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Synthesis and characterization of silver sulfide nanoparticles for photocatalytic and antimicrobial applications

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ABSTRACT

The study describes a simple and novel method for the synthesis of silver sulfide nanoparticles (Ag_2S NPs). The synthesized NPs were characterized by SEM (scanning electron microscope), XRD (X-ray diffraction), particle size analyzer, zeta sizer and EDX (Energy dispersive X-ray). The Ag_2S NPs were spherical in shape with an effective diameter size of 30 nm. The synthesized particles possess photocatalytic activity under visible light and exhibited excellent antimicrobial effect. The photocatalytic property of Ag_2S NPs was also evaluated by the degradation of methylene blue dye under visible light. NPs degraded 87% of methylene blue with in 1 h at pH 8. The NPs of 0.1 μg/mL showed a growth inhibition of more than 75% against *S. aureus* (ATCC 25923), *E. coli* (ATCC 13534), and *E. coli* (ATCC 25922).

1. Introduction

Due to wide variety of potential application in optoelectronic and biological field, nanotechnology is currently an intense area of scientific research. Past few years, the study of semiconductor nanoparticles has been attracted much attention because of their novel optical and electronic properties [1]. Nanoparticles (NPs) such as CdS, CdSe and PbS have narrow band gap semiconductor quantum dots which are used as photocatalyst in last few years. Among the all, silver sulfide (Ag_2S) NPs is an important material as photocatalyst. Ag_2S is a direct, narrow-band gap semiconductor with good chemical stability and good optical limiting properties [2,3]. This NP is solid ionic conductor conducting both ions and electrons at room temperature [4]. Ag_2S has a direct band gap of 0.9–1.05 eV, and large absorption coefficient which shows an effective semiconductor material for photovoltaic application [2]. The unique properties of Ag_2S NPs led to variety of application such as in solar cells, photo-detectors, light emitting diodes and switches, photoconductors, IR detectors, magnetic field sensors, optical filters, super-ionic conductors, solar-selective coatings and room temperature oxygen sensors [1,3,5,6]. Hence, the present study we utilized the photocatalytic ability of Ag_2S NPs for the treatment of textile dye.

The textile and food processing industries released large amounts of dye bearing effluents into the nearby water bodies, since the current methodologies are not capable for the efficient of dye stuffs in the effluents. Due to the higher stability and toxic potential of these dyes, it is inevitable to develop a new treatment methodology to remediate the dyes from the effluents. Photocatalytic process is a photoreaction and it is catalyst dependent reaction because of its ability to create electron–hole pairs and generate free radicals [7]. Many studies have been shown that through light illumination, the heterogenous photocatalysis on a semiconductor surface is an attractive advanced oxidation process. On the semiconductor NPs, the solar spectrum falling are very less i.e. approximately 3–5%, which shows the solar energy utilization by the semiconductor is very limited. Hence it is very necessary to study about new catalysts to enhance the degradation ability.

Ag_2S is an important chalcogenide compound, which has been utilized in various applications, including photoconductors, photovoltaic cells, photosensitive films in optoelectronic devices, solar-selective coatings and infrared detectors [8]. The low band gap energy of Ag_2S makes it an effective semiconductor material for photocatalytic applications due to its high capability of absorbing a broad solar spectrum. However, few studies were reported synthesis of Ag_2S by hydrothermal, sol–gel and solvothermal method [9–11]. Dong et al. [12] synthesized cubic Ag_2S via hydrothermal method by using CTAB as a surfactant. Chin et al. [13] used various stabilizing agent such as hexadecylamine (HDA), octylamine (OA), ethylenediamine (EDA) and dioctylamine (DOA) to synthesize stable Ag_2S NPs. Most of the previous studies in which has a remarkable effect on adjusting the Ag_2S morphology focus on the choice of stabilizers or surfactants, but the reaction condition and process to are complicated. In the present work, Ag_2S NPs were prepared by simple one-step chemical co-precipitation method. This method

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is relatively simple, fast, high yielding and easy to purify the particles. The application of the present study may utilize in dye processing industries or medical application. It was reported that the antimicrobial effect of photocatalytic active particles could be comparatively higher than non-phototocatalytic active particles [14]. Hence the antimicrobial activity of Ag_2S NPs against *Escherichia coli* (ATCC 13534), *E. coli* (ATCC 25922), and *Staphylococcus aureus* (ATCC 25923) was also investigated. So the present study was focused to synthesis renewable, eco-friendly, catalytic active and antimicrobial Ag_2S NPs for possible application in industries and bioremediation.

2. Materials and methods

2.1. Materials

Analytical grade of chemicals includes silver nitrate ($AgNO_3$) and sodium sulfide ($Na_2S{\cdot}H_2O$) and PVP (polyvinyl pyrrolidone) were purchased from Merck (Germany) and Aldrich (USA). Then synthesized Ag_2S was characterized by different instruments includes SEM, XRD, EDX and zeta sizer and particle size analyzer. Lyophilizer was used for drying purpose of NPs.

2.2. Synthesis of Ag_2S NPs

Ag_2S NPs was synthesized by simple chemical co-precipitation method. Silver nitrate was taken as silver source and sodium sulfide for sulfide source respectively. Briefly, 50 mL of sodium sulfide solution (0.001 M) was added drop by drop to 50 mL of silver nitrate solution (0.001 M) at 80° temperature. There after the mixture temperature was brought down to room temperature. PVP solution (20 times higher the amount of Ag) was added to the above mixture, once it attained 60 °C. Then solutions were stirred under magnetic stirrer for 3 h until it reaches light brown color with black precipitates on the surface. Further these solutions were centrifuged at 10,000*g* for 30 min. Then obtained pellet were subjected to lyophilization.

2.3. Characterization of Ag_2S NPs

The optical property of NPs was tested by using UV–visible spectrophotometer (Perkin Elmer, USA). The surface state, morphology and structure of Ag_2S NPs was determined using transmission electron microscope (TEM, Tecnai G-20) and field emission scanning electron microscope (JEOL JSM-6701F, Japan). The surface area was measured using a Smart Sorb 93 Single point BET surface area analyzer (Smart Instruments Co., Pvt., Ltd., Mumbai, India). The lyophilized NPs powder was coated in XRD grid and the spectrum was recorded using Bruker (D8 Focus) diffractometer operated at voltage of 40 kV using Cu Kα radiation. Energy dispersive X-ray (EDX) spectroscopy was used to for the elemental analysis of NPs. The particle size was measured using a particle size analyzer (Microtrac Blue Ware, Nikkiso, Japan). The zeta potential was measured using Malvern (UK) zeta analyzer. Further, the stability of the synthesized particles was evaluated by measuring the size and zeta potential of the particles up to 30 days under static condition.

2.4. Adsorption of dyes

Adsorption studies were carried out by interacting 5 mg of NPs with an initial concentration of 250 mg/L dye for an hour under dark condition. At various time intervals the interaction mixture was centrifuge at 10,000*g* for 20 min. The supernatant were collected and amount of dye left in supernatant was determined by visible spectrophotometer by measuring absorbance at 665 nm. The amount of adsorption was calculated at time t, q_t (mg/mg) by following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 (mg/L) is the initial dye concentration, C_t (mg/L) is the amount of dye left at time t, q_t is the amount of dye adsorbed at equilibrium at time t, V is the volume of solution in L and W (mg) is weight of NPs used. The effect of pH on adsorption was evaluated at different pH.

2.5. Photocatalytic property of Ag_2S NPs

The photocatalytic activity of Ag_2S NPs was evaluated by measuring the ability of NPs to degrade the dye (methylene blue) under visible light. The dispersed nanoparticles were mixed with methylene blue solution and the solution was exposed to a light source at ambient temperature using a 300 W Xe lamp with a cutoff filter ($k > 420$ nm) for an hour. A small portion of the samples were removed periodically and centrifuged. Thereafter the amount of dye left in the supernatant was determined by measuring the absorbance at 665 nm using UV–visible spectrophotometer. The effect of pH on photocatalytic activity was determined at different pH level. The percentage degradation was calculated by following the equation,

$$\text{Degradation } (\%) = \left(\frac{A_c - A_t}{A_c}\right) \times 100 \tag{2}$$

where A_c is the absorbance of blank (control) (only dye solution exposed to visible light) and A_t is the absorbance of test (dye solution contains NPs exposed to visible light). A blank (dye solution without NPs) test was run parallel to this experiment in order to evaluate the self degradation of methylene blue under visible light. The photocatalytic effect of NPs was calculated by subtracting from self degradation of methylene blue under visible light.

The rate of ·OH formation during photocatalytic degradation under visible light was evaluated by the photoluminescence technique. The excitation wavelength and the scanning speed were adjusted to 332 nm and 1200 nm/min respectively. After visible light irradiation, the solution was filtrated to measure the photoluminescence intensity at 456 nm.

2.6. Antimicrobial effect of Ag_2S NPs

The antibacterial effect of Ag_2S NPs was examined by interacting different concentration of NPs with *E. coli* (ATCC 13534), *E. coli* (ATCC 25922), and *S. aureus* (ATCC 25923) bacterial cells. 10 mL of log phase cultures were centrifuged at 5000*g* for 10 min and the pellet was suspended in sterile saline (0.75 mM NaCl) containing different concentrations of Ag_2S NPs (0.1, 0.5 and 1 μg/mL) and adjusts the cell number to 1×10^8 CFU/mL. After 4 h of interaction, the cultures were plated on nutrient agar plates. The number of colony forming units was examined after 24 h of incubation. The same procedure was adopted in the control experiment (without Ag_2S NPs). Six replicates were kept for each concentration.

3. Results and discussion

3.1. Characterization of Ag_2S NPs

The preliminary characterization of NPs was performed using UV–visible spectrophotometric analysis. The results show that a broad peak in between 450 and 550 nm (Fig. 1a) indicates the presence of Ag_2S NPs. Further, TEM and SEM were used to characterize the micro-surface structures and morphologies of chemically syn-