



# Plasmon based metal-graphene nanocomposites for effective solar vaporization



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## ABSTRACT

Graphene-silver nanoparticle composites for effective solar absorption are prepared by coupling surface plasmon and optical absorption of individual phases as low cost materials. Optoelectronic and morphological properties are studied with varying synthetic conditions to optimize their photothermal response. Plasmonic silver nanoparticles encapsulated in graphene layers act as localized solar heating elements of its surrounding medium, because of which a significant heating is observed. The tested composites are quite stable under prolong exposure to solar radiation and hence may find potential applications in various fields.

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## 1. Introduction

The energy generation, conversion and utilization via clean, cost effective, abundant and renewable resources have always been subjects of scientific interest due to their potential applications both in industrial and non-industrial processes [1]. Solar energy is one of the most abundant renewable resources that fulfills all greener requirements, can be collected using concentrators and converted into useful forms of energy for human benefits [2]. With the development of nanoscience, various applications including photovoltaic, thermo-photovoltaic, solid state lighting and photocatalytic energy conversion are studied extensively using nanoparticles [3–6]. The recent proposal of solar steam generation utilizing surface plasmon resonance (SPR) properties of gold nanoparticles (GNPs) has gained a much interest [7–9]. The usefulness of these nanoparticles (NPs) in such processes is highly influenced by their intensive properties of low light emission, controlled modification of optical density of states (DOS), and tunable SPR [1,10].

It is well known from the literature that noble nanomaterials with tunable SPR are highly capable of tailoring their DOS, light trapping and light conversion properties to generate the heat at

nanometer length scale by various processes [11–16]. Hence, they serve as highly efficient localized heating elements for many potential applications, these include photothermal therapy, nanosurgery, photothermal imaging, photoacoustic imaging, and plasmon assisted optofluids. Therefore, attempts are being made by scientific communities to use metal nanoparticles (MNPs), especially Au, Ag & Cu, in this direction [9,10]. Further, the increasing demand of these NPs in medical fields also has received a considerable interest [17–20]. The phenomenon that follow in such processes include effective absorption of incident photons, conversion of photon energy into heat energy and finally the effective diffusion of generated heat into the appropriate surrounding media [10]. The amount of heat generated here highly depends upon various factors such as the size, shape and number of nanoparticles present in the reaction matrix. Therefore it is highly desirable to make an appropriate selection of nanoparticles based on the requirement of energy conversion process under the consideration. It is well reported that silver nanoparticles (AgNPs) are capable of generating ten times stronger heat than gold nanoparticles due to their high absorption by SPR [10,21]. Further, the silver has also advantage of being a low cost and abundant material as compared to gold. In order to achieve an efficient and broadband absorption by SPR the other materials are also studied, these include titanium nitride [22], TiO<sub>2</sub>-Ag nanocomposites [23], the effect is also quantified in case of isolated gold nanowires [24]. Recently an interesting review has been published on the various theoretical and experimental aspects

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of thermoplasmonics along with their various possible applications [25].

Graphene, a carbon based nanomaterial, with exciting electrical, thermal, and mechanical properties has been explored as a potential candidate for a large number of applications [26–39]. Recently, carbon based materials along with MNPs have been explored towards the solar steam generation process [7,40,41]. To date, various methods utilizing different reducing agents are used to prepare graphene but among all, the chemical reduction using sodium borohydride is considered as most effective, which is low cost, simple and provides a large yield [42,43]. Considering all these factors, including importance of carbon and MNPs in photothermal processes, here it is decided to prepare and utilize graphene-AgNPs composites for solar to thermal energy conversion process. In this communication, a simple synthetic approach for the preparation of graphene-AgNPs composites by chemical reduction process has been reported. The effect of reducing agent on optoelectronic and morphological properties of these composites has been investigated. Finally, the thermal response of the most efficient composite is studied under the concentrated solar illumination.

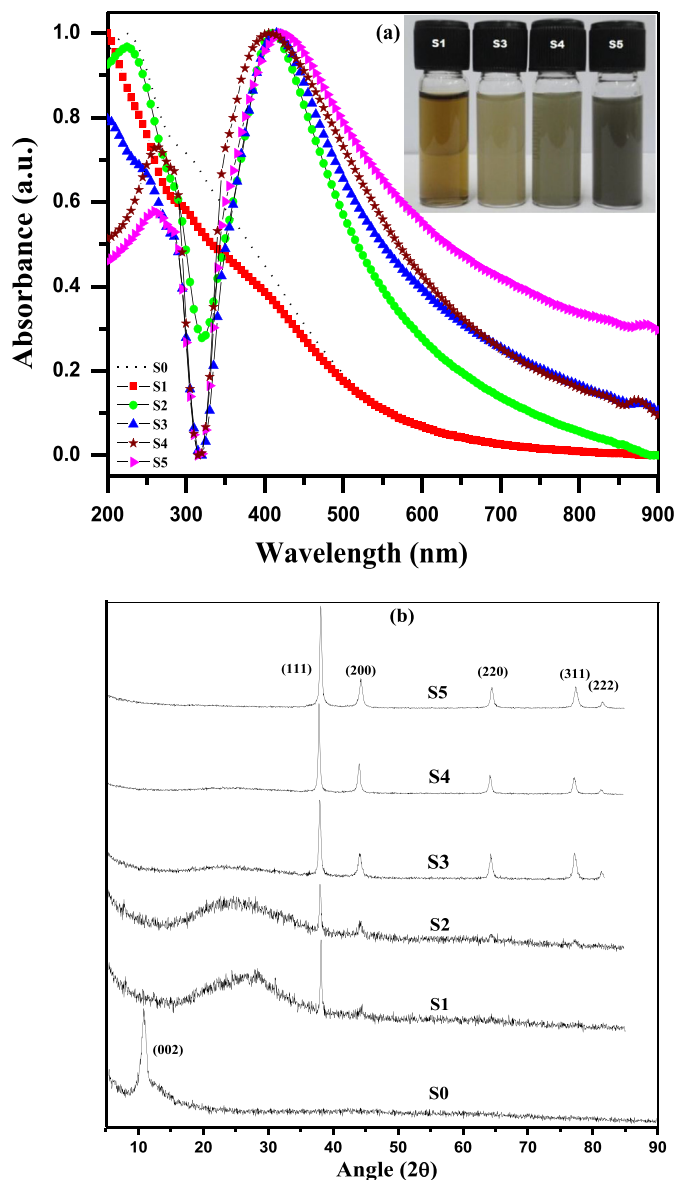
## 2. Experimental details

### 2.1. Materials

Graphite powder, sulphuric acid ( $\text{H}_2\text{SO}_4$  98% AR) and sodium borohydride ( $\text{NaBH}_4$ ) (AR) were obtained from sd-fine chemicals, India. Potassium permanganate ( $\text{KMnO}_4$ ) (AR) was purchased from Himedia, India. Silver nitrate ( $\text{AgNO}_3$ ) was taken from Sigma Aldrich. All these reagents were used as received without further purification. Milli Q water was used in the synthesis of present composites.

### 2.2. Formation of graphene-silver nanoparticle composites

The stock aqueous solution (2.4 L) of graphite oxide (S0) was prepared from the 2 gm of graphite powder using well known Hummers method followed from literature [44]. The formation of graphene-AgNPs composites was achieved by a simple reduction method for the five different concentrations of sodium borohydride in an aqueous environment. The concentrations chosen for this work were 1 mM, 25 mM, 100 mM, 200 mM and 500 mM respectively. In our typical synthesis procedure, equal amount of GO (10 ml) from its stock was taken in five different conical flasks and are labeled as S1, S2, S3, S4 and S5. In a separate container stock aqueous solution of  $\text{AgNO}_3$  (200 mM in 50 ml) was prepared which was added to all the above flasks in equal proportion to each of 10 ml GO at room temperature. These mixtures were then well sonicated for 15 min in ultrasonication bath in order to attain proper mixing of the two phases. To form composites, aqueous solutions (10 ml) with different molarities of sodium borohydride were prepared in five separate beakers and stirred, each one of which was mixed with different solution of  $\text{AgNO}_3$  and GO. The addition of sodium borohydride in all the cases (S1–S5) was carried out in water bath conditions with continuous stirring, samples were then left for a longer duration (5 h) to attain complete reduction. This process has resulted the different colored precipitates of graphene-AgNPs composites which were further washed thoroughly with copious amount of distilled water to remove unreacted products. The resultant precipitates were then dried under table lamp and preserved at room temperature. The Digital photograph of as prepared colloids of composites S1, S3, S4 and S5 are shown in the inset of Fig. 1(a). In addition to this, a direct reduction of pure GO solution (stock) and pure silver nitrate (200 mM) were also carried out with 100 mM sodium borohydride



**Fig. 1.** (a) Normalized optical absorption spectra of graphene-AgNPs composites S1 to S5, prepared with different molarities of sodium borohydride reduction. Dotted dashed line in the spectra represents the absorption of pure graphite oxide (GO) solution whereas the inset of the same figure provide digital photograph of as prepared graphene-AgNPs composites S1, S3, S4 and S5 (left to right) under room light, and (b) Compared X-ray diffraction spectra of pure graphite oxide (GO) with graphene-AgNPs composites S1 to S5 (down to up).

exactly in the similar way as described previously for independent colloids. Resultant materials obtained in these two cases were also preserved and used for the further characterizations.

### 2.3. Characterization techniques

Optical absorption spectra of the prepared composites were recorded using Analytikjena Specord 200 plus spectrophotometer. X-ray diffraction pattern were recorded using Philips X'pert powder diffractometer with  $\text{Cu } k_{\alpha 1}$  radiation ( $k_{\alpha 1} = 1.54056 \text{ \AA}$ ). Thermogravimetric analysis (TGA) of the samples were carried out with SDT – Q600 thermal analyzer (TA instruments, USA) to investigate thermal degradation of prepared composites. Scanning electron microscopy (SEM) was done using a field emission gun (Quantan

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