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Influence of gold core concentration on visible photocatalytic activity of gold–zinc sulfide core–shell nanoparticle

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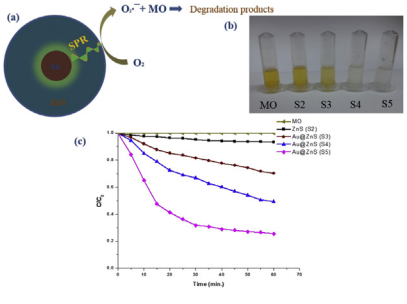
HIGHLIGHTS

- Synthesis of novel Au@ZnS core–shell nanoparticle by chemical precipitation method.
- The Au core enhances the charge separation process and quenches emission of ZnS shell.
- Visible photocatalytic activity enhance with Au core concentration.
- SPR generated photo-current improved with Au core concentration in Au@ZnS nanoparticle.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research work, we have proposed a facile route for synthesis of Au@ZnS core–shell nanocomposite with single or multiple cores. The ZnS nanostructure shows a broad visible photoluminescence that gets quenched with an increase in Au core concentration. The photoconductivity under visible light exhibits a 21 fold increase in photo current density (0.068–1.43 μA) when there is a four-time increase in Au core concentration. The visible photocatalytic activity for the degradation of methyl orange dye is found to be much higher for Au@ZnS nanocomposite with multiple cores. The electrochemical impedance study show that the charge transfer resistance of Au@ZnS thin film gets reduced with an increase in concentration of Au core.

1. Introduction

ZnS is a well-known material for its unique properties, such as wide band gap (3.7 eV), luminescence and photocatalytic activity under UV light irradiation [1–3]. It has been widely investigated for application areas, such as sensors, lasers, light-emitting diodes, field emission devices and coating material [4–8]. However, since ZnS can only absorb UV light and due to its higher recombination rate of electron-hole pairs, its application as a visible light photocatalyst gets restricted. To overcome this limitation, several studies have been reported, such as doping ZnS with metal/non-metal ion, and combination with narrow band gap semiconductors like CdS, CuS, Fe_2O_3, CdTe, CdSe and $CuInS_2$ [9–16]. The photocatalytic performance of ZnS after being modified with novel metals, got enhanced with an improved light harvesting efficiency. The Fermi level gets shifted to more negative potential, resulting in

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prolonging the lifetime of photo generated carriers. Furthermore, in the case of metal-semiconductor core–shell structure, stability in chemical composition is achieved since the shell is able to electrically insulate the metallic core from its surroundings [17]. A very thin shell layer of semiconductor in close proximity to the metal NPs can further enhance the plasmonic features of such structures through coupling of plasmon-excitons. This also controls the charge separation at the interface of metal semiconductor [18,19].

As we know that under UV light absorption the semiconductor materials like ZnO, ZnS and TiO_2 show photocatalytic activity and produce photo generated electrons in the conduction band and holes in the valence band. These photo generated electrons are trapped by O_2 to form superoxide radical ion ($\cdot O^{-2}$), and hole can react with absorbed water to form very reactive hydroxyl radicals, which further react with the absorbed pollutant molecules to produce oxidized species and/or decomposed products. However, these hydroxyl radicals have very short lifetime, so it is very difficult to detect them directly. For the detection of hydroxyl radicals generally probe molecule were introduced in the medium but it takes long time for measurement. Recently, it has been observed that the luminescent test molecules such as terephthalic acid (TA) and coumarin (COU) can react with hydroxyl radicals and produce luminescent compounds [20]. Therefore, these molecules can be used for the detection and quantification of hydroxyl radicals. The hydroxyl radicals have two kinds of forms, one is free in solution and other is surface-bound. The above mentioned PL method primarily detect hydroxyl radicals freely present in solution.

Till date, different synthetic routes for various morphologies have been reported for the synthesis of Au–ZnS NPs. For example, Du and co-workers have reported the growth of Au–ZnS core–shell on ITO thin film-coated glass surface. This was carried out by successive electrodeposition of Au and ZnS in cyclic voltammetry for an enzyme-based electrochemical biosensor [21]. Chen and co-workers have prepared core-satellite ZnS–Au nano-assemblies by employing the hydrothermal method, in which each of the ZnS nanospheres was surrounded by a few Au NPs. It was further used as a photocatalytic material for degradation of cationic dye (TH) under UV light [22]. Bose and co-workers have reported $Au_xZn_yS_{x/2+y}$ class of nanomaterials and have studied their optical and electrical behaviour [23]. In addition, Zhang and co-workers have prepared Au NPs decorated with ZnS nanostructures through hydrothermal approach, followed by a deposition-precipitation method. They have observed photocatalytic hydrogen evolution under a 350 W xenon arc lamp and found that the samples did not exhibit any remarkable activities in the visible light region ($\lambda > 420$ nm) [24]. Geng and co-workers have synthesized Au–ZnS nanocomposites in a fast one-step resign microwave assisted hydrothermal route. They have further studied the optical properties with different Au doping concentrations [25]. Cushing and co-workers have reported that the Au core has the ability of converting the energy of incident photons into localized surface plasmon resonance oscillations and transfer the plasmonic energy to the Cu_2O semiconductor shell by resonant energy transfer (RET). This can generate electron-hole pairs in the Cu_2O semiconductor by dipole–dipole interaction between the plasmonic metal (donor) and semiconductor (acceptor), which greatly enhance the visible-light photocatalytic activity as compared to Cu_2O alone [26]. Xiang and co-workers have prepared Ag–TiO_2 hollow nanocomposite spheres by a template-free chemically-induced self-transformation strategy under microwave-hydrothermal conditions. The photocatalytic activity of the prepared samples was evaluated by photocatalytic decolourization of Rhodamine B in an aqueous medium in the presence of visible-light irradiation [27]. Anpo and co-workers have studied the photocatalytic activity of TiO_2 powder and found that small amounts of Pt can enhance the charge separation of photo generated electron-hole pairs under visible light irradiation. According to our recent observations, Au@ZnO core–shell NPs in visible light irradiance under the effect of surface plasmon resonance (SPR) leads to generation of electrons in Au nanocore that further gets transferred to the conduction band of ZnO shell in order to drive the chemical reaction. This has a direct influence on photo catalytic activity due to its strong absorption between 510 and 530 nm [28]. Chen and co-workers have prepared Au/ZnS core/shell nanostructure with controllable shell thicknesses using a cysteine-assisted hydrothermal method. Further they study the photocatalytic properties of Au/ZnS core/shell nanoparticle toward methanol oxidation and used it as an anode photocatalyst in the half-cell reaction of direct methanol fuel cells [29]. Stefan and co-workers synthesised and characterised the magnetite based Fe_3O_4@ZnS and Fe_3O_4@Au@ZnS core–shell nanoparticles. They have found that the photoluminescence response was enhanced with inserting a gold shell between the magnetite core and ZnS outer shell [30]. Low and co-workers prepared silver–graphene–bismuth tungsten (Ag-G-$B_{i2}WO_6$) nano composite through chemical route. Further they studied the photocatalytic activities of the prepared nanocomposite by the photocatalytic degradation of rhodamine B (RhB) under visible-light irradiation. They found that the photocatalytic activity of Bi_2WO_6 was considerably enhanced by the loading of Ag and grapheme [31]. Praus and co-workers prepared CdS/ZnS core–shell nanostructure using one-pot procedure and they calculated the dispersions transition energies of CdS and ZnS nanostructures from the UV–vis absorption spectra of the CdS@ZnS colloid. The photocatalytic activity of different ZnS shell thickness and a degree of the CdS core coverage of CdS@ZnO core–shell nanoparticle were characterized by the photocatalytic decomposition of Methylene Blue (MB) [32]. Bredol and co-workers prepared carbon/ZnS-based electrocatalysts for ethanol oxidation in complete membrane electrode assemblies. The maximum overall conversion efficiencies they have achieved was up to 25% from fuel cells [33]. Yuan and co-workers synthesised thermally stable poly(triphenylamine)-grafted-silica nanoparticle by surface initiated nitroxide-mediated polymerization method and used it in solid-state dye-sensitized solar cell. They found that by combining silica/polymer nanocomposites with spiro-MeOTAD as hole conductor, the power conversion efficiency was improved because the photocurrent comes from an additional light scattering layer formed by silica/polymer nanocomposites [34].

The literature review reveals that not much work have been reported with variations of either the Au NPs core or ZnS shell or vice versa and its effects on visible photocatalytic activity. The effect of Au core concentration on electrical and optical properties of Au@ZnS core–shell NPs have not been reported so far. Keeping this in view, we have proposed a simple, quick and novel preparation of Au@ZnS nanostructure, which contains different concentrations of Au core using a two-step chemical synthesis method. The growth mechanism of Au@ZnS core–shell nanostructures and the effect of absorption and photoluminescence behaviour with respect to Au concentration have been investigated. The visible photocatalytic activity of ZnS NP, Au@ZnS core–shell nanocomposite with single or multiple Au core concentrations were evaluated by photocatalytic degradation of methyl orange (MO) dye. In addition, visible photo conductivity performance of ZnS and Au@ZnS nanostructures coated thin film have also been studied under visible light irradiations. We further used photoluminescence technique to characterize the formation rates of hydroxyl radicals by using coumarin (COU) as a probe molecule. The COU is a poor fluorescent molecule, can react with hydroxyl radicals to form the highly fluorescent 7-hydroxycoumarin (7HC).