Chapter - 9

Silver Vanadate Nanomaterial and its Photocatalytic Application

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Abstract—*Silver vanadium nanomaterial can behave as photocatalyst in various applications such as in the degradation of organic pollutants, oxygen evolution reaction, synthesis of fine chemical, etc. The metal-oxide has suitable band gap which helped the material to absorb both ultra violet as well as the visible light of solar spectrum. The doping of co-catalyst such Ag can further boost the generation of electron and hole pair in the photocatalytic reaction.*

Introduction

The water pollution occurred by drainage of chemicals from different sources like textile industries, paint industries, cosmetics, etc. are threating human life as well as marine species. Dye molecules are usually highly toxic and carcinogenic. The degradation of dye molecules is a difficult process due to their high stability. The conjugated and large structures are generally not decomposed via biological and chemical processes. The releasing of dye molecules to the river or any water sources without any

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treatment usually damaged the environment.[1-5] Till now, different processes have been adopted for wastewater management and some of them are Fenton type oxidation, reduction of dye using $NaBH_4$, catalytic oxidation using H_2O_2, adsorption or photocatalytic oxidation etc.[6,7,8] Photocatalytic degradation is considered as the most suitable among all the advances oxidation processes as the byproduct of this reaction is only water and carbon dioxide. Different types of catalysts have been used in the photocatalytic reaction depending on their capability to absorb the light. In addition to light absorption, the efficiency in the catalytic process is also a key criterion for suitable photocatalyst. Recently, it is found that several defect generated metal oxides are well-known photocatalyst in degradation dye pollutants from water. Chen *et al*. demonstrated the role of oxygen vacancy in TiO_2 nanorod synthesized by annealing the TiO_2 for the degradation of organic pollutant.[9] Various metal oxides such as ZnO, WO_3, etc. can also be used in wastewater treatment via the photocatalytic process and many of them suffer due to its incapability to absorb visible light of the spectrum.[10,11]

In the current scenario of catalytic development, nanoparticles (NPs) of 3d, 4d, and 5d block elements either in homogeneous or in heterogeneous form has found well application in various catalytic transformations. Silver-based nanocatalysts are recently being of high focused owing to its high selectivity and low cost compared to gold and platinum. Over the decade, several reactions carried out using Ag-based nanomaterial with notable results. In some reports Ag alone could not carry out all the

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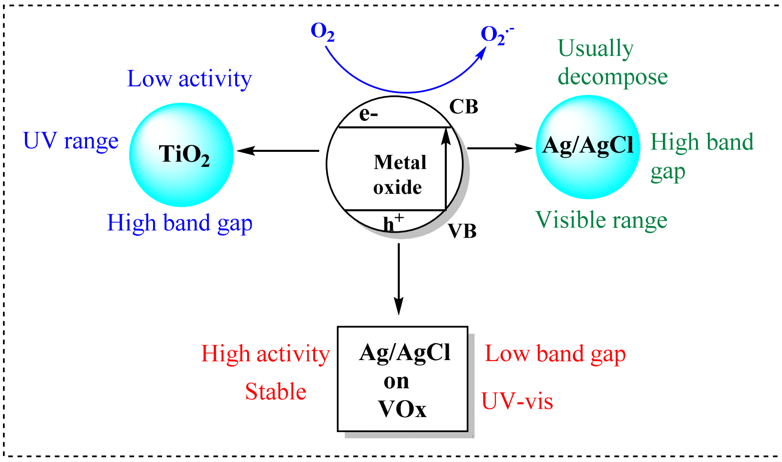
transformations. The noble metal like Ag, Au, or Pt has been used as plasmonic photocatalyst due to their localized surface plasmon resonance (LSPR) phenomenon. LSPR effect depends on the morphology of the nanomaterial, size of the particle, and composition of the material. Besides this, such resonance phenomenon also depends on the band gap of the materials. Band gap of Ag NPs are found to be higher than that of well-known photocatalyst such as Titanium dioxide (TiO_2). TiO_2 is commonly used as a semiconductor in various fields like white pigments, dyes, coatings, cosmetics, and solar cells, etc. Moreover, it can also be considered as an ideal photocatalyst since it completely degrades the pollutant into water and carbon dioxide. TiO_2 also possesses several drawbacks as a photocatalyst in several reactions. The large band gap associated with TiO_2 makes it inappropriate to use as a photocatalyst. However, by doping with some co-catalyst like coinage metals, the activity of TiO_2 material can be increased. Therefore, Ag NPs are supported in various metal oxides such as TiO_2 in order to enhance the catalytic activity of those semiconducting materials in the visible range.[12,13]



On the other hand, the band gap of AgX (X= Cl, Br) is comparable to that of TiO_2. Ag/AgX nanocomposites show plasmonic resonance band which induces electron promotion for photocatalytic reaction in visible range.[14] Ag/AgCl/TiO_2/PM modified material shows strong absorption in UV, as well as in the visible region of the spectrum. However, TiO_2 supported on magnesian (PM), was found to show strong absorption only in the UV region.[15] The band gap of AgCl is found to be in the range of 3.25-3.85 eV and its combination with Ag NPs exhibits surface plasmon resonance. In AgCl surface, SPR peaks of Ag NPs can be significantly influenced by tuning their shapes and diameters and thereby leads to its broad surface plasmon resonance peaks for Ag NPs which covered the wide range of the visible spectrum. Besides photocatalytic activity, it also has wide applicability as catalysts for the different chemical reactions. Owing to its good optical behaviour, it has also been extensively used in different applications.

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Recently, silver-based catalysts such as Ag_3PO_4, AgX (X = Cl or Br) and Ag_2CO_3 are considered as an efficient photocatalyst under visible light. Due to several factors, there is a limitation in its applicability. In the photocatalytic process, Ag-based compounds are usually decomposed to form silver particles on the photocatalytic material. Moreover, silver-based materials have more positive conduction band potential, which restricts its use in photocatalytic reactions.[16] Therefore, advance research can be made for Ag-based material to improve its activity as well as stability. For this purpose, Ag/AgCl NPs that has been synthesized supported in various metal oxide surfaces such as WO_x, TiO_2, VO_x, SiO_2, rGO, etc. Ag/AgCl supported in rGO, TiO_2 also shows very good photocatalytic activity as the band gap decreases in the supported systems. Ag supported photocatalyst such as Ag(GeO_4) also found its application in hydrogen generation from water which is termed as a prominent field in cleaner fuel generation technology.[17] Apart from being used as a photocatalyst, these Ag-based NPs entrapped in metal oxides have recently been found to be highly applicable in the lithium-ion battery. Among all the metal oxides, vanadium oxide (VOx) is also familiar as an effective nanomaterial with proper band gap. Yan *et al.* synthesized $BiVO_4/BiPO_4$ NPs using green hydrothermal process without using any templating agent for photocatalytic degradation of organic dye.[18] The mixture of Ag or any other co-catalyst with VOx shows high activity in oxidation of alcohol, degradation of organic pollutants, water splitting, etc.

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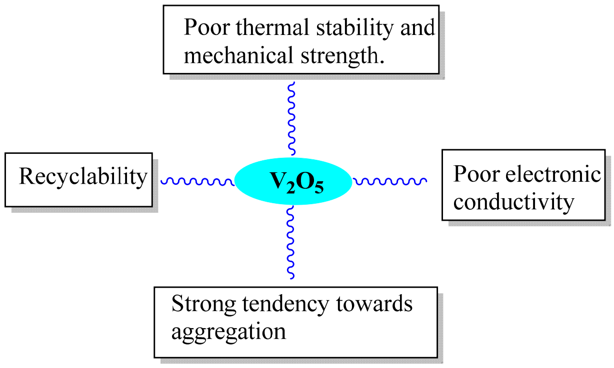
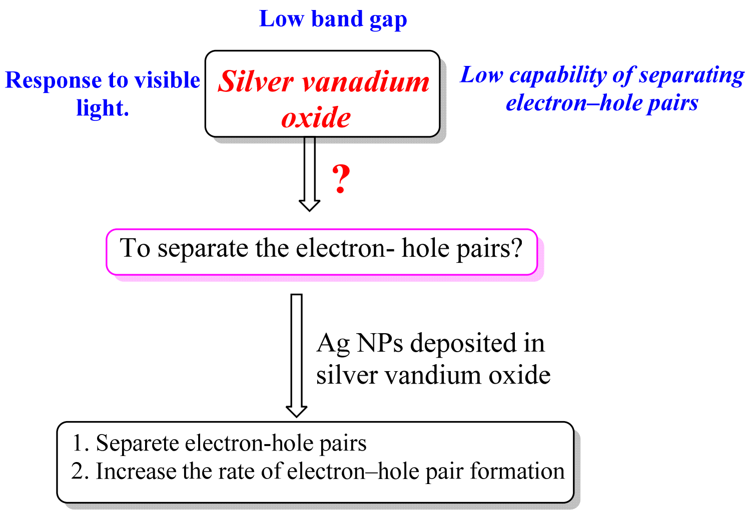
The modified silver-based compound such as β-$AgVO_3$ gained special interest due to its excellent use in rechargeable lithium batteries and many more areas. $AgVO_3$ materials are used a visible light photocatalyst as it has a narrow band gap and highly dispersed valance band due to its unique hybridization of valance band orbitals, i.e., V_{3d}, O_{2p}, and Ag_{4d}.[19] The size, morphology and the surface property of the synthesized silver vanadium oxide depends on the synthetic procedures and conditions. These SVO materials are usually prepared via hydrothermal method that changes the size, morphology, and crystallinity of the SVO depending on the condition. The 1D nanostructures such as nanowires, nano-belts, nano-ribbons from β-$AgVO_3$, SVO and VO was well reported in the literature, and these nanostructures can be used as semiconductor materials in nano-scale electronics. Furthermore, this 1D nano-structures increase the diffusion of lithium-ion, as a result, the reactivity against organic chemicals of SVO materials can be increased. However, a very less number of works has been reported in designing of silver/silver halide material doped on vanadium oxides. Apart from these materials, silver sulfide having composition like Ag_2S, Ag_2S_2 has also been found to act as a catalyst for water splitting reaction for hydrogen fuel generation.[20-22]



Carbon nanotube (CNT) is considered as an excellent support due to its high thermal stability, high purity, and interaction with metal providing high surface area. This material has good adsorption properties and the presence of conjugated structure help in promoting the electron in a different process. One of the major advantages of using CNT is the modification of its surface with different functional groups which changes the properties of the material. The modified CNT can provide a site to interact with the metal; as a result, the selectivity and activity can be tuned easily.[23] The encapsulation of NPs in the MWCNTs provides a new direction in different filed like controlled delivery of drug molecules as well as in various organic reactions. As the MWCNT can adsorb the dye molecules very fast and as a result, it approaches the catalyst surface leading to enhance activity.[24] Sathiya *et al.* reported that V_2O_5 supported over MWCNTs increases the energy storage capacity of the overall material.[25] Recently, 1-D silver vanadate over MWCNT has been found to exhibit higher efficiency as well as stability over the unsupported materials for the degradation of organic pollutants.

Degradation of organic pollutant

The semiconductor material has a suitable band gap, and it can be used as a photocatalyst in different dye degradation processes. The combination of some noble metal such as silver, gold with metal oxide like vanadium oxide can be used as an effective catalyst in dye degradation. The presence of noble metal like silver enhance the visible light capability of vanadium oxide as well as reduces the electron/hole pair recombination. Vanadium oxide has several advantages as a photocatalyst due to its suitable band gap, and its morphology can be altered with different capping agents. Different types of silver vanadium oxide like α- $AgVO_3$, β–$AgVO_3$, Ag_3VO_4, $Ag_4V_2O_7$, $Ag_2Sr(VO_3)_4$ have been already found to demonstrate higher photocatalytic activity.[26,27] F. Wang and his coworkers reported for a new group of silver-vanadate clusters type material (AgV_7O_{18}) which possesses better photo-degradation ability on dyes under visible light irradiation. The incorporation Ag in vanadium oxide matrix lowers the band gap due to hybridization between 4d and 2p orbital of silver and oxygen, respectively.[28]

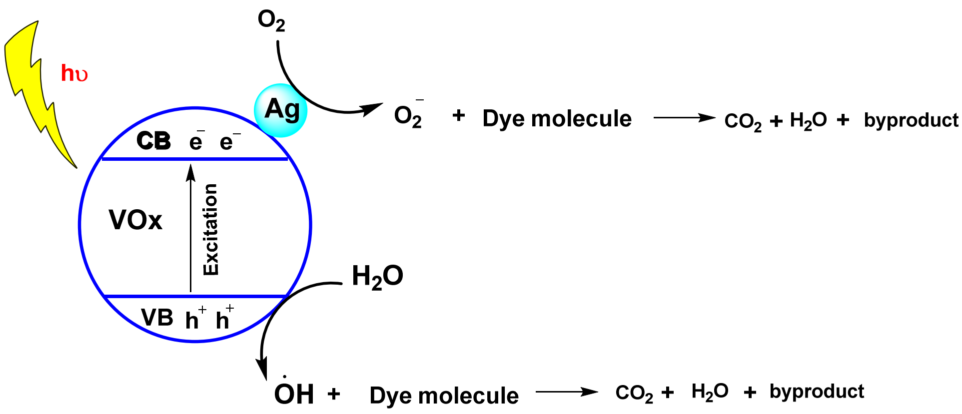


Hollow α-$AgVO_3$ nanomaterial shows better photocatalytic activity in the degradation of RhB than the bulk α-$AgVO_3$ under solar light. The photocatalytic efficiency of the material was efficient up to 90% with 2 h of reaction. The superior activity of hollow α-$AgVO_3$ in comparison to bulk α-$AgVO_3$ was due to the synergistic effect which enhanced the visible light absorption and electron transfer ability as well as reduces the electron-hole recombination.[29] $AgVO_3$ materials hybridized with carbon nitride as support was reported different groups using hydrothermal methods. The material shows photo activity in the degradation of Bisphenol A (BPA) and Basic Fuchsin (BF) under visible light. The hybrid material exhibits better catalytic activity and stability than the unsupported $AgVO_3$..[30] Wu *et al.* prepared a photocatalyst composed of g-C_3N_4/Ag/Ag_3VO_4 material for the degradation of RhB. The presence of Ag NPs in the material helped in increasing the recombination time of photogenerated electron and hole pairs.[31]

Chen *et al.*[32] synthesized $Ag/AgBr/AgVO_3$ materials for photocatalytic degradation of rhodamine B (RhB). This material shows excellent activity as well as it reduced the recombination of electron and hole pair during the photocatalytic reaction. The presence of AgBr helps the generation of electron and hole pair during the reaction. AgBr is n-type photosensitive material with band gap 2.6 eV. Recently, Ag/AgCl/VOx shows excellent photocatalytic activity in the degradation of methylene blue dye. The material was synthesized using two ligands that leads to an alteration in the morphology of the materials. The efficiency of photocatalytic degradation was enhanced when the Ag/AgCl/VOx material was synthesized over MWCNT.

Mechanism of the dye degradation

The noble metal increases the light absorption capability of the material and also reduces the band gap of the material due to the localized surface plasmon resonance effect. When the light falls on the material surface, the e^- from the conduction band excited to the valence band and creates an h^+ on the conduction band. The presence of Ag NPs reduces the recombination of e^- and h^+ pair during the reaction. The exact species responsible for the photo-degradation can be investigated using different types of scavenging agents. When tert-butanol was used as·OH scavenging agent, the rate of degradation was almost the same as that without the scavenging agent which implies that OH radical was not involved in the reaction. When other scavenging agents such as ammonium oxalate, silver nitrate, and p-benzoquinone the rate of degradation was employed their is decreased in the reaction rate which suggested that the degradation of a dye molecule was proceeded via the generation e-, h+ and superoxide as shown in Scheme 1.



Scheme 1. Photocatalytic degradation of organic dye under visible light.

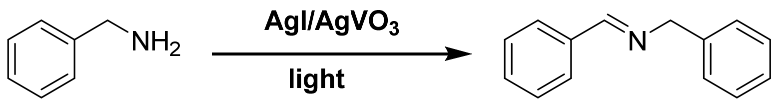
Oxygen evolution reaction

The decrease of fossil fuel as well as increasing greenhouse gases forces the researcher to think of some alternative source of energy. Among the different processes, photocatalytic water splitting has attracted the eyes of different research groups. In general water-splitting reaction is carried out in alkaline or acidic medium. Most of the catalysts suffer due to its low stability in this medium. Therefore synthesis of the photocatalyst in generation hydrogen and oxygen is considered as a beneficial process. Therefore, designing a catalyst for oxygen evolution is a challenging task. The photocatalytic oxygen evolution has been investigated with various silver vanadate catalysts such as α-$AgVO_3$, β-$AgVO_3$, Ag_3VO_4, and $Ag_4V_2O_7$ catalyst.[26] Among all the catalyst the activity of oxygen evolution is observed in case of Ag_3VO_4 catalyst under visible light. Sahoo *et al.*[33]

synthesized Ag@Ag_3VO_4/ZnCr LDH material via hydrothermal methods in which Ag^+ was reduced to Ag°. The surface plasmon resonance phenomenon of silver enhances the visible light-harvesting ability of the material.

Organic Transformations

With silver vanadate composites, less numbers of reduction reactions are so far studied in comparison with oxidation reaction due to their positive conduction band potentials and decreasing reduction properties. Wang and his co-worker prepared AgI/$AgVO_3$ nanoribbon composites that acts as an excellent visible light redox photocatalyst for selectively imine synthesis from its corresponding of benzylic amine.[34]



Scheme 2. Selective oxidation of benzylic amine under visible light irradiation with AgI/$AgVO_3$.

Conclusion

From the above discussion, silver vanadate-based nanocatalysts can be used in different photocatalytic applications owing to their ability to harvest visible light. Moreover, encapsulation of nanocatalyst further enhances the efficiency and stability of the catalyst in different photocatalytic processes.

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