Enhanced photocatalytic activity of Ag-ZnO hybrid plasmonic nanostructures

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Abstract: Noble metal/semiconductor oxide nanocomposites have considerable interest on degradation of pollutants from textile wastewaters. Ag-ZnO, as one of the noble metal/semiconductor oxide nanocomposite, is highly efficient catalyst in textile pollutant degradation that allows irradiation wavelength towards visible light region. Application of Ag on the surface of ZnO nanoparticles has caused enhanced photocatalytic activity of the Ag-ZnO composite owing to its greater degradation efficiency. Oxidation of the methylene blue consumes photo-generated holes and/or •OH radicals efficiently, blocking the electron-hole recombination and thus, increasing the total efficiency and acted as an efficient scavenger of the photogenerated electrons.

Introduction

Textile industries use various dyes, of which 65–75% are azo compounds, and approximately 2% of these dyes are estimated to be lost annually during manufacturing and processing operations (Zhang and Zeng, 2012). The direct discharge of these dyes into the ecosystem without treatment creates pollution problems that have become a major threat to the lives of humans (Zhang, 2010, 2011). Hence, the disposal of waste water is a worldwide environmental concern and its treatment is of the utmost importance. Methylene blue (MB) is one of the thiazine dyes which is hard to be degraded, and it usually acts as the model object of photocatalytic degradation with TiO_2 (Tang et al., 2003) and has harmful effects on living things. For example, during inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea and gastritis (Abdullah et al., 1990). Therefore, decolorisation and detoxicity of these dyes containing effluents have received increasing attention.

Conventional methods used to treat dye effluents are classified as physical, biological or chemical methods (Robinson et al., 2001) each of which having its own drawbacks. Physical methods such as chemical or electro-flocculation, reverse osmosis and adsorption are not destructive and mainly create pollutant concentrates. Activated sludge process does not work efficiently due to high solubility of synthetic dyes and their resistance to aerobic degradation. Furthermore dyes, although not directly toxic, may generate carcinogenic

compounds such as aromatic amines from azo dyes during their anaerobic treatment (Ledakowicz et al., 2001). New treatment methods are therefore necessary for the removal of persistent dye chemicals or converting them into harmless compounds in water. The low-cost and environmentally friendly process of semiconductor photocatalysis thus appears to be a viable method for destroying dyes. Semiconductor photocatalysis is a promising technology for harvesting clean solar energy, and it could help to solve the global energy crisis and environmental pollution (Jiang et al., 2010; Zhang et al., 2011, 2013; Qiu et al., 2014; Qi et al., 2014). Photocatalysis in heterogeneous systems mainly depends on the generation, migration, and separation of electron-hole pairs (Dong et al., 2012; Zhang et al., 2013) There are three major material requirements for photocatalysis: (i) a semiconductor with a suitable band gap that will allow a significant fraction of the solar spectrum to be utilized; (ii) chemical and structural stability under irradiation; and (iii) high electron and hole mobilities on the surface to reduce/oxidize the targets before recombining (Castelli et al., 2012; Qi et al., 2014).Therefore, to effectively solve these problems, nanocomposite photocatalysts have been explored in detail (Li et al., 2013).

In particular, ZnO has attracted much attention with respect to the degradation of various pollutants due to its being relatively cheap, stable and high photocatalysis. One of the main problems associated with the feasibility and viability of ZnO semiconductor photocatalytic oxidation is represented by a high tendency of photo induced hole-electron pairs to recombine, which implicates deactivation of the photocatalyst. Unfortunately solar spectrum consists only 5-7% of UV light, the other 46% and 47% of the spectrum are visible light and infrared radiation, respectively. This minimal extent of UV light in the solar spectrum has particularly ruled out the use of natural source of light for photocatalytic decomposition of inorganic contaminants and bacteria disinfection from water and air on large scale. Therefore, in order to shift the optical absorption of ZnO into the visible region and

prevent charges from recombination on the photocatalysts surface, various attempts have been made. ZnO has been extensively studied as a photocatalyst for environmental remediation because of its low cost, excellent electrochemical stability, and high electron mobility (Lai et al., 2010), as well as its large surface area when fabricated as a nanomaterial (Sarkar and Basak, 2013). However, the rapid recombination of photoexcited electrons and holes reduces its photocatalytic efficiency. Moreover, ZnO is unstable; it easily agglomerates and is difficult to recycle after use (Deng et al., 2012).Thus, preventing the agglomeration of these nanostructures is the main reason for preserving the high photoactivity of nanoscale photocatalysts. To overcome the problem of agglomeration, one of the most efficient methods is to use semiconductor-based heterostructures with desirable compositions and/or morphologies (Zhang, 2010). The properties of these semiconductors can be modified by adding noble metals with complementary properties to form core-shell, hetero-, and/or doped structures (Yu et al., 2010; Lupan et al., 2010; Guo et al., 2011). Besides allowing the properties of the materials to be finely tuned to meet certain specifications, this method also makes them multifunctional. In the literature, noble metal (Au, Pt, or Ag)/semiconductor nano-structures have been extensively studied because of their excellent catalytic activity (Zhang, 2012; Jiang et al., 2013 ; Li and Zhang 2014). Because of its good chemical stability and high electrical conductivity, Ag is one of the most promising noble tested metals and thus, it plays an important role in the collection of electrons from photovoltaic cells and concentrating them into currents (Li and Li, 2001; Height et al., 2006; Zheng et al., 2007) Ag NPs, in Ag-doped metal-oxide nanostructures, can significantly enhance the interfacial charge-transfer kinetics between the metal and semiconductor. This can cause a substantial increase in the photoactivity of the Ag-doped nanostructures compared to that of the undoped metal oxide. During the exposure of the Ag-ZnO nanostructures to visible light, charge carriers are formed in the noble metal by the

absorption of visible light, and are directly injected from the optically excited plasmonic-metal nanostructures into the semiconductor (Furube et al., 2007; Kochuveedu et al., 2013).The surface plasmon resonance of Ag nanoparticles helps in extending the light absorption of ZnO from near UV to the visible region, leading to an improved sun-light utilization efficiency. The decoration with Ag nanoparticles significantly improves the charge separation in ZnO. This characteristic makes Ag-ZnO nanostructures a potential candidate for photocatalysis. Ag NPs have been successfully attached to ZnO NPs with different geometries/morphologies, including hollow spheres (Zeng et al., 2008; Wang et al., 2012), cauliflowers (Zeng et al., 2008) and 3D flowerlike ZnO hierarchical microstructures (Fageria et al., 2014). But, the fabrication of Ag-ZnO nanostructures is still difficult for two reasons: (i) the self-nucleation of Ag NPs, and (ii) controlling the surface states of the ZnO nanostructure seeds to be suitable for the growth of Ag NPs (Gao et al., 2011, Patil et al., 2014). ZnO photocatalysts decorated with Ag NPs showed increased photocatalytic performance when applied to the degradation of organic contaminants, such as methyl-orange, MB, rhodamine B, and orange G.

The mechanisms underlying the enhanced photocatalytic activity of Ag-ZnO hybrid plasmonic nanostructures towards the degradation of MB can be understood as follows: When ZnO absorbs photons of energy greater than or equal to its band gap, electrons are promoted from its valence band to conduction band, creating an equal number of holes in the valence band. As the energy level of conduction band of ZnO is higher than the Fermi level of Ag-ZnO hybrid structure, the flow of electrons occur from ZnO nanostructures to Ag nanoparticles. This way Ag nanoparticles act as efficient sinks for the photogenerated electrons, preventing their recombination with holes. The direct electron transfer from semiconductor to the plasmonic nanostructures is dependent on the alignment of electronic band structure of the noble metal and semiconductor. The irradiation with sun light leads to the excitation of MB dye molecules adsorbed onto the ZnO nanostructures. The photoexcited MB molecules transfer electrons into the conduction band of ZnO (Garg and Bhakuni 1984).The photogenerated electrons created by the above mentioned processes react with dissolved O_2 molecules forming superoxide anion radicals, while holes react with H_2O leading to the formation of hydroxyl radicals, both of which cause the degradation of the MB dye. These reactions can be summarized as follows (Deng et al., 2009, Simon et al., 2012) and are schematically illustrated in Fig. 1.
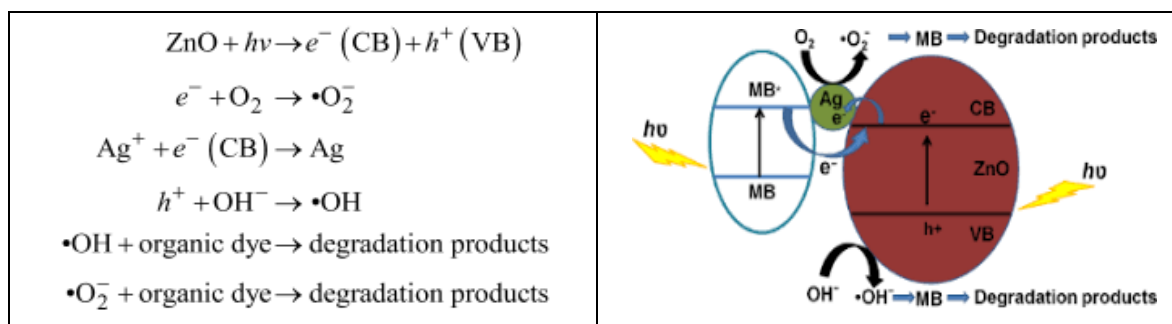

$$ZnO + hv \rightarrow e^- (CB) + h^+ (VB)$$
$$e^- + O_2 \rightarrow \cdot O_2^-$$
$$Ag^+ + e^- (CB) \rightarrow Ag$$
$$h^+ + OH^- \rightarrow \cdot OH$$
$$\cdot OH + \text{organic dye} \rightarrow \text{degradation products}$$
$$\cdot O_2^- + \text{organic dye} \rightarrow \text{degradation products}$$

Figure 1 Summary of Reactions.

Because the modified surface plays a key role in the photoresponse, the Ag-ZnO nanostructures may be useful for the degradation of other organic pollutants. The enhanced photo response of the Ag-ZnO nanostructures can be attributed to their hierarchical nanostructure that forms a closely packed inter-penetrating network, which results in improved charge carrier separation and surface

properties. The closely packed interpenetrating network could have more active sites, further enhancing the efficiency of photocatalysis process. The photocatalytic activity of ZnO nanostructures can be significantly enhanced upon decoration with Ag nanoparticles, which suppress the recombination of photodegenerated electrons and holes and improve sun-light utilization due to plasmonic response of Ag nanoparticles.

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