

One dimensional efficient photocatalyst based on plasmonic grating

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Abstract

We can summarize the benefits of the water photocatalysis by two words: clean energy and purification of pollutants, and its problems as the large energy gap and electron-hole recombination. Scientists are still looking for a semiconductor whose energy gap lies in the visible region, with electron-hole pairs of longer life time. One of the proposed solutions in this field is combining the available semiconductors (such as TiO_2) with a metal of plasmonic properties. The existing of the plasmonic metal will ensure that the visible portion of the solar region will involve in the photocatalysis action. It will be absorbed by the plasmonic metal, be transformed into a local energy that leads to excitation processes in the semiconductor. Also, the existing of the metal will guarantee a longer life time for the electron-hole pairs generated in the semiconductor, as the metal acts as a sink for the electrons generated in the semiconductor. In this paper, we created a unique photocatalyst based on one dimensional grating coated by gold thin film and covered by TiO_2 cap layer. By examining the sample with visible radiation, we obtained a rate of degradation of 25 percent within three hours.

I. Introduction

Since the discovery of photocatalysis of water by Fujishima and Honda in 1979 [1], scientists move towards the investing of solar energy to obtain the hydrogen gas, which has wide applications in the field of clean energy and fuel in addition of basic chemical industries such as ammonia [1–3]. Now days, semiconductor photocatalysis have entered into very important applications like water treatment, removing of trace metals, water splitting, self-cleaning, antifogging, Antibacterial and cancer treatment and self-sterilization [3, 4]. The importance of photocatalysis processes is laying under that it is a cheap process comparing with other oxidation processes [4]. The process of photocatalysis of water itself leads to the disassociation of biological and chemical pollutants in the water, as the generation of strong oxidizer OH^- will lead to the disassociation of the most prevalent chemical dyes in water such as methylene blue and methylene orange and others [3–5]. The quality of catalysts has the first effect on the efficiency of the process of photocatalysis, where several factors is determining the efficiency of the photocatalyst, including the extension of its energy gap within the visible range of UV and solar radiation, cost efficiency, non-toxic, resistant to corrosion [3, 6].

The TiO_2 has been an ideal semiconductor for the photocatalysis action according to its efficiency in photocatalysis interactions, high stable, non-toxic and available [4, 7]. In addition of that, the high oxidation power of TiO_2 [4] makes it suitable for the degradation of organic and inorganic compositions [4, 7]. TiO_2 is both interstice and n-type semiconductor (inadvertently anesthetized), due to oxygen vacancies in the TiO_2 lattice [4, 8]. By a certain energy of light, jumping the electron between valence band (VB) and the conduction band (CB) and stay the holes in VB, yield to the reduction (form a superoxide radical O_2^- with H^+ and dissolved O_2 in the aqueous solution) and the oxidation (oxidize OH^- to produce hydroxyl radicals OH^\cdot) reactions [3–5, 9, 10].

The using of the photocatalyst as a powder has its benefits and disadvantages, the powder has high specific area, high quantum yield and efficient photocatalytic activity, in spite of these benefits, the TiO₂ powder is of hard recycling and expensive treatment [11]. By using the depositing TiO₂ films, large mechanical strength substrates must be used with high physical or chemical bonds between the film and substrate body [11].

In spite of all above mentioned benefits, there is main important problem to use TiO₂ as a photocatalyst working with visible sunlight which is explained as its band gap at the beginning of the ultraviolet part of solar spectrum (3.2 eV for anatase) [4–6, 12, 13]. There is an additional problem, the rapid recombination rate of the photo-generated electron-hole pairs, which lowering the photocatalytic efficiency [12, 13].

To solve above bottleneck, Multiple solutions have been proposed such as its combination with other semiconductors (co-catalyst) [4, 13], adding impurities [4, 6] alloying [4] or metallic substances to use amplification due to plasmonic of that metallic ones.

This new field in the photocatalysis named as plasmonic indicates the coherent collective oscillation of free electrons in metal nanoparticles in response to an external oscillating electric field, such as solar radiation in the case of photocatalysis [14, 15]. Here, photo-generated electrons have higher negative potential than the CB of the semiconductor, thus causing electron transfer from excited metal to the CB of the semiconductor [4, 14, 15]. Photocatalytically, the nanoparticles of noble metals can act as active sites to capture the photo-generated electrons and reduce the recombination rate, in addition of that, the plasmonic nanoparticles can be employed to increase the absorption of visible light because of their photo-activity in the visible range [16, 17].

As explained in the above paragraph, due to those efficient properties, among the most prominent proposed modern solutions is the use of the plasmonic properties of noble metals to absorb visible rays and convert it as electrons or excitation energy to the semiconductor.

When the metals are doped on semiconductors it would enhance the activity of photocatalyst by formation Schottky barrier in the interface between the metal and the semiconductor [15, 16]. The property of the metal as a sink of electrons and the drifting of the electrons generated in the semiconductor towards the positive metal will increase the life time of the electron-hole pair, which provides more time for the electron to travel to the surface of semiconductor and participate in the interaction [16–18]. Among the noble metals, gold is distinguished by its resistance to oxidation and its activity within visible light, which makes it a good candidate to work with TiO₂ [18–19]

All of above mentioned papers work onto the effect of LSP onto the photocatalyst; we want to exam the propagative surface plasmon resonance to use in the portable and solid samples. Thus we create a unique photocatalyst consists of one dimensional plasmonic grating piece over lied by a thin film of gold and a thin layer of TiO₂ on top of it, this will overcome the problem of disusing of the visible light and will increase the efficiency of our TiO₂ catalyst.

II. Experimental Part

We made our plasmonic photocatalyst by using an optical disc, DVD, to get grating coupled plasmon resonances. DVD consists thick layers that protect the recording layer, the inner surface was exposed first by mechanically cutting a notch into the side of the disc and then by applying mechanical force to peel the two sides apart. The initial cut provides a location for separation, which can be initiated from the side by a sharp cutter. After peeling off the top surface, the DVD was cut into four rectangles by scissors then its color was removed by washing it with once by methanol then twice by distilled water (Fig. 1(a to k)). Layers compositions and structural parameters were extracted by scanning electron microscopy (SEM) and also energy dispersive x-ray (EDX) analysis.

The second step is the coating of the Au over the residual clean piece of DVD as a plasmonic layer. An Au thin film was deposited on the DVD substrate by evaporation method, the thickness of the layer was 25 nm. The TiO₂ layer was deposited over Au by spin coating (4000 rpm), the thickness of TiO₂ layer was 200-250 nm. We also prepared another sample of just DVD and TiO₂ comparison. Rhodamine-B of 10 ppm was prepared by adding 2.5 mg of rhodamine-B powder in 250 ml of distilled water then we use 10 ml of it for the test.

As shown in Figures (1L, m and n), the sample was putted with rhodamine-B in the tube test with nearly 30° angle, to make more opportunity to generate the SPR. The test tube then putted between two simulated sun light sources under room temperature (~25 °C). There was an air stream applied on the rhodamine-B solution, the presence of dissolved oxygen is extremely important during photocatalytic degradation as it can make the recombination process on TiO₂ difficult which results in maintaining the electro neutrality of the TiO₂ particles [20].

The absorption spectrum of rhodamine-B was tested every 30 minutes to calculate the degradation rate from the maximum absorption value. The degradation rate of a solution is obtaining usually by comparing the initial and final (after photocatalysis) concentrations by using the law:

$$Deg. = \frac{C_0 - C}{C_0} \% \quad (1)$$

Where C₀ and C is the concentration before and after the photocatalysis process respectively; but it can be calculated also by using the maximum absorption value of the initial and final concentrations:

$$Deg. = \frac{C_0 - C}{C_0} \% \approx \frac{A_0 - A}{A_0} \% \quad (2)$$

Where A_0 and A is the absorption before and after the photocatalysis process respectively. The test was done after three hours by getting UV-Vis spectrum every half hour.

iii. Results And Discussion

To ensure and show the metallic surface and the periodicity in the grating, Scanning electron microscopy (SEM) images were obtained by using Hitachi SU3500 Scanning Electron Microscope (Figs. 2a and b). These pictures approve 650 nm periodicity and thus availability to excite surface plasmon resonance in the visible region.

The sample of 1D grating-TiO₂ was tested firstly under EDX evaluation to ensure TiO₂ layer coated on the grating surface as shown in Fig. 2(c). The effect of irradiation time on photo-degradation of rhodamine-B with 1D Grating-Au-TiO₂ sample examined for three hours. Every thirty minutes we get the UV-Vis spectrum of rhodamine-B solution and the maximum absorption values and the degradation rates for 0, 0.5, 1, 1.5, 2, 2.5 and 3 hours. After 3 hours we get a degradation rate of about 25% as shown in Fig. 2(d).

The ability of degradation of Au-TiO₂ sample can be related to the plasmon resonance energy transfer (PRET) mechanism which consider the intense oscillating electric field about the metal [16]. According to PRET, the power is transferred from plasmon to absorbent (semiconductor) across electric field. The light also illuminates the metal and the electricity the field will be created around the metal and this electric field it will enhance the rate of formation of electrons and holes. The existence of gold is also supported the separation life-time of the generated electron-hole pairs in TiO₂ due to the formation of Schottky barrier (the metal will be act as an electrons sink); this will also enhance the photocatalytic activity of TiO₂. The mechanism of the photocatalytic process under visible light of the 1D Grating-Au-TiO₂ photocatalyst can be resumed as reported in Fig. 3.

In this structure, the plasmonic structure as one dimensional grating plays main role instead of thin metallic film in which the diffraction of grating helps us to excite the plasmon. This method doesn't use total reflection and thus the limitation of the incidence angle and the detection range are solved. This gold layer instead of the excitation of plasmon and enhance the visible activity of the TiO₂ grating layer, yields to the more separation of electron and hole based on Schottky junction.

In addition, due to the grating form of Au and also TiO₂ layer, we can decrease more times the electron – hole recombination of the photo-generated charges at the Au – TiO₂ interface specially in the valley region of grating.

This prevention yields to the presence of more electrons in the TiO₂ CB and thus enhance the rate of production for O₂⁻ and OH radicals and finally more photo-degradation activity. The photocatalytic degradation of rhodamine-B in our measurement setup can occur through both oxidation and reduction processes involving photo-generated electron and hole pairs and also electro activity of rhodamine-B.

IV. Conclusion

We prepared our plasmonic photocatalyst by depositing Au then film on cleaned extracted DVD as a grating, then we deposited a TiO₂ layer on the Au. The photocatalysis activity was tested over rhodamine-B dye. By using simulated sun light source, we get a degradation rate of about 25% after 3 hours, where there was no any activity of DVD- TiO₂ sample for the same conditions. We attributed the photocatalytic activity of DVD-Au- TiO₂ sample under visible light to the plasmon resonance energy transfer mechanism which can excite the TiO₂ to generate e-h pairs and start the reaction. The formation of Schottky junction is also enhanced the photocatalysis activity of TiO₂ by extent the life time of e-h pairs.

Declarations

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Figures

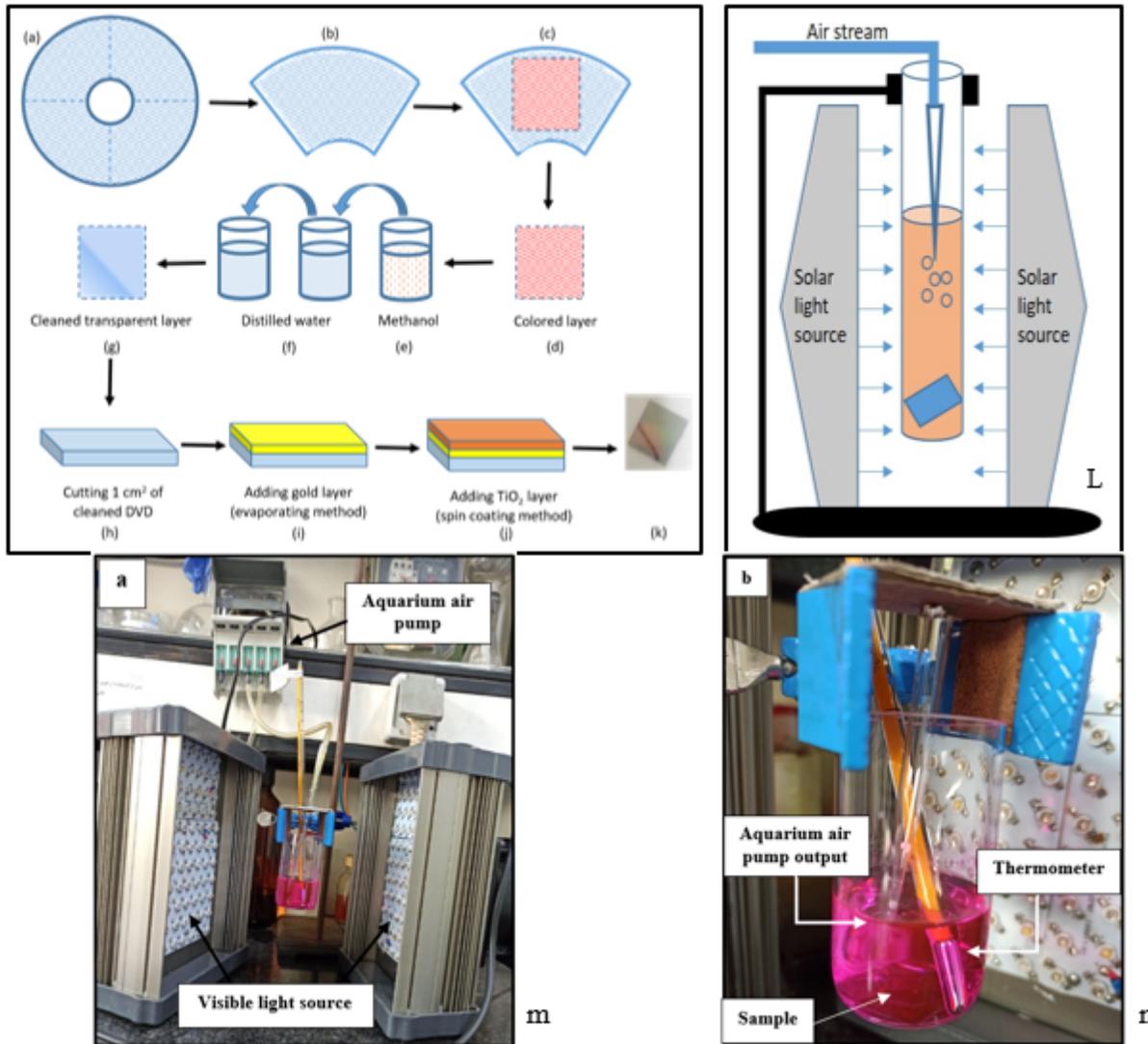


Figure 1

Preparation steps of the sample. (a, b) DVD divided into 4 quadrants, (c, d) cutting a regular shape, (e, f, g) washing the DVD by methanol and distilled water and the result, (g) 1 cm² of the washed DVD, (i, j) adding Au thin film and TiO₂ layer, (k) the final sample, (l) photocatalyst experimental setup, (m) real picture of the whole setup (visible light source, air-pump, quartz test tube with contents) and (n) the contents of the test tube (rhodamine-B, thermometer, out-put of air-pump, 1D grating/ Au/TiO₂ sample).

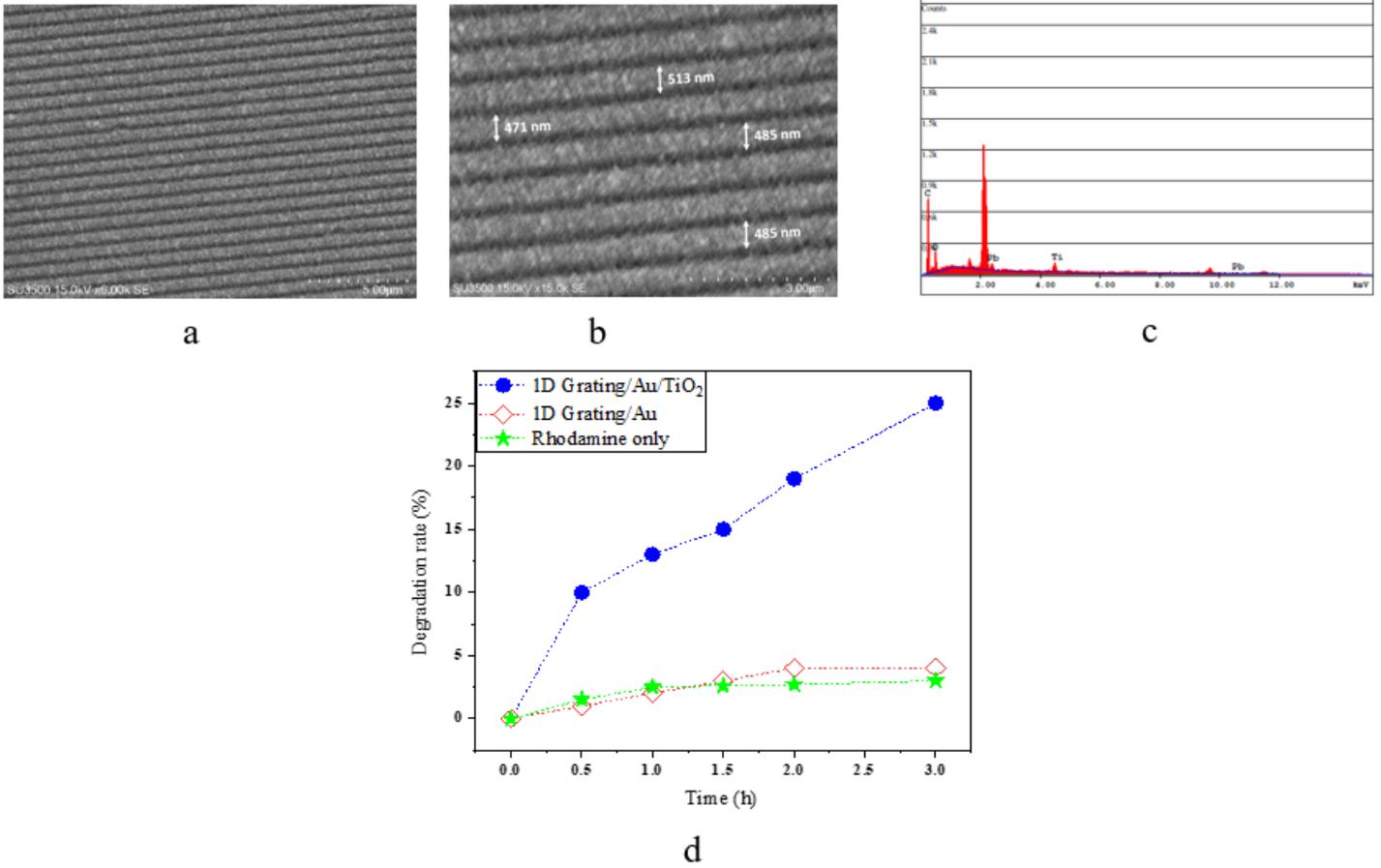


Figure 2

(a and b) SEM image of prepared sample 1D grating/Au/TiO₂, (c) EDX diagram of the sample, (d) the degradation time of the main sample with 1D grating/Au and Rhodamine only.

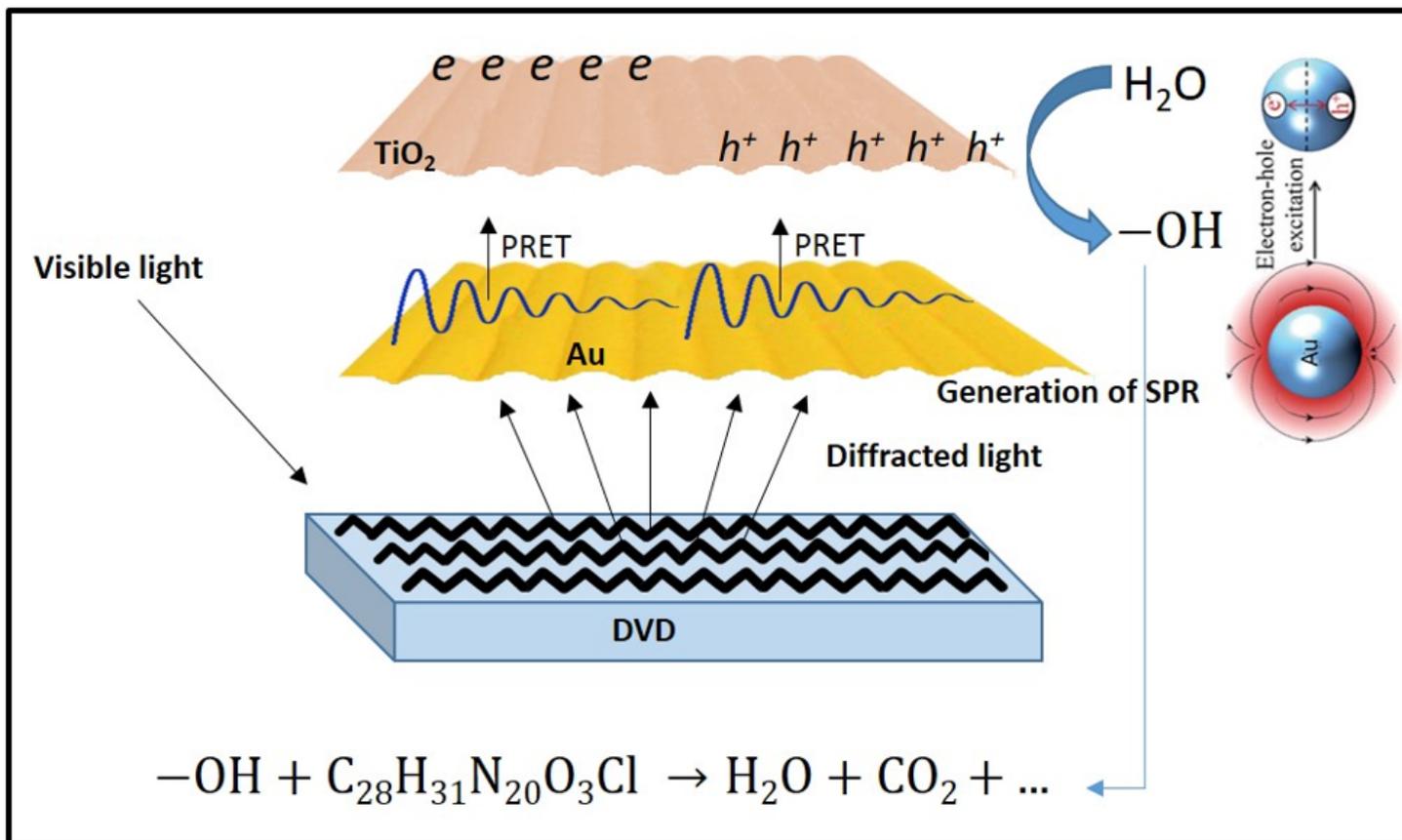


Figure 3

PRET mechanism in 1D Grating-Au-TiO₂ photocatalyst and the chemical reaction