Investigation of photothermal effect in nanomaterials

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Abstract. The thermal emission dependence on various nanostructural materials absorption of electromagnetic irradiation was investigated. Nanomaterials containing Au and Ag nanoparticles, and CuO nanorods have been studied by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy. These nanomaterials were synthesised by physical vapour deposition and by a thermal oxidation process. The preliminary results of a photothermal experiment for all these materials are presented. The temperature increase due to this effect was observed.

1. Introduction

The photothermal effect has been investigated and developed in recent decades, especially with the current of nanotechnology. Although the photothermal effect is mainly utilized for medical therapeutics, it can be further developed for energy-efficient applications. There is still a large amount of “free” energy that has not yet been fully utilized, so new materials are explored and design for this purpose. In materials which absorb light, electrons make transitions from the ground state to the excited state. The excitation energy subsequently relaxes through nonradiative decay channels. This results in the increase in the kinetic energy leading to the overheating of the local environment around the light-absorbing spaces. The heat produced can be employed for energy savings or medicine.

The photothermal effect is the simplest way to utilize solar energy by using an absorption device to convert absorbed solar energy directly into heat energy. This effect is caused by localized surface plasmon resonance. Some materials can absorb substantial radiation in a wide frequency range and convert it to thermal energy [1].

A variety of materials exhibiting the photothermal effect, such as metallic materials, carbon-based materials, and organic materials, have been reported in the literature [2,3]. Up to now, there have been a lot of investigations on the photothermal properties. In the previous reports, most photothermal conversion heterostructures contain plasmonic metal nanoparticles as crucial components. The superior performance in photothermal conversion has been mainly ascribed to the enhancement of surface plasmon resonance [4].

In ref. [5] the photothermal effects of various Fe₃O₄ nanoparticles in both solution and thin film forms under white-light and NIR laser irradiation have been investigated. The much stronger photothermal effect was found for Fe₃O₄ under white-light irradiation as compared with the NIR laser irradiation. Also, the photothermal applications of SmCoO₃/SBA-15 catalysts synthesized by impregnation method were investigated by Zhang’s group [6]. The temperature of SmCoO₃/SBA-15 rose to 85 °C under the irradiation power density of 0.5 W/cm². In paper [7] a new approach of thermal insulation via the photothermal effect of the nanostructured thin films and coatings for the energy-efficient window was presented. Upon irradiation solar light simulator, the surface temperature of composite poly(acrylic acid)-Fe₃O₄ considerably increased resulting in reduced convective heat loss. The key that limits the
heat flow through windows is the thermal insulation, which is traditionally constructed by multi-pane structures with an insulating layer.

Highly cross-linked and monodispersed poly(cyclotriphosphazene-co-4,40-sulfonyldiphenol) (PZS) with silver and gold-silver bimetallic nanoshells were investigated in [8]. PZS@gold nanoshells show very strong absorption in the NIR region and thus can effectively convert NIR laser energy into heat. Therefore, fine-structured PZS@gold nanoshells may be an ideal candidate for photothermal imaging and therapy under NIR laser irradiation and have great potential as a combined platform for therapeutics and diagnostics. The sudden temperature increase leads to hyperthermia, rapidly resulting in cell death.

Gold nanoparticles have a wide absorption range and are efficient heaters. Depending on the size and shape, Au has an absorption peak between 500 and 600nm. This tunable feature appears not only in Au nanoparticles, [9-12] but also in other metal nanoparticles including Ag, Cu, and Pd. An alternative to metals, metal oxides is also a widely used group of photothermal nanomaterials. For example, copper oxide is a narrow bandgap semiconductor with excellent absorption properties in visible light, thus it can be expected to have significant photothermal conversion properties [13].

In this work different type of nanomaterials are purposed and the effect of metal (Ag, Au) and metal oxide (CuO) on photothermal conversion was considered. These materials contain gold or silver nanoparticles and copper oxide nanorods. They were characterized by scanning electron microscopy, infrared absorption and X-ray diffraction.

2. Experimental

2.1. Nanomaterials synthesis

Two type of nanomaterials were prepared. The nanocomposites containing metal particles (silver and gold) were synthesized using physical vapour deposition. As a result the carbon films with silver (nano-Ag-C) and gold (nano-Au-C) nanoparticles were obtained. Material with copper oxide in form of nanostructures was prepared by thermal oxidation process. Samples were prepared on Al and Si substrates.

2.1.1. Nano-Ag-C and nano-Au-C films synthesis

Thin films with metal particles in the carbonaceous matrix were obtained using two separate sources in the PVD method. As precursors of these films fullerene C_{60} (99.95%) and metal acetate were applied. Both compounds were evaporated from separate sources heating by electrically resistive. The silver and gold acetate was used for preparing nano-Ag and nano-Au particles respectively. The processes were performing under dynamic pressure 10^{-3} Pa. Duration time of PVD process for nano-Ag-C films was 10 min and for nano-Au-C films was 8 min. The distance between substrate and sources was 80 mm for both types of films. The process of preparing such films is based on the method described in ref. [14] and [15].

2.1.2. CuO nanorods films synthesis

Films composed of copper oxide nanostructure especially in form of nanorods were synthesised by thermal oxidation process. The process was performed in the air atmosphere at 600°C for 30 min.

2.2. Structural characterization

SEM studies were performed with JEOL JSM-7600F field emission scanning electron microscope equipped with EDX (Energy Dispersive X-ray) spectroscopy.

FTIR spectra were obtained with ThermoScientific Nicolet iS10 FTIR spectrometer, using ATR (Attenuated Total Reflection) technique, in the spectral range 600-4000 cm^{-1} and transmission technique, in the spectral range 400-4000 cm^{-1}.

X-ray diffraction (XRD) technique was applied to study crystal structure form of obtained films. XRD data were obtained with Rigaku SmartLab 3kW diffractometer. Diffraction measurements were performed in grazing incidence primary beam geometry (GIXD).
2.3. Photothermal experiment
The photothermal conversion properties of the nanomaterials were recorded using a self-built photothermal conversion set-up. The experimental set-up utilizes a lamp as a light source and thermocouple for temperature changes measurements.

3. Results and discussion
Various nanomaterials were prepared and characterized in terms of the molecular and crystalline structure as well as surface topography. All samples were tested towards the photothermal effect. The detailed results are presented below.

3.1. Structural characterization of nanomaterials

3.1.1. Nano-Ag-C and nano-Au-C films
Figure 1 presents SEM imaging of surface topography of nano-Ag-C (1a) and nano-Au-C films (1b). Both types of nanocarbon films were deposited on an aluminium substrate. Such films are composed of metal nanoparticles within amorphous carbon matrix. It is noticeable that depend on metal the surface of films is different. For the nano-Ag-C films densely packed silver nanoparticles were observed whereas for the nano-Au-C films gold nanoparticles were much bigger and rarely distributed on the surface. Ag nanoparticles are very dispersed and have a few nm while Au nanoparticles have diameters between 30 – 60 nm. However, in higher magnification tiny Au particles on the film’s surface are also visible. The carbon matrix also differs for these films – for nano-Ag-C seems more solid-like structure and for nano-Au-C large, irregular pores are visible.

Molecular structure was studied using the FTIR spectroscopy by ATR technique. In figure 2 spectra of infrared absorption of samples with Ag and Au nanoparticles are presented. Due to organic precursors used during PVD processes (metal acetate) some of active modes of functional groups in IR range are found. In FTIR spectra for both nanomaterials narrow bands at 1183 and 2328 cm\(^{-1}\) associated to stretching vibration of C\(_{60}\) are visible. Bands in the spectral range between 1300-1654 cm\(^{-1}\) are corresponded to stretching modes of CH, CH\(_2\), C=O, C-C. There were found bands at 2850 and 2920 cm\(^{-1}\) related to stretching bond CH and CH\(_2\). There are also observed broad band at 3423 and 3367 cm\(^{-1}\) in nano-Ag-C and nano-Au-C films respectively. These bands are connected to O-H stretching vibration in water molecules adsorbed on the film’s surface.

At the diffraction pattern are shown reflections from Ag-acetate (§), fullerene (+) and Ag nanoparticles (■) with crystalline structure (figure 3a). The estimated size of Ag nanoparticles is in the order of several nanometers.

The diffraction pattern shows reflections from the fullerene phase (+) and Au nanoparticles (*) with an estimated size of several dozen nanometers (figure 3b).

![Figure 1. SEM image of nano-Ag-C (a) and nano-Au-C films (b).](image-url)
Figure 2. FTIR spectra of nano-Ag-C (a) and nano-Au-C films (b).

Figure 3. XRD diffractograms of nano-Ag-C – ■ – Ag nanoparticles, + - fullerite, • - Ag acetate (a) and nano-Au-C films - • – Au nanoparticles, + - fullerite (b).

3.1.2. CuO nanorods films

Copper oxide nanorods films growth in thermal oxidation process in the air atmosphere and at temperature 600 °C for 30 mins. Figure 4a shows a typical topography of such film surface. Nanorods are densely distributed and grow perpendicularly to the surface. They are very long – the length exceeds several µm and diameters are in the range from several to hundreds nm (figure 4b).

Figure 4. SEM image of CuO nanorods film (a) and individual nanorods in higher magnification (b).
A molecular and a crystalline structure of CuO nanorods is presented at figure 5. The vibrational modes in the CuO nanorods network are related to the relative motion of Cu and O atoms, which contain asymmetric Cu-O stretching vibration and asymmetric O-Cu-O bending vibration. FTIR spectrum of prepared CuO nanorods is shown in figure 5a. The high-frequency mode around 461 cm\(^{-1}\) is reported as Cu-O stretching along the (\(\bar{1}10\)) direction and the mode at 540 cm\(^{-1}\) is attributed to Cu-O stretching along (101) direction [16,17]. The band at 626 cm\(^{-1}\) can be attributed to the stretching vibrations Cu(I)-O, occurring, around 625 cm\(^{-1}\) [18]. This also confirms the existence of the Cu\(_2\)O phase. The bands with wavenumber higher than the CuO vibration modes are observed, like a band around 876 cm\(^{-1}\) which is probably associated with the occurrence of various forms of copper compounds with oxygen and hydrogen occurring in the form of nanostructures. In work [19], there was also observed band at 881 cm\(^{-1}\) for vibrations coming from Cu-OH structures and its existence was connected with oxidation process in the air. The bands in the spectral region between 1000-1500 cm\(^{-1}\) are associated to C-O stretch and CH bending vibrations modes of the hydroxyl group combined with copper atoms. There is also a band at 1637 cm\(^{-1}\) corresponds to C=O stretching vibration and broad band around 3400 cm\(^{-1}\) connected to O-H stretching vibration. Bands in the range of 2850-2950 cm\(^{-1}\) are attributed to vibrations modes of CH and CH\(_2\).

A diffractogram of CuO nanorods film is presented in figure 5b. The diffraction pattern shows reflections from two crystalline copper oxide phases: cuprite Cu\(_2\)O and tenorite CuO. The content of both phases is similar and the size of the crystallites also.

![Figure 5](image)

**Figure 5.** (a) FTIR spectrum of CuO nanorods, (b) XRD diffractogram of CuO nanorods film \(\bullet\) – Cu\(_2\)O, + - CuO.

### 3.2. Photothermal effect

Photothermal conversion properties were performed for all nanomaterials films. The scheme of the experimental set up for photothermal measurements is presented in figure 6. To evaluate the photothermal performance of nano-Ag-C, nano-Au-C and CuO nanorods films, the sample was placed under a lamp to test its temperature variation with irradiation time and the results of the tests were shown in figure 7. Samples were irradiated by a white-light from LED lamp. The value of illuminance on the sample surface was \(4 \times 10^4\) lx. The temperature of the sample’s surface was measured by the thermocouple with a diameter of 0.2 mm, located directly on the films’ surface. The light was turned on for few min, but the thermometer continued to record the temperature after the light was turned off.
All experiments were performed in the same condition and investigated samples had the same dimensions. The samples were placed on a specially designed frame, and all of the samples' area was in the air during the measurement. The graphs show the temperature changes of the surface of the illuminated nanomaterials as a function of time (blue line) together with the temperature changes only for the sample substrates (black line). Comparing these plots allowed to determine the photothermal effect of nanomaterials films.

Samples exhibited a similar increase in the temperature. The maximum temperature was 26.2°C and 26.6°C for nano-Ag-C and nano-Au-C films respectively while for CuO nanorods films this temperature was 27.2°C. After the light was turned off, all samples exhibited approximately the same cooling rates indicating their emissive properties are similar. The difference of the temperature changes of a nanomaterial as against temperature of substrates is about 2°C. It is not a significant rise cause here were measured thin films deposited on substrates. The substrates alter photons absorption, therefore, lowering the photothermal heating efficiency.
Similar methodology of photothermal measurements were performed in ref. [20] where gold nanoshells with a size of ~20 nm. The temperature increase of the gold nanoshell hydrosol induced by photothermal conversion was as high as 30°C under exposure of an 808 nm coherent diode laser with a power density of 5 W/cm². The difference between results presented in this work and results from the literature are crucial. Most investigations are concentrated on samples in the form of fluids as well as various research groups perform experiments using a different radiation source. Therefore, it is difficult to compare these results.

4. Conclusion

In this study, the experimental measurements have been conducted to evaluate the photothermal effect of the various type of nanomaterials with Ag and Au nanoparticles and CuO nanorods. Samples with metal nanoparticles were obtained by PVD method and CuO nanorods by thermal oxidation process in the air. The structural characterization was performed by SEM, XRD and FTIR technique and allows to determine the topography and the morphology of films surface as well as the crystalline and molecular structure.

The results of this study conclude that both nanomaterials with Ag and Au nanoparticles and CuO nanorods change the temperature under light irradiation. The change is not spectacular probably because the measurements were performed on the thin films. To solve this issue it is necessary preparation samples in a different way. A solution could be separation the thin film of nanomaterial from the substrate and then measured the photothermal effect only for films material.

Although the photothermal effects of transition metal nanoparticles and copper oxide nanostructures have previously used for cancer treatment, new studies, also in this paper, suggest possibilities for applications in energy-efficient structures.

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