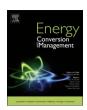
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Enhancement of spectral absorption of solar thermal collectors by bulk graphene addition via high-pressure graphite blasting



Abdul Hai Alami^{a,*}, Kamilia Aokal^b

- ^a Sustainable and Renewable Energy Engineering Department, University of Sharjah, P.O. Box 27272, Sharjah, United Arab Emirates
- ^b Center of Advanced Materials Research, University of Sharjah, P.O. Box 27272, Sharjah, United Arab Emirates

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ABSTRACT

This work presents the results of construction and testing of a flat plate thermal solar collector with an absorber section that has enhanced radiative properties through the modification of its surface properties. A copper oxide layer is grown on top of the copper absorber by chemically treating it in an ammonia atmosphere. Then, a novel graphene mechanical deposition technique is employed that uses compressed air to deposit few layer graphene on top of the copper oxide substrate. In total, three absorbers are made, one features the copper oxide layer, the second has graphene on top of copper oxide and the third is the reference absorber covered with a black matt paint. The radiative properties of the absorbers are assessed, as well as their thermal efficiencies. The best performance was recorded for the graphene-clad copper oxide collector, with a maximum efficiency of 69.4% compared with an efficiency of around 39.5% for the reference collector.

1. Introduction

Flat plate solar thermal collectors are the simplest and probably oldest technology of converting solar radiation into sensible heat through a working fluid [1]. Their utilization covers a wide range of applications that have been reported in literature. For example, Bellos et al. have investigated a Fresnel solar collector with a flat plate for domestic water heating [2]. Shojaeizadeh et al. used a binary fluid to supply thermal energy to industrial processes [3]. Also, the cooling of photovoltaic panels while utilizing rejected heat within the working fluid have been investigated by Ibrahim et al. [4]. Fang & Li reviewed localized investigation of similar solar thermal application for China [5]. Kalogirou has also reviewed their applications in power generation as well [6]. Flat plate collectors still receive interest from R&D to arrive at better efficiencies and lower costs through augmenting various technologies applied either on a system level, such as the work of Bakos in incorporating tracking to enhance efficiency [7], or enhancing one or all of its components. These components are the absorber section, glazing, insulation and auxiliary components, such as circulation and pumping systems, tubing, and solar tracking as reported by Abdallah [8]. Also, incorporating CO2 gas within the glazing as reported by Alami [9] helps enhance the efficiency by reducing the heat transfer from the absorber to the glazing. Each component of the collector has been investigated for enhancing its contribution to the overall efficiency of the solar collector. For example, researchers have investigated enhancing the energy properties of the working fluid to increase the efficiency. This has ranged from the addition to various nano-particles, such as graphene in the work of Verma et al. [10] with a reported overall efficiency enhancement of 29.3%. Metal oxides such as MgO are investigated also by Verma et al. [11] which provided an enhancement of 9.3% from the base case.

Another key component in flat plate solar collectors is the absorber plate, since it is the part that interacts with electromagnetic energy carried by incident solar radiation and converts it into thermal energy. This energy is eventually transferred to the working fluid and into the application. Absorbers thus must possess good radiative and thermal properties because the overall efficiency will depend on the quality of this energy conversion [12].

Enhancing the radiative properties of the absorber is well researched in recent literature. The aim is to utilize thin coatings for selective absorption enhancement, mainly in the visible spectral range. These coatings are mainly metallic oxide materials with direct optical bandgaps such as cobalt silicon oxide reported by Barrera et al. [13]. Nickel-alumina is used in the work of Bostrom et al. [14] to enhance the optical absorptivity up to 0.83 of the incident radiation. Karlsson & Roos [15] used copper oxides on stainless-steel to enhance absorptivity, especially after applying an anti-reflection coating. In the same vain, Hottel & Unger [16] applied copper oxide on aluminum. Cupric oxide coatings applied by arc deposition presented by Marquez et al. [17] not only is shown to enhance the selective absorptivity of the coating, it

E-mail address: aalalami@sharjah.ac.ae (A.H. Alami).

^{*} Corresponding author.

Nomenclature		$I_{ m G}$	intensity of the G peak on Raman plot, AU
		L	length, cm
Greek symbols		m	mass flow rate, kg/s
		q	useful energy collection rate per unit area
σ	absorptivity of absorber	T	temperature, Celsius
ρ	reflectivity of glass and absorber	t	thickness, m
τ	transmittance of glass	U	overall heat loss coefficient, W/m ² ·K
ω_{g}	number of layers of graphene	w	width, cm
Latin symbols		Subscript	
Α	collector area, m ²	а	ambient
$c_{ m p}$	specific heat of water, 4185 J/kg·K	in	inlet water
F_R	heat removal efficiency	m	water average
G	the average solar radiation during the test period, W/m ²	out	outlet water
$I_{ m D}$	intensity of the D peak on Raman plot, AU	p	plate

also adheres better to the surface due to the deposition technique. This has the added benefit of prolonging the useful life of the absorber. Schere et al. [18] investigated copper-aluminum composite films that enhanced absorptivity to 0.89 and emissivity to 0.1. It is understandable why copper oxide appears in many of the literature as a surface optical enhancer since it is the most compatible with the copper-based solar thermal plates, tubing and fittings. Copper oxides are sometimes used in conjunction with aluminum to decrease the cost and enhance the material stability as reported by Sathiaraj [19]. The selective absorbers can be synthesized in a variety of dip coating as reported by Rizzato et al. [20]. Sputtering is another technique used in the work of Lu et al. [21]. Others used evaporation and co-evaporation as seen in the work of Niklasson [22]. Chemical solution deposition is investigated by Bostrom et al. for nickel-alumina in [23]. The latter work also presented results for testing the durability of these films in their earlier work [24]. All authors report on significant gains in efficiency due to these thin film incorporations regardless of the method with which it has been applied. Other methods of promoting selective absorptivity are used to modify the absorber surface microstructure to allow internal refraction of incident radiation and to minimize reflection losses. These modifications are incorporated by either mechanical means as reported by Konttinen et al. [25]. Nickel pigment plating is another method reported in the work of Wazwaz et al. [26]. Depositing nano-structured materials on the absorber has also been successfully used and reported by Oelhafen & Schüler [27]. Lastly, carbon nanoparticles is also used for surface modification as seen in the work of Katumba et al. [28].

Graphene is a two-dimensional material that received significant attention ever since its discovery, with wide spectrum of applications, especially in micro- and nano- devices [29]. The original work on graphene by Ferrari et al. [30,31] has introduced facile and effective production techniques of graphene flakes. The graphene road map, reported by Novoselov [32] discusses various graphene production techniques and direct applications as well. Graphene properties are extremely sensitive to the number of layers that stack during production, according to Machado et al. [33]. The produced graphene materials also has intrinsic structural defects present, that affects many structural and optical properties according to reports published by Malig et al., who reported on multifunctional wet functionalization of graphene [34]. Thus, researchers have reported on many methods to produce graphene while controlling its stacking, such as Sahoo et al. who investigated pristine graphene exfoliation with lithium [35]. Thus, the synthesis routes and conditions are important in tuning its optical and thermal properties as reported by Kim et al. for semiconductor applications [36]. Other potential applications are presented in the review of Soldano et al. [37]. Historically, graphene has been synthesized by various methodologies that are documented in literature, such

as dry exfoliation as reported by Guermoune et al. [38]. It is also produced via photoexfoliation in the work of Li & Cai [39]. Wet exfoliation techniques from graphite and graphite oxide reported by Huang et al. [40] is another route to produce few-layer graphene. Graphene has also been grown on substrates, mainly silicon, and by chemical vapor deposition (CVD) as in Bonaccorso et al. report [41]. It can also be produced via plasma enhanced CVD reported by Yavari F, Koratkar [42]. Lastly, a facile production technique involves producing graphene nano-platelets mechanically by high-energy centrifugal milling investigated by Alami et al. [43]. As an application, some authors [44] have incorporated graphene nanoplatelets with the working fluid for enhancing the efficiency of the collectors, which enhanced the reported efficiency by 18.7%.

In this work, the enhancement of the absorber section is investigated by chemically growing an adherent copper oxide layer, followed by the deposition of a graphene bulk layer using a novel process that uses a compressed air stream to mechanically exfoliate graphite. Three absorber plates are prepared and are mounted in three identical solar thermal collectors. One absorber has its surface coated with a commercial black matt paint (the reference collector), while two others had either an adherent layer of grown black copper oxide (CuO) and or a graphene substrate air-blasted over the CuO layer. The radiative and thermal properties of these absorber substrates are examined, as well as their effect on the thermal efficiency of the respective collectors is also investigated and reported. Although graphene has been used in flat plate collectors as an enhancer of the working fluid, it has never been applied in its solid state and on a scale larger than macroscale. The air blasting technique is investigated in this work as it provides a homogeneous layer of nano-graphene, which is expected to enhance the radiative properties of the absorber.

2. Theoretical model

The modeling of flat plate collectors is a well-established area in literature. From the simple energy balance of the following two equations for the energy carried by the fluid and the solar energy incident on the collector, respectively:

$$\dot{q} = \dot{m}c_p(T_{out} - T_{in}) \tag{1}$$

$$\dot{q} = GA(\alpha \tau) - U. A(T_p - T_a) \tag{2}$$

The plate temperature, T_p is difficult to estimate, and thus the useful heat can be expressed as a function of the water temperature. An interesting 1963 study by B. Liu and R. Jordan [45] defined the rate of useful energy collection to be the difference between the rate at which electromagnetic radiation is absorbed by the absorber section and the rate at which energy is lost due to the difference in temperature of the

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