* shows an SEM image of some of the 0.5 micron grade.

The most interesting aspect of this process is that the manner in which lithium is co-ordinated on the surface and within the bulk appear to be markedly different. For example, when adsorbed onto certain diamond surfaces, a negative electron affinity three times as large as that produced by a hydrogenated surface may be obtained leading to much larger reductions in effective work function. Efficient incorporation into the bulk is dependent on the number and type of other impurities present in the diamond lattice and the nature of the lithium entering the lattice.

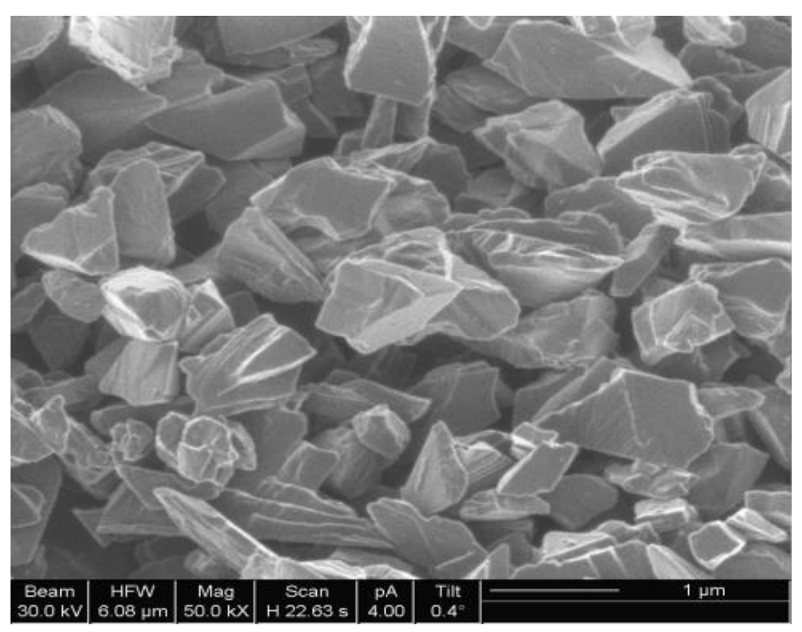


FIG.3.Mono-crystalline grade of lithiated diamond particles with a range of particle sizes.

Experimental Results

A number of grades of lithiated powder from 500nm down to 30nm have been tested for emission in a vacuum chamber, at 1x10⁸ torr. They were heated from room temperature to 850°C in steps. At each temperature step, a voltage was applied to give the current-voltage (IV) curves shown in FIG 4 (a). Work-functions were found to be 1.37-1.41eV using equation (1), as shown in FIG 4(b). The acid washed material emitted less current but showed an improved work-function of **0.91eV**. Electrodes incorporating this material are being fabricated to determine their performance in a demountable paper prototype device.

Large area cathodes have been made and set to work in thermal diodes with inter-electrode separations of less than 100µm. Under 'field-free' conditions, current densities of tens of mA/cm² have been achieved at 700ºC. Application of a small electric field (<0.2V/µm), to mitigate space charge raises the current density to several A/cm².

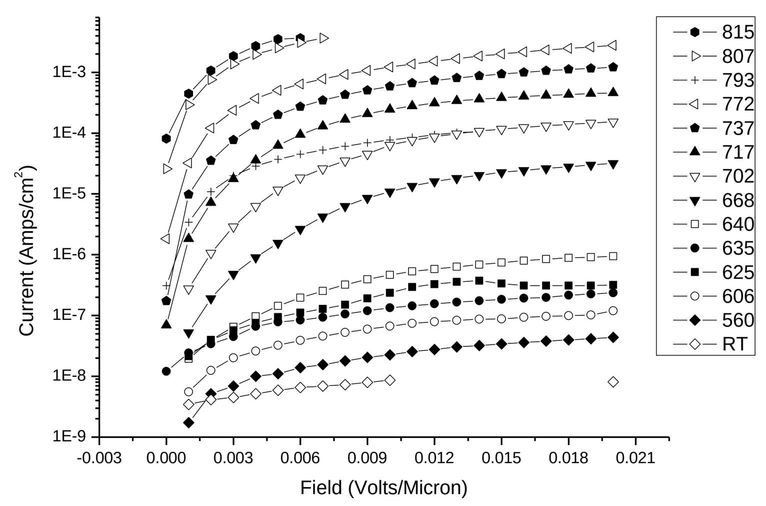


FIG.4 (a) IV curves showing emission current with applied field for 500nm grade of lithiated diamond material .

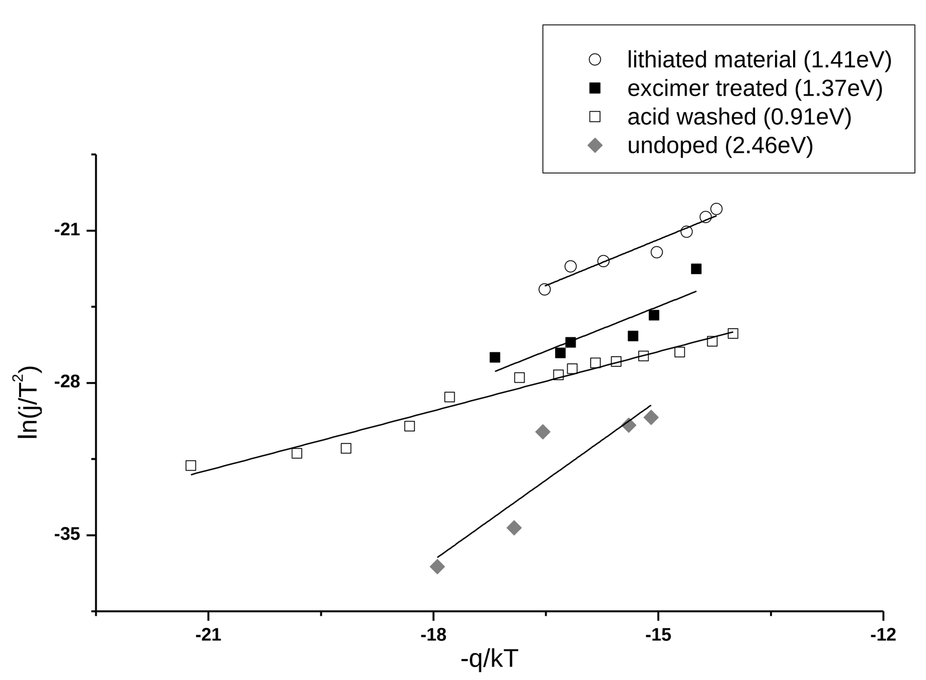


FIG 4(b) Richardson plots for un-doped, lithiated and acid-treated nanodiamond materials , with work functions detailed in the legend.

Model Results

The modelling work has been organised so that the adsorption of lithium onto the three principal crystal planes found on the diamond surface is tackled first. This provides predictions that can be compared with experimental work. The second phase of this work will examine the role of lithium in the bulk lattice of diamond. Here the degree of activity will be mediated by the number and location of other impurity atoms. A summary of some of the findings from the first phase of work conducted on the C(100)-(1x1):O diamond surface are presented in Table1 and FIG 5.

Coverage	Structure	E_{abs} (eV/ads)	d_{CO} (Å)	$d_{11(C-C)}$ (Å)	d_{Li-O} (Å)	$\Delta\phi$ (eV)	χ (eV)
0.5 ML	OP	4.71 (K), 4.07 (E)	1.27	No dimer	1.87	-2.70	-2.08
	OB	3.54 (K)	1.25	No dimer	1.74	-1.87	-1.25
1 ML	HH + T3	4.70 (K), 4.38 (E)	1.40	1.65	1.81, 1.86	-4.52	-3.89
	HB + T3	3.90 (K), 3.76 (E)	1.36	1.66	1.67, 1.86	-3.00	-2.38
	HB + T4	3.36 (K)	1.35	1.62	1.67, 1.75	-2.30	-1.67

Table 1 Calculated structural and electronic properties of the Li-adsorbed C(100)-(1x1) :O surface.

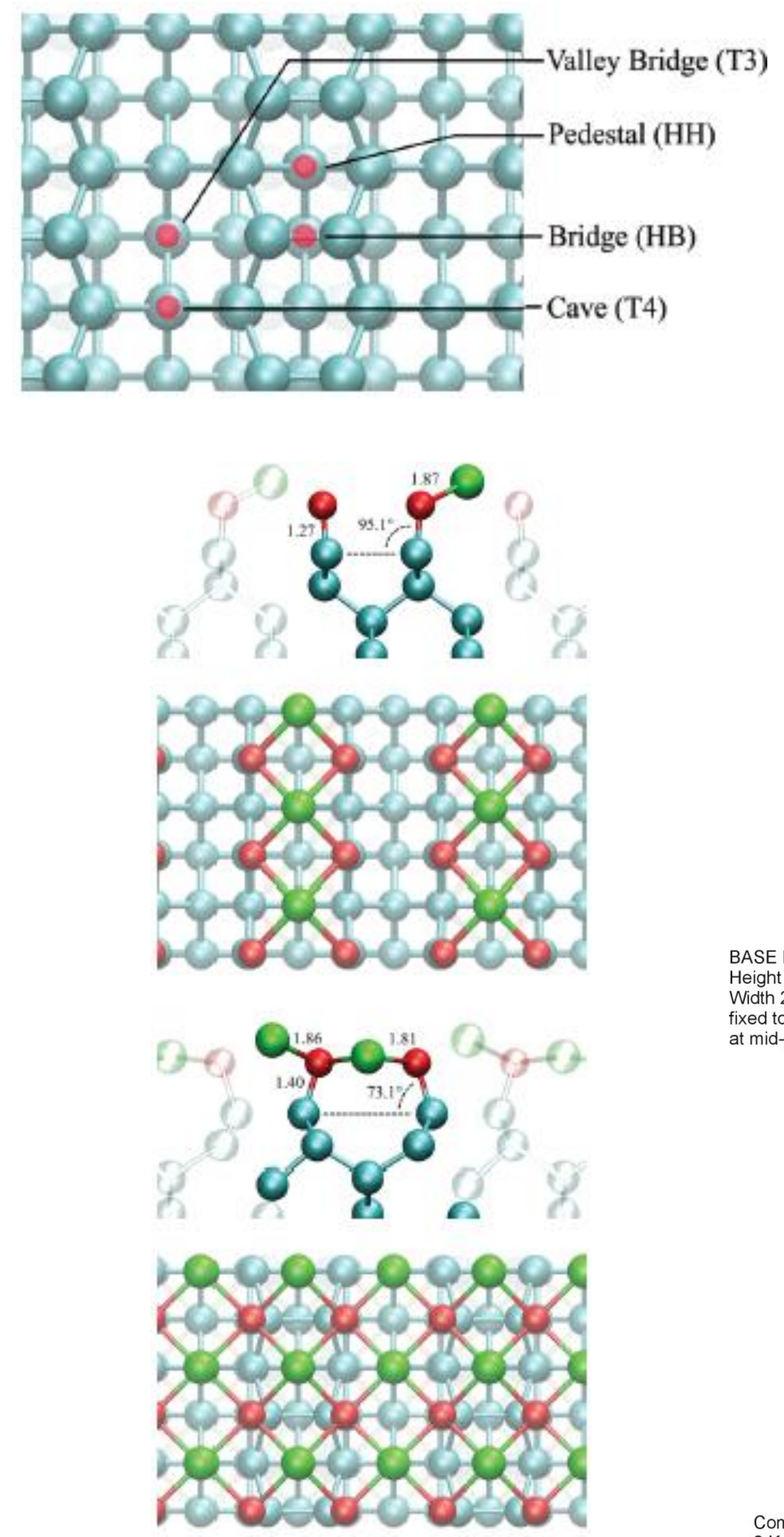


FIG 5 Lowest energy structures for 0.5 ML and 1 ML Li adsorption on C(100)-(1x1):O, with reference to the lithium lattice positions considered.

Key Laboratory Facility

Omicron Ultra High Vacuum Variable temperature Scanning probe microscope is installed in the Bristol Nano Science and Quantum Information Centre- the quietest laboratory in the world. The low noise lab is pictured in FIG 7. This equipment is wholly funded by E.ON IRI project and is used to map the location and stability of lithium and other dopant atoms on the surface of diamond. It is equipped with a scanning Kelvin Probe allowing maps of work-function to be generated with nm precision and compared with topology and surface conductivity.

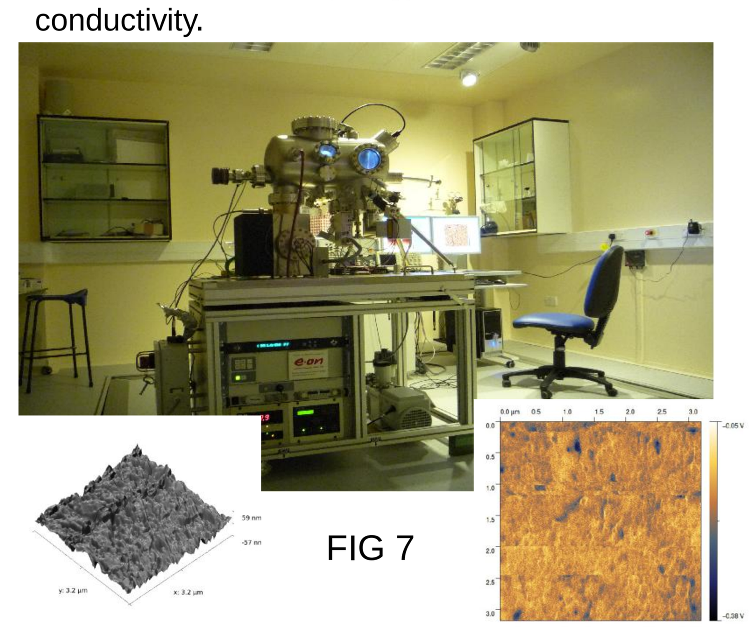


FIG 7

On-sun Trials Activity

In addition to advancing the state-of-the-art in thermionic converters through the characterisation of new semiconducting diamond nano-materials, an integral part of the E.ON project is the testing of prototype devices on a customised Deger sun-tracking platform, (FIG 6, left). The prototype devices (FIG 6 right) will be demountable vacuum diodes with active areas of 45cm². Prototype and platform fabrications are already underway.

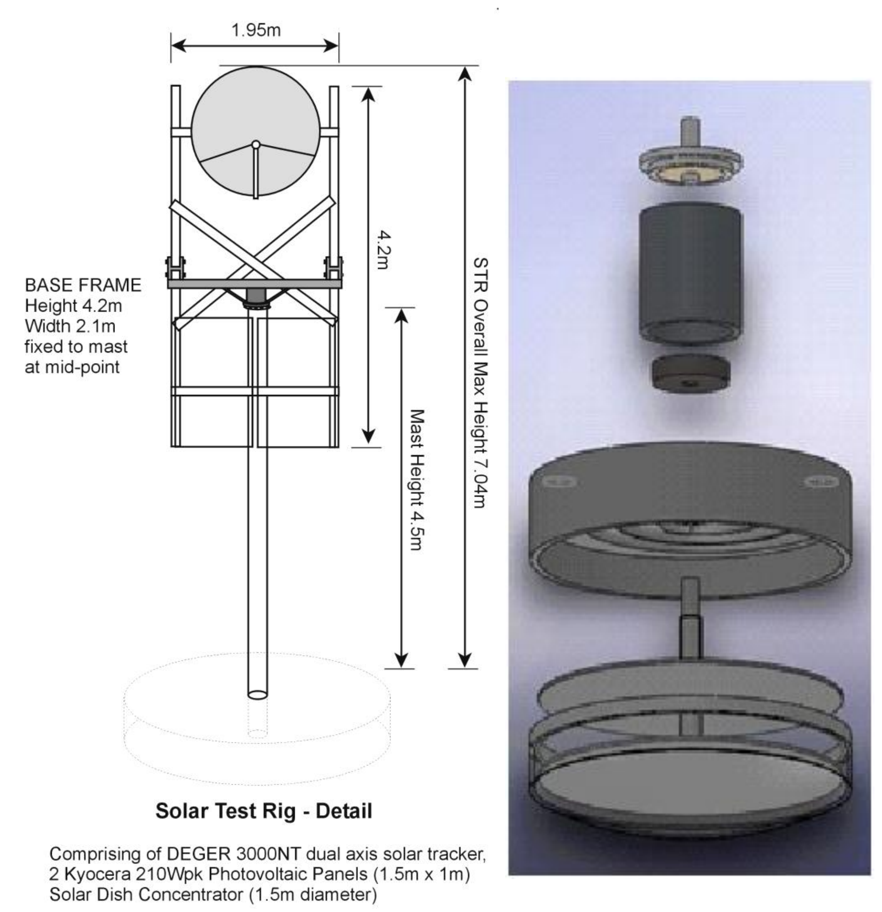


FIG 6 (Left)Drawing of custom sun-tracker with dish and solar panels. (Right)Exploded view of prototype.

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