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MOS HYBRID MATERIALS FOR APPLICATIONS IN PHOTOCATALYSIS

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Abstract: As public awareness of climate change and global warming has grown, research into photocatalysis has once again accelerated because of the development of renewable energy. Since photocatalysis enables the direct conversion of (sun)light into chemical energy, its successful use on a larger scale may be able to address two issues at once: the production of energy carriers and their storage. The establishment of a methanol-based economy independent of the use of fossil fuels could be one example. Methanol may be a good fit for this use since it has a high potential for being produced from renewable resources (such as biomass or photocatalysis) and is easily transportable and stored.

Keywords: Metal Oxide, Semiconductor, Photocatalysis, Charge Carriers

I. Introduction

In order to convert sunlight into chemical energy, research efforts have been concentrated on two primary strategies: The first seeks to create molecular hydrogen from water by facilitating the whole photocatalytic water splitting reaction, while the second tries to leverage photocatalytic reduction reactions to transform greenhouse gas CO2 into useful feedstock molecules like ethylene or methanol. There are two distinct tactics for both approaches that aim to accomplish these goals. The first method (bio-or metal-based) uses organic systems as photocatalysts. Historically carried out in an enous catalytic manner, it attempted to emulate photosynthesis in nature, but in a different approach (e.g., aiming for different reaction products by the use of other materials, such as iridium complexes). Semiconductors are used for the heterogeneous analogs. For the majority of reactions and catalysts, it has been found that adding a so-called "co-catalyst" to these semiconductors is advantageous for photocatalysis. Since these photocatalysts are typically either metal or metal oxide particles, the majority of them are hybrid systems made up of semiconductors and metal (oxide) particles. Metal (oxide) particles are typically supplied at the nanoscale (also known as "nanoparticles") or even smaller scales (also known as "clusters"). Similarly, methods have also been tried where semiconductor materials were utilized as photocatalysts with and without co-catalysts and were nanostructured.

II. Related Work

This section focuses on two distinct aspects: Initially, generic mechanisms that may be pertinent to the activity of such heterogeneous photocatalysts will be presented. Second, the photocatalytic total water splitting reaction is used to illustrate two distinct concepts and the complex materials that result for the potential applications [1]. Light absorption and subsequent chemical reactions are the two distinct phenomena that can always be separated out of a photocatalytic system. Semiconductors are used for light arvesting in the vast majority of semiconductor/metal (oxide) hybrid systems. They are ideal for this function due to a number of qualities: First, in semiconductors with a direct bandgap, photons with energy above the bandgap are often very efficiently absorbed. Second, a wide range of materials with various bandgaps are available [2]. The majority of them are chemically stable, and the qualities of the materials can be adjusted in many ways.

For instance, alloying, the electrical properties of these semiconductors, semiconductor doping, and various semiconductor morphologies can all cause a shift in the bandgap and the migration of charge carriers can be obtained by different growth methods and the semiconductor's surface can be tuned by chemical manipulation. While the band gap determines the semiconductor's properties, the position of its bands, the conduction and valence band, governs its redox properties [3]. Thus, the band position is of similar importance and has to be considered when choosing a particular material. An electronhole is created when a photon with energy higher than the semiconductor's band gap is absorbed. The hole is in the valence band while the electron is excited into the conduction band. Consequently, the semiconductor's reduction strength is correlated with the conduction band's position, whereas its oxidation strength is determined by the valence band's position [4]. The band gaps and band locations of a few semiconductor materials, which are connected to the energetic required for the water splitting reaction, are depicted in Fig. 1. To compare the bands to the corresponding redox couples, they are displayed in relation to the reduction potential with reference to a standard hydrogen electrode operating at pH zero. The conduction band edge of the semiconductor must be greater than the halfreaction's reduction potential, which is determined using the Nernst equation and the standard electrode potential, in order to permit the hydrogen evolution reaction at pH 7. On the other hand, the semiconductor's valence band edge needs to be smaller than the water oxidation reaction's potential [5]. Rutile and the semiconductors on its left side are only appropriate to facilitate one of these reactions, but TaON and the semiconductors on its right side meet these requirements for both halfreactions.



Fig.1. Semiconductor Materials and Their Band Gap

By releasing heat or light, carriers with opposing charges can recombine. This process can take place on the surface of the semiconductor (surface recombination, or SR) or in the bulk (volume recombination, or VR). Conversely, the charges might move to reaction centres and start the intended chemical reactions there. Reaction centres typically serve as trap states at the same time, and it's thought that several charges may occasionally be held there. Either structural flaws in the semiconductor or, in hybrid materials, co-catalysts on the semiconductor's surface typically serve as the centres themselves [6]. Electrons start reduction reactions like the creation of molecules, whereas stored photo holes drive oxidation events like the oxidation of water.

The semiconductor's surface characteristics and doping have an impact on the charge carriers' trajectories. The Charge redistribution occurs in the semiconductor even when it is already dark due to contact with localized states (such as surface defects, deposited particles, or adsorbed molecules). The relative location of the Fermi-levels determines whether the electron density moves to the states nearby or outside of it. Consequently, the semiconductor's bands either bend upward or downward (Fig. 1). Differently doped semiconductors result in a varied charge redistribution and, as a result, variable band bending characteristics because doping modifies the location of the semiconductor's Fermi level [7]. On the other hand, band bending affects how photogenerated charge carriers migrate. The bands of semiconductors flatten as a result of majority charge carriers moving into the bulk and minority charge carriers generally preferentially moving toward the surface. This indicates that migration of photo-

holes to the surface is favored for negatively charged surfaces with upwardly bent bands, whereas photo-electrons are favored for positively charged surfaces with downwardly bent bands.



Fig.2. Semiconductor Materials and Band Positions

Consequently, n-type doping of the semiconductors may be advantageous for reaction rate in photooxidations, which are triggered by photo-holes, whereas p-type doped systems may be advantageous for reduction reactions driven by photons [8]. It must be mentioned, nevertheless, that the chemical reactions that are involved might vary greatly depending on the system under study and are also controlled by the reactants' dark adsorption characteristics. Because the migration of the photongenerated charges may not always be the step that determines the rate, it may not be entirely evident which sort of doping is favouring the overall reaction rate [9].

The scenario is a little different for nanostructured semiconductors because of the size of the semiconductor, which may cause the space charge region to be much shortened or the wave function of the charges to already be stretched over the entire semiconductor [10]. Therefore, band bending's contribution to the photoactivity of catalysts is greatly diminished or even nonexistent for thin semiconductor films or tiny particles in the range of a few nanometers. Due to the loss of the advantageous impact of band bending for charge separation, trapping of the charges may become much more crucial in certain situations, as recombination may become more probable [11]. As an alternative, the rapid elimination of a certain kind of charge carrier is another option that can be carried out by the addition of sacrificial agents to the reaction environment.

III. Properties

The primary function of the co-catalyst is to propel the actual chemical reaction, whilst the semiconductor is typically employed for light collecting. The co-catalyst must meet a few conditions in order to do this:

- A. Trapping of Charges: To ultimately start the chemical reaction, the minority charge carriers that are moving out of the semiconductor must be effectively trapped at the co-catalyst [12]. Trapping may be essential in nanostructured semiconductors in particular to lessen undesired charge carrier recombination.
- B. Selectivity: Which products are generated is also determined by the co-catalyst. In certain situations, it is crucial that a different product be produced than what would be expected from the bare semiconductor (for example, H2 gas rather than surface-bound hydroxyls on oxidic semiconductors); in other situations, it is necessary to prevent successive reaction steps (for instance, the unintended overreduction of methanol to methane in the conversion of CO2).
- C. Interaction with reactant molecules: In order to facilitate the following transfer of charges, the reactant molecules must be adsorbed. Certain bonds in the reactant molecule may already be weakened as a result of contact with the co-catalyst.

D. Suppression of the back-reaction: This is especially important in photocatalysis in particular [13]. First off, photon energy is frequently utilized to produce products that are thermodynamically less stable than the reactants (referred to as "up-hill reactions"); the CO2 conversion and the water splitting reaction are two well-known instances of this tactic at play. Second, unlike photo electro chemistry, the molecules that are produced by disproportionation processes (such the water splitting reaction) probably cannot be isolated from one another using a membrane, for instance. By drastically reducing its activation energy, a co-catalyst that is also serving as a thermal catalyst for the back-reaction would likewise greatly accelerate the back-reaction's rate of reaction.

IV. Light Absorption

As previously stated, a semiconductor's absorption characteristics are just as significant as the energy location of its bands. Because of their availability and chemical characteristics, some semiconductors (like TiO2) appear to be ideally suited for photocatalytic applications; nevertheless, they only absorb ultraviolet to their notably large band gap. light in the due But specifically.

The goal of research efforts for photocatalysis-based renewable energy generation is to fully utilize the sun spectrum. Alloying is one way to enhance the large band gap semiconductors' spectrum of light absorption [14]. The employment of ZnO to move GaN's absorption into the visible spectrum is one well-known example. An additional strategy to enhance semiconductors' absorption capabilities. The dye's stability and possible deterioration under UV light are its biggest drawbacks, despite its low cost and high adsorption capabilities. Plasmonic nanoparticle application is an alternative to dye use and an effort to get beyond some of its drawbacks. The absorption spectrum of these particles shows a band known as the localized surface plasmon resonance (LSPR). The collective movement of electrons in a metal particle with a frequency similar to the absorbed photon explains the well-understood LSPR mechanism [15]. Because of the enormous electric dipole created by this movement, the cross section for light absorption is often high. A number of variables affect the location and form of the plasmonic particles' LSPR absorption band.

V. Proposed Application

There are a number of situations in which renewable energy sources could replace fossil fuels. One strategy is the creation of a hydrogen economy, which requires overcoming challenges in both the production and storage of H2. There are various methods for both problems. The photocatalytic total water splitting process is a direct conversion mechanism for the synthesis of hydrogen from solar energy [16]. It must, however, be economically competitive with a benchmark system that combines photovoltaics, which generates energy from sunshine, with water electrolysis, which converts hydrogen.

When employing semiconductors loaded with co-catalysts, two distinct approaches can be used in light of the aforementioned effects, which are crucial for photocatalyst efficiency. One method is to customize catalysts by concurrently taking into account the physical and chemical needs of each component to identify the most effective material [17]. Another idea is centered on the creation of systems with multiple components, each of which performs a certain function. The first method requires a thorough, molecular-level understanding of each component's characteristics and how they interact, which is currently only feasible for extremely basic systems at most. In complex processes, the second method is typically used for total water splitting.

Using semiconductor materials for light harvesting is the "traditional" method of heterogeneous photocatalysis. The overall photocatalytic water splitting reaction without sacrificial agents was conducted using two distinct methods for semiconductors loaded with co-catalysts, which are detailed in this section. Conversely, two-step systems have been created, utilizing two distinct semiconductors, each of which serves as a co-catalyst for either the reduction or oxidation reaction [18]. A GaN semiconductor alloyed with ZnO to move the absorption edge into the visible region (to roughly 500 nm) is one example of such a one-step photocatalytic device. It has been discovered that manganese

oxide nanoparticles, which have a diameter of roughly 10 nm, effectively promote the oxidation reaction. About 2 nm chromium oxide shell-coated rhodium nanoparticles were placed on the semiconductor for the H2 evolution process.

For a wide range of uses, including optical sensing, gold nanoparticles and nanostructures show intriguing optical characteristics [19]. In the visible spectrum, gold-based materials typically provide good optical transitions and chemical stability, with the exception of very small clusters. As a result, studies have been conducted to employ them as light harvesters, much like dyes in dye-sensitized solar cells. For an effective chemical reaction that results in already complex systems, co-catalysts may be needed in addition to a semiconductor and a plasmonic particle.

VI. Conclusion

Future photocatalytic systems are represented by semiconductor/metal (oxide) hybrid materials. The mechanisms at play are complicated, though: the light harvesters' absorption characteristics must be taken into account, charges must be transferred by avoiding undesirable de-excitation pathways, and the chemical reaction must produce the desired product, at most, without producing undesirable byproducts. Although it is challenging to accomplish, knowing the characteristics of a possible system could be a crucial first step in creating customized photocatalytic materials. Clarifying the underlying reaction mechanics has greatly benefitted state-of-the-art systems, as demonstrated by the overall water splitting reaction.

The benchmark system of water electrolysis in conjunction with solar cells is still unbeatable, despite the systems' significant rise in complexity and component usage. However, the fixation of carbon from CO2 has been the continual focus of research, and it is likely that the water splitting reaction is not the best area for photocatalysis. Furthermore, the use of semiconductor/metal (oxide) hybrid materials may not be restricted to the production of renewable fuels, as demonstrated by the use of titania for water treatment and self-cleaning windows. Alternatively, these systems might facilitate the development of new synthetic pathways for molecules of interest or assist in the replacement of hightemperature catalytic methods with photocatalytic ones.

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