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Laser Induced Plasmonic Heating with Au Decorated TiO_2 Nanoparticles

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Abstract

In this study, we explore the feasibility of laser as source of photons for plasmonic heating of metal nanoparticles. Au decorated TiO_2 nanoparticles with different Au wt.% loading were prepared using deposition-precipitation method and their physical and optical properties were characterized by X-Ray diffraction (XRD), Diffuse reflectance spectra (DRS) and Raman spectroscopy. The enhancement of the optical properties of Au plasmonic nanoparticles arises from localized surface plasmon resonance (LSPR) effect achieved under 532 nm laser irradiation. Additionally, the photothermal performance of Au/TiO_2 nanofluid was tested compared with other nanofluids under visible laser irradiation. The results revealed that the temperature of Au/TiO_2 nanofluid was significantly higher compared to that of bare TiO_2 and pure milli-Q water, attributing to the plasmonic excitation of Au nanoparticles under laser irradiation.

Keywords: Plasmonic nanoparticles; laser irradiation; photothermal;

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1. Introduction

Due to the increasing energy crisis and environmental problems, the development of energy efficient technologies has attracted great research interest by both scientific community and industry over the last decades. The use of light-harvesting energy systems is a promising strategy to develop a large number of sustainable and environmental friendly applications, such as photovoltaics, photochemical and photothermal processes [1, 2]. Among these, photothermal conversion is one of the simplest processes, in which incident photons are absorbed and then converted into heat energy.

The utilization of plasmonic metal nanoparticles (NPs) with metal oxides has been widely applied in light-driven processes because they can enhance all the radiative properties, including absorption of photons and scattering [3]. Nanostructured plasmonic metals, such as Au, Ag and Cu, are able to induce Localised Surface Plasmon Resonance (LSPR) upon the absorption of their corresponding wavelength and subsequently enhance the local electromagnetic field [4]. LSPR is an optical phenomena, which occurs when the size of the metal NPs is smaller than the wavelength of the incident light [5]. This effect can be described as the collective resonant oscillation of free conduction electrons confined in metallic NPs stimulated by incident light [4, 6]. The LSPR can be tuned by tailoring several parameters, such as metallic material, size, shape, inter-particle distance and the nature of the surrounded medium [5, 7, 8]. Laser light has been used for the excitation of plasmonic NPs due to its unique properties, including monochromaticity, high intensity and directionality. The novel aspect of this process is that the directionality and high intensity of laser light as excitation source allows localized heating in space and time, which could result in highly-efficient energy processes. [9].

In this study, we investigate the effect of using laser as light source for efficient localized heating of plasmonic Au NPs. Au decorated TiO_2 nanoparticles with different Au loading were characterized using XRD, DRS and Raman spectroscopy. The temperature increase of different nanofluids under laser excitation and the photothermal effect of Au NPs in aqueous solution were observed. Additionally, parameters that influenced the photothermal performance of nanofluids such as the concentration of Au NPs was evaluated.

2. Experimental section

2.1. Preparation of Au/TiO_2 photocatalyst

A series of Au/TiO_2 (i.e., different concentrations of Au loading) photocatalysts were prepared by deposition-precipitation (DP) method [10]. For the DP method, $AuCl_4{\cdot}3H_2O$ was used as a precursor. Degussa P25 TiO_2 was dried in an oven for 24 h before use. Different weight percentages (1 and 3 wt.%) of Au NPs supported over P25 TiO_2 were obtained by stirring 100 ml solution containing different concentrations of $AuCl_4{\cdot}3H_2O$. The pH of the different solutions was adjusted to 9 by adding NaOH 0.1 M. 500 mg P25 TiO_2 were then added to the solution and the pH was re-adjusted at 9. The DP was done at 80 °C under sonication for 2 h while maintaining the pH constant and then the slurry was stirred overnight. The photocatalysts were washed repeatedly with milli-Q water by centrifuge and then placed in an oven for drying at 100 °C overnight. The fabricated samples calcined in the air at 300 °C for 4 h with a ramping rate of 5 °C/min. Finally, the samples were cooled and kept inside a desiccator in the dark to prevent photo-decomposition and moisture. The final Au/TiO_2 powders obtained had purple color.

2.2. Characterization and measurements

X-Ray diffraction (XRD) patterns were recorded using a D8 ADVANCE (Bruker AXS) diffractometer with Cu Kα radiation and a nickel beta filter (2θ = 10-80°). Raman spectra were collected with a Renishaw using 532 nm laser excitation. Diffuse reflectance spectra were obtained using a spectrometer (Perkin Elmer Lamda 950) equipped with a 150 mm integrating sphere. Temperature measurements were recorded with PicoLog thermocouple data logger (TC-08).

2.3. Experimental set-up

A schematic representation of experimental set-up is shown in Fig. 1. A reactor made of Poly (methyl methacrylate) (PMMA) sheet was fabricated using Trotec Speedy 300 laser cutter. The total volume of the reactor was 7 ml. During the experimental procedure, the fabricated reactor was kept in the air using a clamp to avoid heating and was covered by insulated material. A solution comprising 5 ml milli-Q water in the presence of 3 mg photocatalyst in the PMMA reactor was stirred throughout the experiment and irradiated from the top using 532 nm laser light. Two thermocouples were connected to a data acquisition unit plugged in a computer and were installed in different heights of the solution to monitor the temperature. Temperatures were recorded every 2 min for a total period of 80 min until a thermal steady state has been achieved.

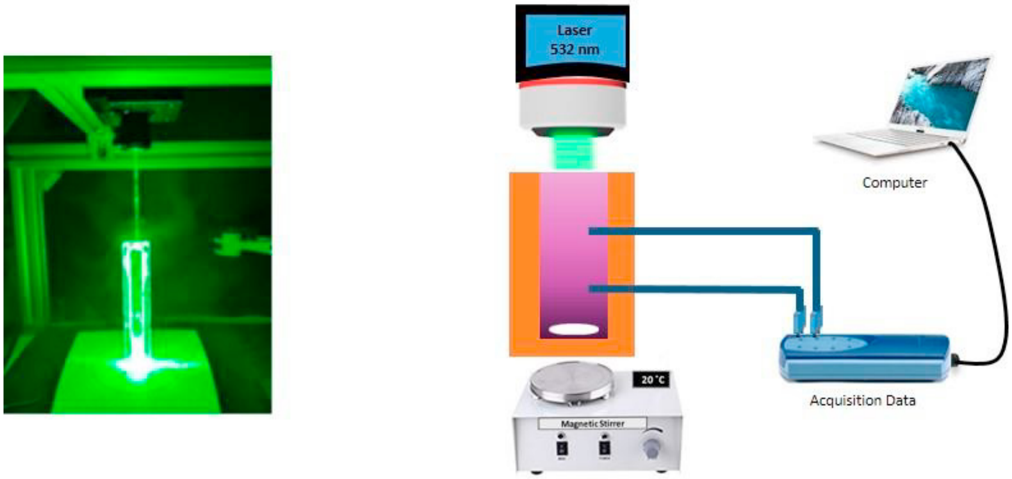

Figure 1. Photo of the fabricated reactor (left) and schematic representation of the experimental set-up (right) for the plasmonic heating experiment.

3. Results and discussion

3.1 Characterization of the prepared photocatalysts

The XRD pattern confirmed the presence of both anatase and rutile phase of P25 (Fig. 2). Diffraction peaks of 25, 38 and 48 ° correspond to anatase phase, whereas 27, 41, 54 and 63 ° correspond to rutile phase of TiO_2. No Au pattern was observed in the Au loaded TiO_2 samples. This was probably due to low Au concentration. The presence of Au NPs was confirmed from Transmission electron microscopy images and the average Au NP diameter was determined 3.1 ± 0.4 nm.

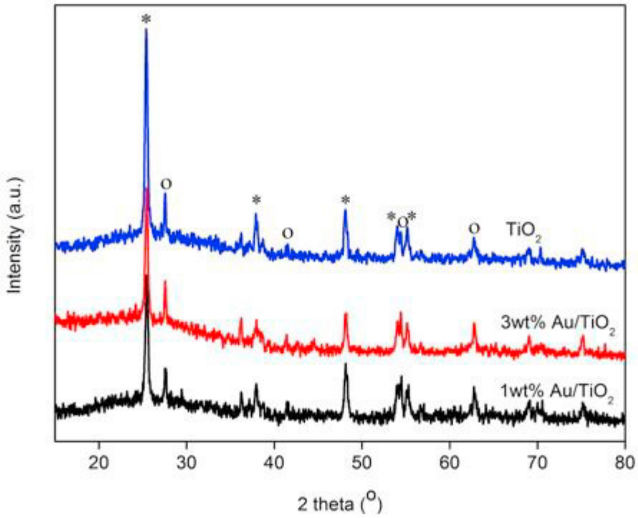

Figure 2. XRD pattern of pure TiO_2 anatase (*) and rutile (o) and Au/TiO_2 samples.

The diffuse reflectance spectra (DRS) of pure TiO_2-P25 and Au/TiO_2 nanoparticles are shown in Fig. 3a. The pure TiO_2-P25 powder showed intense absorption in the UV region (below 400nm). In contrast to pure TiO_2, Au/TiO_2 catalysts (purple colour) exhibited an enhancement absorption in the visible region, particularly between 500-550 nm, which is attributed to the localised surface plasmon resonance (LSPR) of Au nanoparticles supported on TiO_2. Additionally, a higher intensity of LSPR band at 532 nm was observed when Au loading increased from 1 to 3 wt.%. This happens because the surface plasmon resonance wavelength depends on the metal content and particle size of noble metal [11]. The plasmon peak of Au nanoparticles is in resonance with 532 nm laser excitation used in our experiments.

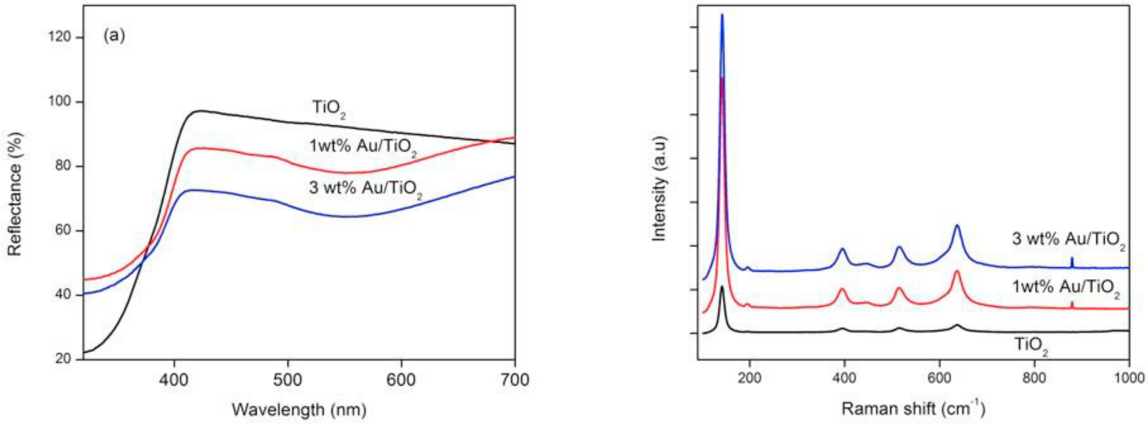

Figure 3. a) Diffuse reflectance spectra and b) Raman spectra of pure TiO2 and Au/TiO2 samples.

Fig. 3b shows the Raman spectra of pure TiO_2-P25 and Au/TiO_2 nanoparticles measured at room temperature under 532 nm laser irradiation. The characteristic bands at 150, 395, 515 and 638 cm^{-1} correspond to anatase phase of TiO_2, whereas a rutile phase peak appears at 445 cm^{-1}. Additionally, a peak at 879 cm^{-1} corresponds to gold nanoparticles. The peak intensity increased with increasing Au loading from 1 to 3 wt.%.

3.2 Plasmonic heating effect

An experimental investigation of the effect of localized plasmonic heat generated by Au NPs was performed under 532 nm laser excitation. Fig. 4a shows the recorded temperature profile of the different nanofluids under 532 nm laser irradiation. The temperatures between different thermocouples were almost the same. For pure milli-Q water, the temperature increase was ~0.9 ºC over 60 min of visible irradiation. A logarithmic increase in temperature of Au nanofluid under laser irradiation, reaching a steady state after 20 min is shown in Fig. 4a. The temperature of Au/TiO_2 nanofluid was significantly higher compared to pure TiO_2 nanofluid (22.5 ºC), indicating a higher optical absorption of the nanoparticles. Additionally, it is worth mentioning that the temperature reached up to 28.5 ºC when 3 wt.% Au/TiO_2 nanofluid was used instead of 1 wt.% Au/TiO_2. This result confirmed that the presence of plasmonic nanoparticles in water enhanced the light absorption and thus the photo-thermal conversion. The novel aspect of this process is that the directionality and high intensity of laser light allows rapid localized heating on micro or nanoscale.

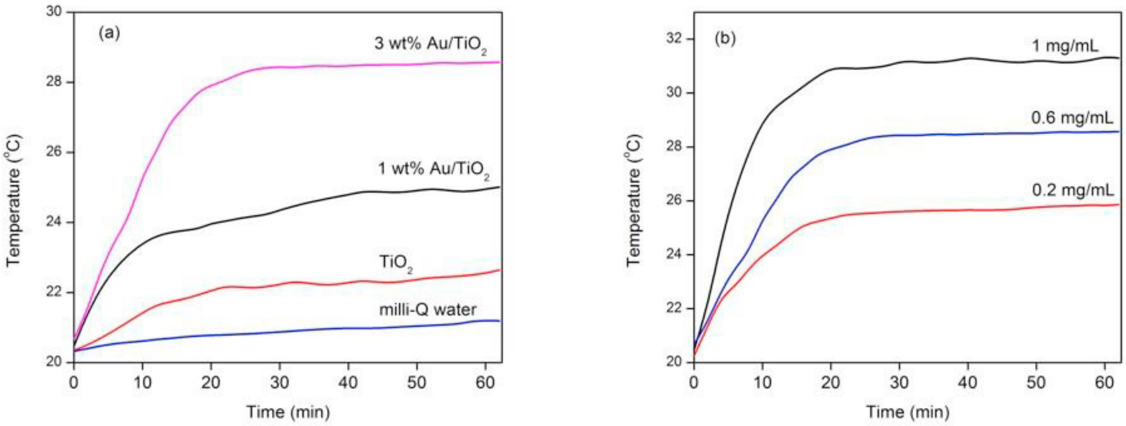

Figure 4. a) Temperatures of different nanofluids as a function of time (0.6 mg/mL) and b) temperatures of 3 wt.% Au/TiO_2 nanofluids with different concentrations as a function of time.

Further investigation on the effect of concentration of Au/TiO_2 NPs was carried out. 3 wt.% Au/TiO_2 nanofluids with different amount of catalyst were prepared and tested under the same conditions as described above. As it can be seen in Fig. 4b, the temperature increased significantly with the increase of Au NPs concentration. Among the tested nanofluids the sample with higher concentration (1 mg/mL) exhibited the highest temperature up to 31 ºC in 20 min of laser excitation after which an equilibrium state was reached. This was due to the fact that when the concentration of Au/TiO_2 NPs increased, the amount of suspended nanoparticles in milli-Q water was higher, so more light was confined in the nanofluid, resulting a higher temperature.

4. Conclusions

In summary, the localized plasmonic heating effect of different plasmonic nanofluids including Au/TiO_2 with different Au loadings, pure TiO_2 and pure milli-Q water were tested under 532 nm laser irradiation. A significant increase in the temperature of Au/TiO_2 nanofluid by ~8 ºC was recorded compared to bare TiO_2, which was just ~2 ºC. The temperature difference was attributed to the remarkable light absorption of Au NPs that led to the LSPR effect on their surface. Additionally, the effect of concentration of Au/TiO_2 catalyst was investigated and the results showed that the temperature of the fluid increased up to 31 ºC with higher concentration of catalyst due to the enhanced absorption at higher volume fraction. The results indicated that localized heating of plasmonic metal NPs under visible laser irradiation has potential applications in effective photothermal and photocatalytic processes.

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