

Chapter 1

PLASMONIC PHOTOCATALYSIS

1.1 Introduction

The anxiety to make use of the visible and low energy photons of the solar radiation has led to the development of plasmonic photo-catalytic systems based on metal nano-particles deposited on the surface of polar semiconductors or insulators. Nano particles (NP) of noble metals especially (Ag, Au and Pt) can strongly absorb visible light due to their Surface Plasmon Resonance (SPR) which can be tuned by the control of the size or shape or surroundings of NPs. Conventionally, the visible light plasmonic photo-catalysts is a composite system composed of noble metal NP and a polar semiconductor (like AgCl, AgBr)but however, other materials like carbon, graphene oxide (GO), graphene and a few other insulators which are used as supports and or charge carriers to form the plasmonic photo-catalytic systems.

1.2 Phenomenon of SPR

The conducting electrons of NPs undergo collective oscillation (excitation) by the oscillating electric field of the incident light. When the frequency of the incident light coincides with the resonance conditions of the noble metals NPs, the SPR appears because of the light (regions of visible, infrared or near IR) absorption. [7] The SPR of mostly spherical metal particles is dominated by the dipolar mode and is described in terms of the polarizability. The SPR frequency depends on the nature of the metal, the size and shape of the metal NP and the dielectric property of the surrounding medium, these variables can be used to tune the NP optical properties [15, 28, 30] The noble-metal NPs deposited on the surface of support (example polar semiconductor) possibly charge-polarized work as light trapping, scattering and concentration centres. The SPR of the noble-metal NPs can induce electron transfer from the photo-excited noble metal NP to the support to which the NP is attached. The presence of noble metal NPs in contact the support surface can also facilitate the redox reaction between the support and the substrate.

1.3 Types of plasmonic photo-catalysts

There are various combinations of support and metal can be exploited as plasmonic photo-catalysts. These can be grouped as follows: (1) A semiconductor or insulator (A) with NPs of the metal(M) on the surfaces of the support, designated as M-A (2) Noble metals M with nano-particles of the support (either a semiconductor or insulator) possibly deposited on the surface denoted as A-M. (3) A combination of the support A/A' with NPs of metal deposited on the surface is referred to as M-A/A' (4) Sensitizer molecule S anchored on the surface of noble metal and the noble metal supported on the semiconductor referred as S-M-A (5) A noble metal M coated with an insulator A is denoted as A(M) and any other combination with support is designated as A'-A(M) These designations are only indicative and one can generate many other combinations and they can be conveniently abbreviated using this type of notation.

1.4 Process of Plasmonic Photo-catalysis

In this mode of action, the Metal NPs absorb the visible light, the resulting photo-generated electrons and holes are separated by the metal support interface and the redox reaction take place on the surface of the plasmonic photo-catalyst. Alternatively, there can be radiative energy transfer between the noble metal NPs and the semiconductor in which the strong SPR induced electric field localized in the vicinity of the noble metal NPs can affect the electron hole formation and their transfer. [25]. If the noble metal especially Au is supported on insulating support like ZrO_2 , SiO_2 , or zeolite, then the support cannot sustain the charge transfer and hence the metal NPs can be quickly heated up by the absorption of the visible light thereby activating the organic substrate. [32]. A listing of the reported plasmonic photo-catalysts have been compiled [28] together with the preparation methods and photo-catalytic reactions like water splitting, oxidation of organic substrates or molecules like methylene blue or rhodamine blue.

1.5 Photo-catalysts based on Silver nano-particles

It has been recognized that small silver clusters upto 8 atoms exhibit molecule-like optical transition. [4, 27] As the size of the silver particles are big enough (more than 2 nm) then they develop optical absorption SPR bands due to their free electrons. [3, 13] Since the complex dielectric constant of silver has small imaginary component, this leads to large local field enhancement and small loss of the surface plasmon propagation. Therefore, the SPR of silver nanoparticles induces large absorption amplitude. A variety of plasmonic photo-catalysts composed of silver nano particles on TiO_2 , silver halides, composite semiconductors, carbon and graphene have been reported in literature.

1.5.1 Plasmonic photo-catalyst composed of Ag NP and TiO_2

Awazu et al. fabricated $TiO_2/SiO_2/Ag$ photo-catalyst. The photo-catalytic activity of this catalyst under UV illumination for methylene blue is enhanced

7 times compared with that of TiO_2 . [14] Controlling the thickness of the SiO_2 shell can be used to further increase in enhancing the photo-catalytic activity. Kumar et al. studied the system $\text{TiO}_2/\text{SiO}_2(\text{Ag})$ by tuning the thickness of SiO_2 layer 2, 5, 10 and 20 nm and showed that the photo-catalytic activity gradually increases with a decrease in SiO_2 layer thickness. [17] Nitrogen containing TiO_2 with silver nano particles showed enhanced water-splitting performance compared to TiO_2 alone. [5] They gave evidence to show that the electron-hole pairs near the semiconductor surface are readily separated from each other and migrate to the surface this accounting for the enhanced performance.

1.5.2 Plasmonic photocatalysts - silver nanoparticles and silver halides

Silver halide (Cl, Br and I) particles generate an electron hole pair on absorption of photon and the photogenerated electron combines with an Ag^+ ion to form Ag^0 atom. Using this principle, Kukuta et al. [20] observed that Ag^0 species are formed on AgBr and is not destroyed under successive illumination. This led to the development of first plasmonic photocatalyst $\text{Ag}@\text{AgCl}$ (i.e. $\text{Ag}-\text{AgCl}$). [22] A variety of $\text{Ag}@\text{AgCl}$ systems have been generated and these systems showed strong absorption in the visible region, which is almost as strong in the UV region. The photocatalytic activity evaluated for the dye degradation is 8 times greater than that observed with N- TiO_2 . It is conceived that the visible light induced electron-hole pair in the Nano silver particle is separated such that an electron moves to the surface of the silver nano particle from the interface, and the hole moves to the surface of the AgCl particle which is then used to oxidise chloride ions to chlorine atoms. The chlorine thus formed will oxidise the dye and thus get reduced to chloride (Cl^-) ions. It is possible that the photogenerated electrons are trapped by oxygen dissolved in solution to form superoxide ions O_2^- ions or other reactive species. [18] The architectures in terms of shape, morphology, (rods, hollow spheres, irregular balls, nanocubes, nano wires) and other features of the AgCl have been shown to have considerable influence in the catalytic decomposition of methylene blue under sunlight and showed high stability and recyclability. [1, 2, 12, 16, 21, 36, 39] The system $\text{Ag}@\text{Ag}(\text{Br}, \text{I})$ or $\text{Ag}@\text{AgBr}$ was studied by [21] Wang et al. and they have shown that the photogenerated electrons at the conduction band of the semiconductor are transferred to the silver nano particles, since the Fermi level of the nano particle lie lower in energy than the conduction band minimum of the semiconductor. Among these two systems, the reducing power of the $\text{Ag}@\text{Ag}(\text{Br}, \text{I})$ is stronger than that of $\text{Ag}@\text{AgBr}$ and the photogenerated electrons could reduce $\text{Cr}(\text{VI})$ to $\text{Cr}(\text{III})$ under visible light with high efficiency. Huang et al. [9] studied silver nano particles supported on silver salts like chloride, bromide, iodide, chromate, phosphate, $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$ and have shown that the charge on the counter anion strongly affects the photocatalytic activity.

1.5.3 Silver nano particles on composite semiconductors

Composite photo-catalysts of the type $\text{Ag}/\text{AgBr}/\text{WO}_3 \cdot \text{H}_2\text{O}$ have been examined since the CBM (conduction band minimum) and VBM (valence band maximum) for these two substances are at -3.7 and 5.95 eV and at -4.404 and -6.574 eV respectively. In this configuration, the visible light can be absorbed

by AgBr or WO_3 and the silver nano particles and hence the oxidizing ability of this system will be higher than that of Ag@AgBr. This superior behaviour of this system has been demonstrated in the photo catalytic destruction of E. Coli. Other systems that have been studied include Ag/AgBr/BiOBr; Ag-AgBr/ Al_2O_3 ; TiO_2 -Ag/AgBr and Ag/AgCl/ TiO_2 . These systems have shown visible light photo activity for the sterilization of pathogenic organisms and also for the degradation of dyes. [8, 11, 33, 35]. Another plasmonic photo catalyst system that has been demonstrated is Ag-AgI/ Al_2O_3 for the degradation and mineralization of chlorophenols (2, 2,4 and tri) which has been identified to perform through two electron transfer process one from the photo excited Ag NP to the AgI conduction band resulting in the formation of O_2^- and the other electron transfer from chlorophenol to the Ag NPs. [34] Another similar system studied is Ag-AgI/ Fe_3O_4 @ SiO_2 . [10].

1.5.4 Plasmonic photo catalysts with Ag NPs and Carbon

Core shell nano composite Ag@C (Ag-C) has been prepared by hydro-thermal process [26]. This system showed strong absorption in the visible region. The prepared Ag@C catalyst exhibits a high photocatalytic activity for the decomposition of tetraethylated rhodamine blue and acetaldehyde under visible light irradiation. A similar system namely TiO_2 @C/Ag showed photo-catalytic activity for the degradation of rhodamine blue and methyl orange [23]

1.5.5 plasmonic photo catalysts with Ag NPs and graphene

A photo catalyst of the composition Ag/AgCl/GO in which Graphene oxide is used as carrier (The favourable properties of graphene like transparency, high surface area, conjugated aromatic system, and unique electronic properties make them as excellent carriers for active components). The systems containing graphene oxide showed 4 time plasmonic photo catalytic activity for rhodamine degradation as compared to the Ag@AgCl system. This enhancement is due to the effective charge transfer from the plasmon-excited Ag nanocrystal to graphene which may suppress the electron hole recombination. [19]

1.6 Plasmonic photo catalysts of Au NPs

Gold nanoparticles have unique place in plasmon resonance phenomenon. They show absorption of visible light and exhibit a variety of colours. Their size, shape and surrounding environment all can change the colour that is exhibited by these nano particles. Particles in the range of 10 nm show strong absorption maximum around 520 nm while increase in size there is a red shift. Another method of tuning the SPR is through the change of the shape of NPs. Depending on the aspect ratio, the rod shaped NPs show two resonances. When the length to radius ratio increases the SPR shows red shift. The surroundings also can change the SPR peak position. Au NPs have been deposited on insulators like Zeolite Y, ZrO_2 and SiO_2 and these systems have been efficient for the selective oxidation of hydrocarbons and volatile organic compounds like CO, methanol and formadehyde. The observed process can be accounted for in the heating up of the nano particles or the interaction between oscillating local

electromagnetic fields and polar molecules may assist in the activation of the molecules for oxidation. The observed catalytic activity can be considered to arise only from the SPR effect of Au NPs.

1.6.1 Plasmonic photo catalysts with Au NPs and TiO₂

Au-TiO₂ system has received considerable attention with respect to plasmonic photo-catalyst. Liu et al. [38] used Au-TiO₂ to split water and demonstrated that Photo catalytic splitting under visible light illumination is enhanced by a factor of 66 with the addition of Au Nanoparticles. It has been proposed that the excitation in the Au Nps and the photo generated electrons is injected into the conduction band of TiO₂. Hou et al [29] reported the use of plasmonic photo catalyst Au/TiO₂ for the reduction of carbon dioxide to hydrocarbon fuels. This plasmonic photo catalyst has been used for photo-degradation of acetic acid and 2-propanol [6]

1.7 Plasmonic photo catalysts based on Pt NPs

There are only limited reports on this system. Li et al. [24] prepared a plasmonic photo catalyst Pt/Bi₂O₃, the conduction band receives the photogenerated electrons from Pt NPs and thus promotes the plasmonic catalysis. This system has also been explored for the photo degradation of benzene and oxidation of alcohols to aldehydes [31, 37].

1.8 Conclusion

Noble metal NPs supported on a variety of insulator surfaces does not operate through the injection of the photo excited electrons from NPs to the oxide and thus the latter does not directly participate in photo-catalysis. However, semiconductor supports can directly participate in the plasmonic photo catalysis since the electron transfer between the photo excited NPs and the semiconductor support can take place. The initial inertia in the studies of plasmonic photo catalysis using visible light has been overcome by a number of studies reported in literature and it is hoped that this field will evolve into an active field in the near future.

1.9 Bibliography

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