

Surface modification of titania experiment



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1. 4 Surface Modification of Titania and its requirement:

The chief active fields of research in non-homogeneous photocatalysis with semiconductor particles is development of a system that is capable of using the visible sunlight to degrade inorganic & organic contaminants. The total photocatalytic activity of a particular S/C system for the discussed purpose is measured by various factors. The major factors include semiconductor stability, photocatalytic efficiency, process, response of wavelength range and selectivity of products .

Modifying the surface of the semiconductor can surmount the limitations and drawbacks of a particular semiconductor as a photocatalyst for a particular use. Various benefits of modifying and changing the surface of titania have been studied. Below is the list as discussed before:

(a) Inhibiting recombination by increasing the charge separation and therefore the efficiency of the photocatalytic process;

(b) Changing yield of the particular product.

(c) Increasing the wavelength response range (i. e. excitation of wide band gap semiconductors by visible light); and

1. 4. 1 Metal Semiconductor Modification

The photocatalytic process is changed after the addition of the noble metals as the surface properties of the semiconductor are modified. The metal generally enhances and changes the output of a particular product . The rate

of photocatalytic reaction is also altered by the metal. Besides, there is also a chance that addition can change the reaction products also.

The electron will migrate to the metal where it gets trapped after the excitation and as a result of this migration, the electron-hole recombination is inhibited. The movement of negatively charged electrons to the metal particles has been confirmed by various studies showing there is a reported reduction in photo conductance of metal which has been deposited on the semiconductor compared to no reduction in photo conductance of the bare semiconductor particles. The hole becomes free to diffuse to the surface of the semiconductor particles. The oxidation can take place on the surface of the semiconductor. Besides, the metal has also got its own photocatalytic activity.

Hence, the metal actually alters the photocatalytic properties of the semiconductor by altering the distribution of electrons. The Fermi levels of the two align in such a way which causes the electrons to flow from the semiconductor to the metal as the two species come together in contact. This reduction in electron density in the semiconductor leads to increase in the hydroxyl group[14]. This in turn alters the photocatalytic process on the semiconductor surface.

The modification (electronic) of the semiconductor surface using metal deposition has witnessed with many noble metals such as gold, silver and platinum.

1. 4. 2 Modification of Titania by Noble metals like Silver:

Ag has been deposited onto TiO₂ in most of the studies as it is more cost-effective than other noble metals such as gold and platinum. Moreover, the Ag nanoparticles also have an intrinsic ability to stop and prevent the growth of bacteria. Also it has a very effective photocatalytic ability at the nanoscale [15]. Ag has formerly been added to TiO₂ nanoparticles, TiO₂ nanofilms and on TiO₂ nanorods. Various studies conducted by Li et al have reported that Ag-deposited TiO₂ anatase nanoparticles have shown an improvement in the photoresponse compared to that of anatase bare TiO₂ nanoparticles [16]. Ag-TiO₂ nanocomposite films have also been used and have showed an increased photocatalytic activity compared to the non-modified material. In fact, UV-illuminated Ag-TiO₂ nano-composite films have been found out to be up to 6.3 times more effective at photo degrading MO than are UV-illuminated bare TiO₂ films [17].

Plasmonic photocatalysis has lately been anticipated to increase and extend the photocatalytic activity of TiO₂ to the visible light range (400nm-800nm). The plasmonic photocatalysts are different combinations of noble metal nanoparticles and semiconductor nanoparticles. The semiconductor nanoparticles absorb UV / visible light. Noble metal nanoparticles usually have very strong absorption in the visible region of solar light due to localized surface plasmon resonance commonly known as LSPR.

If this energy of the absorbed visible light by the noble metal nanoparticles can be exploited to improve the reaction rates of photocatalysis, then the semiconductor/metal system is known as plasmonic photocatalyst. There're different mechanisms for plasmonic photocatalyst to enhance and extend the photocatalytic performance to visible light range of the solar spectrum:

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1. Coupling of noble metal nanoparticles directly with the semiconductor nanoparticles. This will lead to transferring of the photogenerated electrons or holes (due to the LSPR absorbance present in the metal nanoparticles) to the semiconductor, thereby enhancing the photocatalytic performance of the semiconductor [18]. One thing that shall be kept in mind is that the direct contact of semiconductor with noble metal may also lead to back transfer of charges from the semiconductors to nanoparticles of the noble metal.
2. The transfer of the absorbed energy by the noble metal nanoparticles to semiconductors via radiative route using the localized interaction of the LSPR-induced improved localized elec. field with semiconductors. [19].

Ag-TiO₂ composites have been extensively studied & prepared by a lot of methods. Loading of Ag nanoparticles on the surface of TiO₂ is done via different techniques. Photocatalytic activity enhancement has been reported with these samples of Ag-TiO₂. But because of the fact that most Ag is present on the surface of TiO₂ nanoparticles, the exposed TiO₂ surface area to illumination is reduced. It must be noted that the interface between Ag and TiO₂ is also limited. Hence, in order to assist the charge-transfer process, we must maximize the interface between Ag and TiO₂. We can also achieve a better design by simply mixing Ag NPs to TiO₂ structures. This has been successfully done using the sol-gel method [20, 21]. But there is a drawback of the sol-gel method as it typically needs precursors and therefore may have organic residues in the samples. Hence, in order to

achieve a very good control over the structure of samples, we must make Ag–TiO₂ porous nanostructures directly through physical methods.

Also it must be stated that silver metal deposition is of considerable interest because of its excellent potential applications. There are a lot of applications of silver in the medical field and in the anti-microbial field. This has led many researchers and scholars to develop and synthesize silver deposited titania coated sanitary wares [22], food preparation surfaces, air conditioning filters, medical devices etc. Ag traps the excited electrons from TiO₂ and also leaves the holes behind for the degradation reaction of organic species.

Furthermore, it also results in the extending the response of wavelength in the visible region [23–25]. Ag nanoparticles can also facilitate in the process of electron excitation by creating a local electric field [26]. The plasmon resonance effects in Ag nanoparticles show an enhancement in this electric field [27]. The effect of Ag deposition on TiO₂ on the photocatalytic activity of TiO₂ by UV irradiation was studied by Chao et al. [28] (using the sol-gel method). They found that silver promotion also leads to the anatase to rutile phase transformation, which may be credited to the increase in specific surface area. This increase in the specific surface area causes the enhancement in photocatalytic activity and the electron-hole pair charge separation.

Au/Pt deposition onto TiO₂ nanoparticles has also reported an increase in the photocatalytic reactivity of TiO₂. Yu and coworkers reported an enhanced photocatalytic reactivity micro-spheres of Au/TiO₂ nanocomposite compared to bare TiO₂ microspheres and Degussa P25 TiO₂ nanoparticles [29]. In addition, the UV-illuminated nanofilms of titania surrounded with Au

nanoparticles have also shown a better photonic efficiency than the UV-illuminated bare TiO₂ films [30].