SDS coated Gold Nanocatalyst for Degradation of Methylene Blue

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***Abstract*—**Gold nanoparticles have been synthesized using chloroauric acid and sodium dodecyl sulfate (SDS) as the surfactant in water. These nanoparticles are analyzed using UV–vis spectroscopic, Transmission electron microscopy and Dynamic light scattering technique. It is spherical in shape, having a size of 50-280 nm. The result shows that SDS coated gold nanocatalyst is highly active in the degradation of methylene blue (10 mg/L) in sunlight (~75%) for 4.0 h.

***Keywords*—**Gold nanoparticles, SDS, TEM, Photedegradation, DLS, Methylene Blue

I. Introduction

OVER the last 20 years, fabrication of different shapes and sizes of gold nanoparticles (GNPs) has drawn considerable attention in the field of nanotechnology, due to their vast range of applications. Many methodologies have been used to date, including physical, chemical, and biological processes. However, most are not ecofriendly due to high capital costs and the use of toxic chemicals. The advantages of GNPs are the ease of preparation of monodisperse NPs [1], low toxicity [2], intense plasmon resonance in the visible range [3], trigger the drug release at a remote place [4], [5] and catalytic capability of AuNPs in redox reactions like CO oxidation [6], hydrogenation of various compounds [7], [8] and oxygen-transfer reactions near ambient temperature [9] has been reported.

SDS microemulsion system was widely used in the past to prepare metal nanoparticles, e.g., Cu–Ni alloy [10], Pd [11], Ag [12], [13], etc. However, some examples for preparation of silver nanoparticles in SDS microemulsion carried out under γ irradiation [12]. It is relatively less that the silver particles are synthesized by chemical reduction of silver ions in SDS microemulsion [13]. In the process of preparation of gold nanoparticles (AuNps) by chemical method, use of sodium dodecyl sulphate (SDS) as an encapsulating agent is not many in literature [14]. In this present communication we are going to report the synthesis of gold nanoparticle through reduction of Au^{3+} by SDS as reducing and stabilizing agent. The self-assembly of AuNPs formation mechanism is not completely clear.and this nanoparticles were used as catalyst for remediation of methylene blue (MB) in the presence of direct sunlight.

MB is a heterocyclic aromatic, chemical compound with the molecular formula $C_6H_{18}N_3SCl$. This thiazine dye appears as a solid, odorless, dark green powder in room temperature and gives a blue solution in aqueous medium [15]. It is used in the analysis of trace levels of sulfide ions in aquatic samples [16]. The reduction of MB to leuco MB and its reoxidation have found applications in textile industry, analytical chemistry, electro optic devices, oxygen detecting and time monitoring [17].

II. Materials and methods

A. Materials and Synthesis of AuNPs

All chemicals were of analytical grade and used without any purification. Sodium dodecyl sulfate (SDS, >99.0%), $HAuCl_4$ and methylene blue (MB, 99.5 %) were purchased from the Spectrum (USA). Millipore Milli-Q water was used in all experiments. Nanoparticles of gold were prepared using the 0.01mM $AuCl_4^-$ (aq) solution. In a typical preparation, 10 mg of SDS was added in 10 mL of 0.01mM $AuCl_4^-$ at room temperature. After the completion of 12 h of the reaction, the color changed in to light pink color and proof for the formation of AuNps. U.V.–vis spectra were measured using spectrophotometer (Thermo Spectronic, GENESYS^{TM} 8, England, Quartz Cell, path length 10 mm and Graph Plotted on Origin 6.1 program). The particle size distributions of nanoparticles were determined using the HORIBA, Dynamic Light Scattering (DLS) Version LB-550 program. Size and selective area electron diffraction (SAED) pattern of nanoparticles are studied on transmission electron microscopy, TEM (FEI, TECNAI, G2 spirit twin, Holland). A thin film of the sample was prepared on a carbon-coated copper grid by dropping a very small amount of the sample on the grid.

B. Decomposition of MB study

Four separate sets of experiments were performed for study the decomposition of MB in direct sunlight (Table I). In set 1, 5 mL MB (10 mg/L) kept in a vial in direct sunlight. In set 2, 3 and 4, the synthesized Au nanocatalysts were used; 5 mL MB and 100-500 µL Au nanoparticle were mixed and kept in sunlight. All four sets of reaction were observed after 0.5, 2.0, 4.0 and 8.0 hrs. The rate of MB dye decomposition was monitored by taking 4 mL samples from each set and recording the absorbance measurements at the wavelength of maximum absorption of MB (664 nm) before and after degradation.

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TABLE I
PHOTODEGRADATION OF METHYLENE BLUE (MB) UNDER DIFFERENT CONDITION USING AUNPS

MB (10 mg/L),5 mL	**AuNps** (catalyst)	**% Degradation**			
		0.5 h	2.0 h	4.0 h	8.0 h
I	-	-	-	-	-
II	100 µL	29.1	42.9	48.9	58.4
III	300 µL	36.0	50.3	58.2	63.7
IV	500 µL	64.8	71.4	74.8	75.3

III. RESULTS AND DISCUSSION

A. Visual Study

Fig. 1 shows the visual change of gold ion before and after treatment of SDS (24 days).

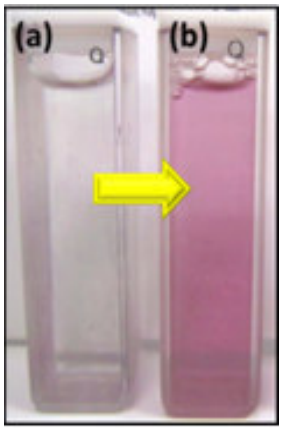

Fig. 1 Visual study of (a) 0.01 mM $AuCl_4^-$ solution and (b) AuNps after 24 days

B. U.V.-vis Study

Fig. 2 shows the U.V.-vis absorption spectra for AuNPs between 350 and 800 nm. Absorption spectra of AuNP synthesized from of 0.01 mM $AuCl_4^-$ in presence of SDS at different time intervals. As the time progresses, position of gold SPR band shifted to the red. It is also observed that the intensity of SPR band (λ_{max}~545–550 nm) increases, reaches a maxima with time. After 7 days, intensity of SPR band increases and absorption shifted 545 to 550 nm, modified Mie's theory which clearly suggests an increase size of AuNPs [18].

It is hypothesized that the formation of AuNPs under light exposure is initiate with the formation of gold dodecyl sulphate (DS) in solution. The gold dodecyl sulphate absorbs a photon and dissociates into metallic gold and a DS free radical. The DS free radical rearranges the S-O bonding and S-O-C bonding of the $-SO_4$ of the SD molecule, therefore making the radical stable. It is clear that the formation of Au nanocatalyst, which was synthesized by using SDS [19]. Thus, UV–vis spectroscopy is a suitable method and an important means for monitoring the nucleation and the formation of AuNPs.

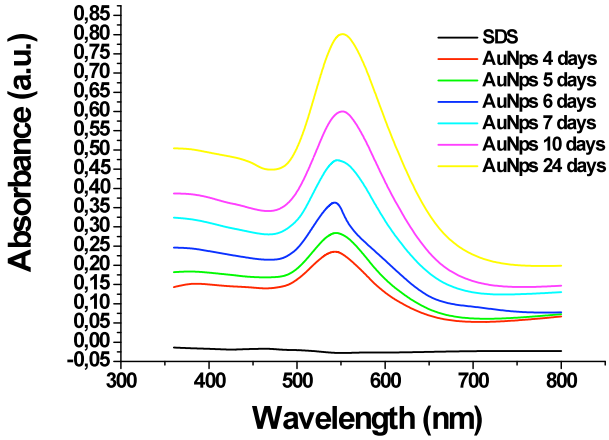

Fig. 2 U.V.-vis pattern of Au nanocatalyst at different time interval

C. TEM and SAED Study

A typical TEM micrograph has taken after 24 days is presented in Fig. 3 illustrate a number of aggregates AuNPs as well as individual. The measurement of size was performed along the largest diameter of the particles. The SAED pattern of AuNP reveals its crystalline nature. It is also believed that SDS micelles are self-assembled into distorted spherical-like aggregations. The particles are found spherical in shape and the average diameter of the particle is found to be about 50-280 nm respectively.

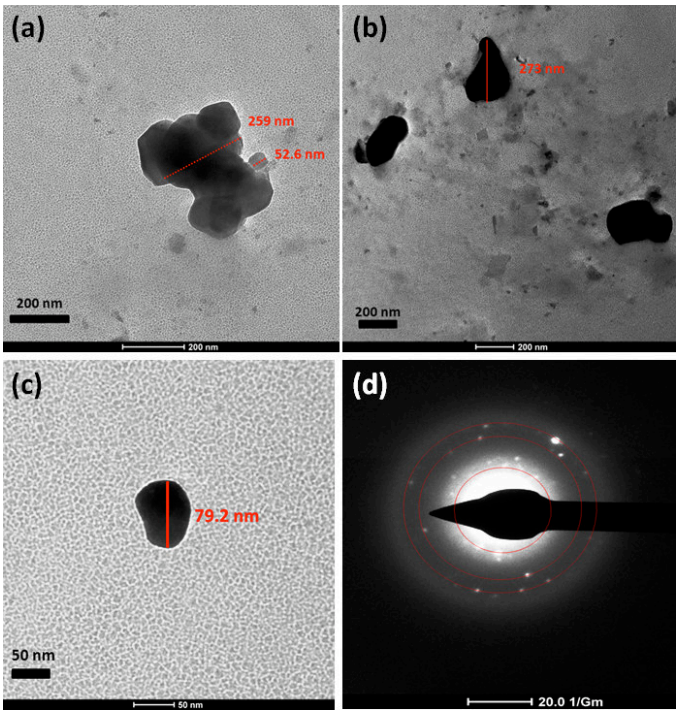

Fig. 3 (a)-(c) TEM image of Au nanocatalyst and (d) SAED pattern

D. DLS analysis

The DLS size distribution image of Au nanocatalyst at time (a) 4, (b) 10 and (c) 24 days is shown in Fig. 4. From the results (4a), the calculated mean particle size distribution of AuNps is 0.0707 µm and the standard deviation (S.D.) is 0.1064 µm for 4 days, the red mark shown near to 0.500-1.000 µm suggests the reaction is incomplete. The average diameters of the as-synthesized gold nanoparticles are 0.0532 µm (Fig. 4b) for 10 days and 0.0453µm (Fig. 4c) for 24 days explains higher stability.

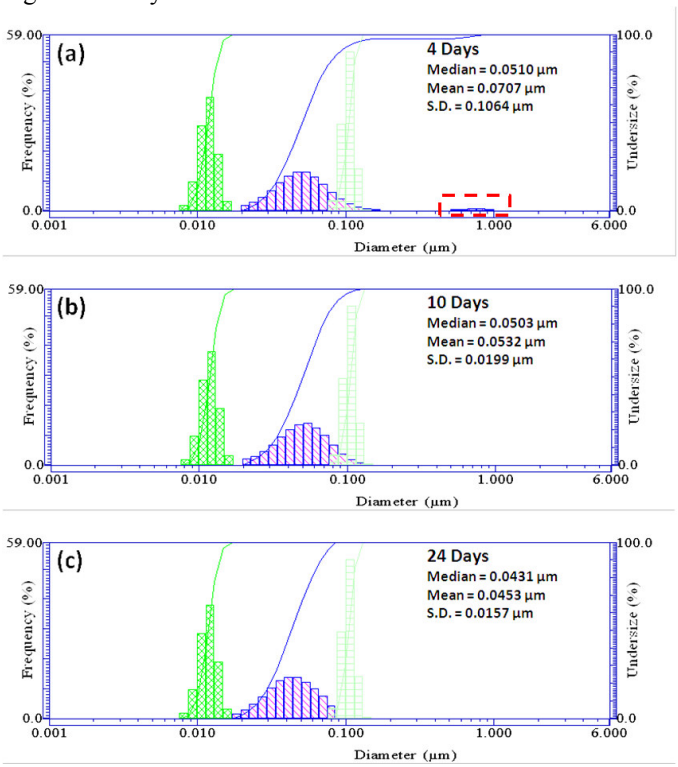

Fig. 4 DLS pattern of the prepared Au photcatalysts at time (a) 4 days, (b) 10 days and (c) 24 days

E. Photocatalytic activity

The activity of the AuNPs as catalyst evaluated for the degradation of MB (10 mg/ L, 5 mL) under direct sunlight and visible light for 2.0 h. Degradation of MB was found satisfactory only under direct sunlight (T = 28-32°C). The reaction parameters were varied to get best results as mentioned in Table I. Fig. 5 shows the visual detection for 8 h and Fig. 6 shows the progression of the MB decomposition for the four different concentration of Au nanocatalyst at 0.5, 2.0, 4.0 and 8.0 h in direct sunlight.

The average decomposition in terms of the percentage of MB in solution was calculated using the following equation:

$$\eta = [A_o - A_t / A_o] \times 100\ \%$$

where η is the rate of decomposition of MO in terms of percentage, A_o is the initial absorbance of MO solution and A_t is the absorbance of the dyes at time t [20]. Initally, there is no degradation of MB (10 mg/ L) observed without use of nanocatalyst (MB 1). The photodegradation capacity increases with an increase in the amount of Au nanocatalyst (100-500 µL).

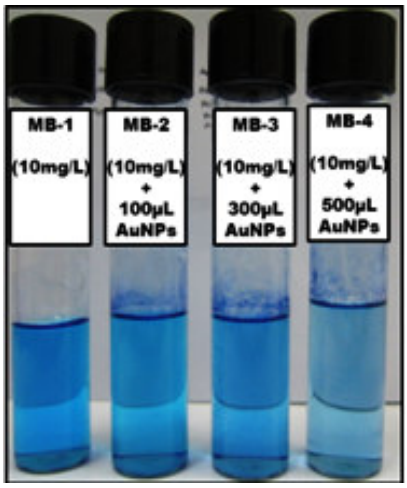

Fig. 5 Visual detection of methylene blue degradation using Au nanocatalyst in sunlight at 8h

Fig. 6 explains that the initial degradation of MB 2, MB 3 is 29.1 %, 36.0% for 0.5 h, when the amount of Au nanocatalyst is 100 µL and 300 µL. MB 4 attains maximum at a catalyst dosage of 500 µL, 64.5% for 0.5 h. It clearly indicates that, MB 4 decomposition increases more than 60% for first half hour on increasing catalyst amount 500 µL. The catalyst amount of 100 µL showed 58.4, whereas 300 µL showed 63.7 % degradation of the MB at 8 h.

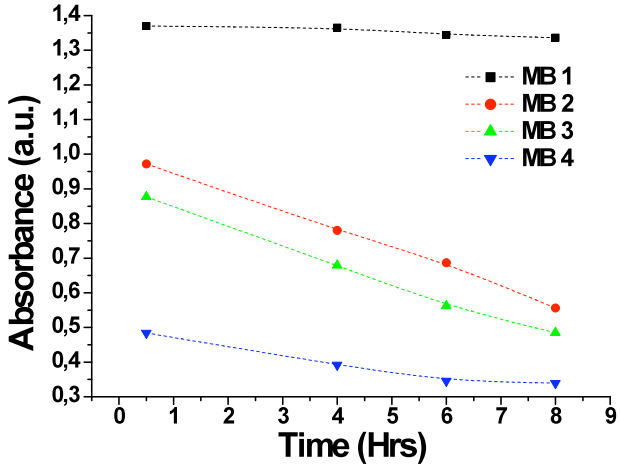

Fig. 6 Degradation of methylene blue using Au nanocatalyst in sunlight at time (a) 0.5 h, (b) 4 h, (c) 6.0 h and (d) 8 h

Fig. 7 explains the U.V.-vis degradation pattern of MB 4 using 500 µL Au nanocatalyst in sunlight at different time interval. The degradation activity of MB is increased and saturated to 74.8 % for 4 h and 75.3 % for 8.0 h. There is no change in shape or position of the absorption bands of MB other than decrease in intensity as a function of time which augur MB is reduced without any side reactions [21]. The degradation of MB was attributed to the higher surface area of nanocatlyst. In the valence band (VB), the holes interact with

water molecules, resulting in the formation of hydroxyl radical (·OH) and proton. We hypothesized that AuNPs act as an electron transfer mediator between the proton and MB by acting as a redox catalyst via electron relay effect. These protons are responsible for the degradation of dye molecules.

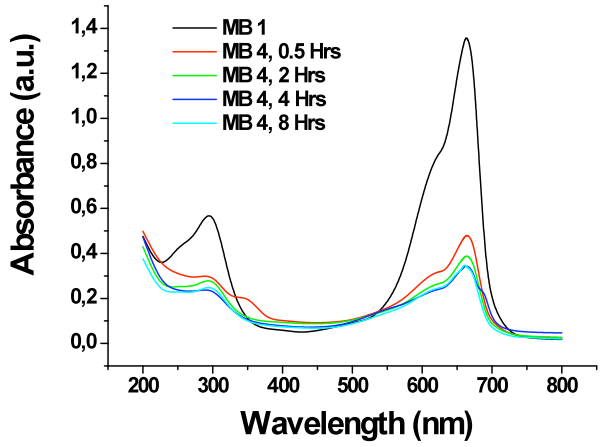

Fig. 7 U.V.-vis degradation pattern of MB 4 different time interval

IV. Conclusion

The present study shows the SDS coated Au nanocatalyst as an effective reducing agent. Sodium dodecyl sulfate (SDS) is used as encapsulating agent. It is also believed that SDS micelles are self-assembled into distorted spherical-like aggregations in the formation of AuNPs. The formed Au nanocatalyst are highly stable and exhibited more than 75 % degradation of MB in sunlight for 4.0 h.

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