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## Review

# **Recent Progress on Ligand Protected Metal Nanoclusters in Photocatalysis**

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**Abstract:** The reckless use of non-replenishable fuels by the growing population for energy and the resultant incessant emission of hazardous gases and waste products into the atmosphere insisted scientists to fabricate materials capable of managing these global threats at once. In recent studies, photocatalysis employed focus on utilizing renewable solar energy to initiate chemical processes with the aid of semiconductors and highly selective catalysts. A wide range of nanoparticles have showcased promising photocatalytic properties. Ultrasmall metal nanoclusters (MNCs) with sizes below 2 nm, stabilized by ligands shows discrete energy levels, exhibits unique optoelectronic properties which are vital to photocatalysis. In this review, we intend to compile information on varying photocatalytic efficiency of metal NCs with respect to changes in their properties. Review discusses about the photocatalytic activity of atomically precise ligand-protected MNCs and its hybrids in the domain of in energy conversion processes like photodegradation of dyes, Oxygen Evolution Reaction (ORR), Hydrogen Evolution Reaction (HER) and CO<sub>2</sub> Reduction Reaction (CO<sub>2</sub>RR), and photosensitizer in solar cell.

**Keywords:** Photocatalysis; Metal Nanocluster; CO<sub>2</sub> Reduction Reaction; Hydrogen Evolution Reaction; photodegradation; Solar cell

### 1. Introduction

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Over the past several decades, rising demands of the ever-growing population, excessive consumption of non-renewable resources and resulting greenhouse gas emissions and improper waste disposal have all been of great concern to mankind. The relentless efforts of scientific community towards this global crisis paved the way for more sustainable solutions like photocatalysis. Photocatalysis appears to be a perfect fit as a greener alternative to resolve energy and pollution related problems simultaneously, it aids the completion of chemical processes with the help of inexhaustible solar power, mitigates hazardous products like CO2 by photoreduction and produces cleaner fuels. In 1972, Fujishima and Honda were first to apply this strategy for hydrogen evolution reaction through photocatalysis[1]. Later, photocatalysis with semiconductors with sufficient bandgaps (i.e., TiO2, CdS, ZnO, Fe<sub>2</sub>O<sub>3</sub> and ZnS) did turn into a promising field of study for researchers[2-6]. Nanotechnology has created revolutionary changes in this dimension, with the help of umpteen number of nanoparticles (NPs) which possess high surface area and plasmonic resonance. Noble metal nanoparticles such as AuNP, AgNP, PtNP, IrNP, OsNP, RhNP, RuNP are largely employed for photocatalysis for the past decades, but the efficiency is not reached the target level[7]. Apart from this, the mechanisms related information in photocatalysis driven by noble metal NPs with huge number of surface atoms did seem vague. Meanwhile, new class of zero-dimensional fluorophores, metal nanoclusters (NCs), proved dominant to their conventional nanoparticle analogues in various applications.

Metal NCs comprises of a core with ten to hundreds of atoms protected by surface ligands like thiols, proteins, peptides, enzymes, polymers, and DNA [8–11]. The emergence of this well-defined aggregates with commendable surface-to-volume ratio, fully reduced atomic core and dispersity on catalysts made them the best available choice for wide range of applications [12]. In comparison to bulk, MNCs being a sub-nanometer sized unit (< 2nm) exhibits quantum confinement effects, as it approaches Fermi wavelength of conduction electrons, thereby splits continuous density of states into discrete energy levels. As a result, metal NCs possess molecule-like behavior and acts as a missing link between atoms/molecules and metal nanoparticles [13]. The atomic level precision of metal NCs assisted in confining size and to analyze involved mechanisms quite understandable. Due to these factors, they have been assigned few other titles too such as Quantum clusters (QCs) and Monolayer protected clusters [14,15]. Initially, gold MNCs were the focus of study due to the simple synthetic routes, commendable stability and novel optical properties presented, even in the absence of plasmonic resonance, are all attributed to their shift in valency from Au (III) to Au (I)/Au(0) in Au NCs [16].

The physiochemical properties of nanoclusters are highly influenced by the size, metal core composition, assembly architecture and surface components [17-19]. In addition, metal NCs are known for their attractive optical characteristics including tunable luminescence, HOMO-LUMO transitions, substantial Stokes shift, two photon absorption, photostability, magnetism, chirality and biocompatibility [20,21]. Their photostability, biocompatibility and low cytotoxicity in turn caused them to be chosen for biomedical applications [22]. Monolayer protected clusters are less aggressive and relatively more stable compared to gas phase clusters containing unsatisfied valence electrons in its free state. Currently, further studies on the factors and their impacts on optical properties set forth new developments in catalysis, biosensing, bioimaging, gene therapy and drug delivery [13,23–26]. Advancements in the preparation of polar or organic solvent soluble NCs, penetrable sized clusters, computational strategies to gain knowledge on surface atom arrangements and instrumentational techniques can build the future of metal NCs. Tailoring cluster's distinctive optical and electronic properties by enhancing parameters like formal charges, geometry, metal composition and ligand, play pivotal role in in photocatalysis [27]. Despite these, metal NCs with fully reduced metal atom cores have relatively low-band gap, thus it indeed inhibits photo-corrosion appreciably. Therefore, metal NCs can be utilized, as photosensitizer and cocatalyst, in energy intensive processes like photodegradation of dyes, ORR, HER and CO<sub>2</sub>RR, photosensitizer in solar cell [28–31]. (Figure 1)

A comprehensive review on metal nanomaterials for heterogeneous catalysis has been written by Liu and Corma [12]. Jianping Xie and colleauges highlighted in a minireview the major important characteristics of MNCs which are vital to photo and electro catalysis [27]. This review aims to update the literature and recent advances with a focus on photocatalysis particularly from 2016 onwards, since a comprehensive review on catalytic applications of ligand-protected, atomically precise MNCs was published in Coordination Chemistry Journal in 2016 to which the readers are referred to [32].



Figure 1. Applications of Metal NCs in photocatalysis.

# 1.1. Chemical Composition and structural properties

The central metal atom, ligands, charge states and composition play significant role in deciding the physiochemical properties of MNCs. In general, MNCs expressed by the molecular formula [Mn  $(SR)_m]^{q}$  (n- represents the number of metal atoms, m- represents the thiolate ligands (staple mottif), and q denotes the net charge of the cluster) [33]. Engineering metal, ligand and charge state on an atomic level can alter the performances and physicochemical properties of MNCs. In addition, the size (~2nm) and structure can be adjusted with atomic precision for new application possibilities in a variety of disciplines [34]. By analogy with terminology employed in protein field, metal NCs is composed of primary, secondary and tertiary structures. whereas metallic core is the primary structure and the repetitive local structural motifs serve as a bridge between the core and the ligands. These motifs are organic ligands and surprisingly, the length or size and structure of these motifs can be easily manipulated, resulting in a wide range of metal NCs. The protective shell's exterior structure is made up of spatial ligands. It has been highlighted that insight of the crystal structure of the material is very crucial as it reveals the information on the atomicity of the core, nature of the Au-S linkage, chirality of the nanoclusters, the arrangements of the ligands around the metal core, and so on [35]. In the recent times, crystal structures of some of the gold nanoclusters such as Au25SR18,[36] Au38SR24,[37] Au36SR24,[38] [Au24 (PPh3 )10 (SR)5 Cl2]+,[39] Au28SR20,[40] Au102SR44,[36] (where SR= thiolate) were resolved using various analytical techniques [41].

The molecular weight of MNCs is identified using mass spectrometry based methods, like matrix-assisted laser-desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS) and electrospray ionization mass spectrometry (ESI-MS) [42,43]. For MALDI analysis traditional weak organic acid used as matrices to recognize the molecular mass of the core of the metal NCs; Even though it's a sophisticated analytical instrument, it also has some limitations. The weak organic acid matrices employed in MALDI do not eliminate ligand fragmentation, The mass accuracy of MS equipment is also decreased by the presence of significant chemical noise and/or an unresolved isotopic pattern, leads to the possibility of numerous molecular formulae being nearly isobaric and the potential for impurities or ligand fragmentation to produce significant chemical noise that makes it difficult to assign atomic information. For instance, isotope-resolved mass spectrometry has been pushed forwards by Antoine's group to unravel the molecular formula of ultrasmall NCs [44].

#### Synthesis of Metal Nanocluster

Gas phase cluster is the first reported nanocluster, where the MNCs are formed by evaporation, and it is unprotected. This unprotected clusters are observed to be very reactive to form larger sized particles. Therefore, proper stabilization techniques should be used for MNC synthesis. The selection of ligand is an important step in the controlled synthesis of the MNCs. The first ligand chosen for the synthesis of MNCs was phosphine due to its high affinity towards metal ions. Followed by phosphine stabilized cluster, various thiol stabilized NCs were reported due to the relatively high affinity of Sulphur towards metal ion. Due to the insolubility of organic thiol stabilized NCs in water, watersoluble thiols were introduced to synthesize the NCs. Later new possibilities has raised to create quantum clusters using macromolecule template. In this green synthesis macromolecules such as various DNA, polymers and dendrimers, have been used for cluster stabilization and protection. Reaction duration, pH, temperature, type of ligand, template structure, reducing agent concentration, and Au3+/ligand ratio are crucial synthetic parameters for influencing the structure, size, surface characteristics, oxidation state, and consequently the optical properties of MNCs. It is necessary that the template or ligand used for the stabilization should have a high binding affinity towards the metals (Au, Ag, Pt etc) in order to prepare highly stable AuNCs with high monodispersed (Figure 2) [45]. Figure 2 depicts core-shell nature of MNCs and can be prepared by selecting appropriate capping ligands [46]. The nanoclusters can be synthesised using different ways such as chemical reduction, photoreduction, hydrothermal, biomineralization and etching, etc[47].



**Figure 2.** shows a schematic representation of the core-shell structure for fluorescent MNCs and the ligands used for the synthesis.

Xie et al. first time developed a biomineralization strategy for the synthesis of highly luminescent gold nanoclusters using BSA as protecting and reducing agent [48]. The red luminescent AuNCs is made up of 25 gold atoms (Au<sub>25</sub>). The same strategy is used for the synthesis of various other protein protected metal NCs [49,50]. Thus, in general, the nanocluster synthesis can be categorized as Top-down approach, bottom-up approach and Inter cluster conversion approach.

Bottom-up method uses metal salt, ligands and reducing agents are used as precursors. In this method, nanoclusters are formed by wet chemical reduction of metal salts with a suitable reducing agent. In the first stage, a Metal(I)\_thiolate complex formed by reacting metal salt with thiolate ligand. Then, Metal(I)\_thiolate complex is treated with a reducing agent such as sodium borohydride (NaBH<sub>4</sub>) or ascorbic acid to reduce M(I) to M(0), and produce M(0)@M(I)-based NCs [51]. In some circumstances, the stabilizing ligand itself serves as a reducing agent, which eliminates the need for a second reducing agent. This technique of synthesis is known as the biomineralization method. Other than wet chemical reduction, photoreduction method is also employed to produce luminescent metal nanoclusters, which in light initiate the reduction reaction.

In Top-Down approach, smaller sized MNCs can be prepared from larger sized metal nanoparticle/MNCs via chemical etching. Here, chemical etching carried out between excess ligands and larger metal nanoclusters to obtain metal NCs with smaller sizes. This usually done in solution phase either in one solution or in the interface of two solution. Based on the use of etching agent, etching method is classified into two categories, ligand etching and solvent etching. One of the major advantage of nanoclusters produced by etching method is the controlled size focusing [52].

In the case of Inter-Cluster conversion method, the NCs formed via seed-mediated synthesis, cluster conversion, metal exchange ligand exchange, and motif exchange. In this process, nanoclusters are used as the starting material, and through the adjustment kinetic or thermodynamic parameters the structure of the nanoclusters are changed. The most common methods for cluster conversion is the ligand exchange reaction [53].Ligand exchange reaction (LER) is a widely used technique for modifying nanoclusters after their creation. The adaptability of the gold and Sulphur interphase makes this possible. The ability to change the size and phase of clusters, as well as the ability to impart fluorescence on nanoclusters for biological labelling purposes, are some advantages of ligand exchange reactions. They can also increase the enantiomeric excess of already chiral clusters

and give chirality to nonchiral clusters. In this way, LER broadens the range of MNCs by forming distinctive and precise nanoclusters [54]

Similarly, an electrochemical method can be used to produce a large quantity of high-quality Au<sub>25</sub>(SR)<sub>18</sub> <sup>0</sup>NC's [55]. This method of crystallisation can aid in determining the structure of new NCs, enabling a deeper comprehension of their molecular physiochemical characteristics.

# 1.2. Key physico-chemical properties of MNCs in photocatalysis

Metal NCs with specific structural design and resultant exceptional physiochemical, electronic and optical properties gave birth to a plethora of distinctive materials capable of driving photochemical reactions. Especially, tailoring their optical and electronic parameters could effectively alter their light harvesting abilities and would render us a method to manipulate certain photocatalytic processes, by inducing electron-hole pairs generation, in order to attain maximum quantum yield. For photocatalysis, the major criteria to choose a materials is strong absorption of solar light [56]. Figure 3 shows the absorption spectrum and solar cells excited with AM 1.5 (100 mW cm<sup>-2</sup>) of Au<sub>25</sub>SG<sub>18</sub>. The overlapping region between these two curves is a key component of photocatalysis. For gold nanoclusters, efficient light energy conversion necessitates a slow rate of excited state relaxation. Indeed, Au<sub>18</sub>SG<sub>14</sub> exhibited the highest electron transfer rate and longest excited state lifetime of the NC series [56].



**Figure 3.** UV-Vis absorption spectrum of Au<sub>25</sub>SG<sub>18</sub>, and solar flux for AM 1.5. (Solar radiation by using a Xe lamp). Reprinted with permission from [56]. Copyright 2012 Royal Society of Chemistry.

# 1.3. Optical Properties

Metal nanoparticles, having size range ~3 nm to 100 nm, obey the plasmonic regime where a single surface plasmon resonance band dominates the optical spectrum and which has a far higher number of atoms than the number of surface molecules that stabilize it (see Figure 4). In such regime (plasmonic regime), nanoparticles interact with the incident light and surface plasmon resonance occurs, causing conduction band electrons to collectively oscillate and forms characteristic peaks (gold nanoparticle shows surface plasmon resonance at 520 nm) [57,58]. On the contrary, the NCs have a very small number of metal atoms (such as 2, 8, 18, 25, 55 etc.), results in an optical spectrum with several bands, distinctive energy levels, and quantum behavior [59].



**Figure 4.** Explains the major differences between MNCs and Metal nanoparticles by Size, and optical absorption. Reprinted with permission from [60]Copyright 2021 Nature.

Figure 4 depicts the electrical transitions between discrete energy levels in metal NCs [61,62]. As the particle diameter decreases, SPR peaks disappear gradually as shown in the Figure 4. In the Kohn-Sham orbital energy diagram of Au<sub>25</sub>SR<sub>18</sub> nanoclusters indicates HOMO composed of triply degenerated 5d10 atomic orbitals and doubly degenerated LUMO, which are 6sp atomic orbitals of gold [63] (Figure 4). The peak 'a' formed due to the HOMO (sp) to LUMO (sp), peak 'b' is a mixed type band (sp to sp and d to sp) transition. The peak 'c' is formed due to (d to sp) interband transition (Figure 4).

The photoluminescence property of metal NCs opens up possibilities and applications in variety of fields including sensing, imaging etc. [64,65]. The luminescence in MNCs are depends on its geometric and electrical structures of the metal core, as well as the ligand shell, alteration in the metal core or ligands, one can tune its optical property. Such nanoclusters can be thought of as a "multishell system," comprising a metallic core containing metal-metal bond, a metal-ligand staple motif as interface, and surface ligand molecules (see figure 4). As observed in metal complexes, metal nanocluster also exhibits the similar charge transfer or electron transfer process. These three shells can interact with each other via ligand to metal core or ligand to metal-metal charge transfer or by directly donating delocalized electrons from the ligands' electron-rich groups [11]. Following visible or near-UV absorption, certain broad tendencies in de-excitation routes have been discovered. The experimental and theoretical data from the literature were used to produce the energy diagram in Figure 5. It is possible for transitions from molecular orbitals with strong ligand contributions to orbitals with high metal character (LMCT) and from metal-to-metal electronic transitions to cause near-ultraviolet and visible absorption. Clusters with a core of metal atoms have an initial decay pathway that could result in an emission in the visible spectrum. All clusters have a charge-transfer component with a long-lived decay [66]. Furthermore, intersystem crossings are associated with multiple energy transfers (reinforced ISC), may result in an overall increase in Photoluminescence (PL) emission and longer PL lifetimes [59]. The luminescence property is affected by temperature in such a way that, on decreasing temperature the HOMO-LUMO gap increases [51].



**Figure 5.** Schematic representation of the relaxation pathways of ligand-stabilized atomically precise gold nanoclusters.

Two-photon Absorption: Two-photon-absorbing (TPA) photocatalyst uses near-infrared lowenergy photons [67] for photocatalysis. The unique Nonlinear optical (NLO) properties of subnanometer core sized clusters of metal nanoclusters exhibits outstanding characteristics [21]. Compared to the conventional organic dyes, NMNCs shows superior two-photon absorption cross section (TPA). Although these two-photon processes in small numbered MNCs are well established, the basic photophysical mechanisms behind them are still poorly understood. Generalizations based on complementary theoretical and experimental studies have been made possible by their twophoton absorption properties [68]. It is reported that, the TPA characteristic of AuNCs and AgNCs can be enhanced by the concept of "ligand-core NLO-phore" [69,70]. The different electron or charge transfer process between metallic core and ligand are essential for boosting the transition dipole moments leading to enhanced TPA cross sections (as exemplified in Figure 6 with Au<sub>10</sub>L<sub>10</sub> nanoclusters).



**Figure 6.** Shows the TD-DFT Two photon absorption spectrum for Au<sub>10</sub>L<sub>10</sub> (L--SCH<sub>2</sub>CH(NH<sub>2</sub>)CH<sub>3</sub>). Bottom panel of figure shows the leading excitations responsible for the characteristic features of TPA.

Chirality: The photocatalytic activity induced by chiral metallic particles varies with the helicity of the illumination light [71]. MNCs such as gold quantum clusters display fascinating chiral properties [72]. Moreover, the chirality depends mainly on three factors, (a) fundamental chirality is

induced first by atomic packing mode, (b) the geometrical isomerisms of the surrounding motifs and (c) the natural chiral characteristics of the protective ligands and their arrangements covering the metal core [51] (Figure 7). Commonly, the SR-Au-SR units of AuNCs display chirality, a chiral center at each Sulphur atom and can exist in either a (R,R)/(S,S) trans-configuration or a (R,S) cisconfiguration.



**Figure 7.** Schematic representation of hierarchical structure of AuNCs and emergence of chirality. Reprinted with permission from [73] Copyright 2021 Nature.

## 1.4. Stability

Metal clusters shielded by thiolates or polymers are attractive possibilities for nanoscale devices [74]. For instance, among various GSH-protected AuNCs, Au<sub>25</sub>SR<sub>18</sub> is the most stable one [75]. The isolated Au<sub>55</sub> clusters exhibit an amazing resistance to oxidation, even when exposed to oxygen atoms and radicals produced by oxygen plasmas, [76]. When the particle size is decreased to 1.6 nm, the metallic component's spectral weight increases rapidly, indicating that these particles are more oxidation-resistant. This resistance is much more for the case of naked Au<sub>55</sub> clusters. In addition, ligands influence on the stability of metal NCs such that thermal stability of captopril-protected Au<sub>25</sub> is more when compared to GSH-protected AuQCs [77].



**Figure 8.** The NMR spectra of captopril before (A) and after heating (B) and glutathione before (C) and after heating (D)respectively Reprinted with permission from [78] Copyright 2007 Royal Society of Chemistry.

NMR measurements [Figure 8(A, B and C, D)] of equal amounts of glutathione and captopril after heating for 2 hrs. at 80°C showed no significant spectral changes for captopril, while new peaks

were observed for glutathione due to degradation. This proves the enhanced stability of Au<sub>25</sub>(Capt)<sub>18</sub> over Au<sub>25</sub>(SG)<sub>18</sub>.

Doping the central metallic core Au<sub>25</sub> with other elements like Cu, Pd alters the geometric structure and increased the resistance to deterioration, respectively [78]. To illustrate this, Negishi, Y., Kurashige and co-workers [79] doped the Au<sub>25</sub>(SG)<sub>18</sub> with Pd leading to the formation of Pd<sub>1</sub>Au<sub>24</sub>(SC<sub>12</sub>H<sub>25</sub>)<sub>18</sub>. The Pd doped gold nanoclusters exhibited increased thermodynamic stability and stability against degradation.

The spectral profile evolves with time, and after 30 days, it resembles that of Pd1Au24(SC12H25)18 rather closely and the ESI MS spectrum shows just a single peak that may be ascribed to Pd1Au24(SC12H25)18 [80]. The strong interaction energy between Pd and Au24(SC12H25)18 was proved by the DFT calculation of Jiang et al. Consequently, with the Au24(SC12H25)18 frame, Pd develops an intermetallic structure and on the strength of this Pd1Au24(SC12H25)18 presents higher thermodynamic stability than Au25(SC12H25)18. On the other hand, doping the Au25(SC2H4Ph)18 with Copper reduced its overall nanocluster stability [81]. Doping with copper formed Cu-1Au-24(SC2H4Ph)18. In comparison to Au25(SC2H4Ph)18, the optical absorption spectra moved toward lower energy, suggesting that the HOMO-LUMO gap has shrunk.

From the electronic density of states study of Au<sub>25</sub>(SR)<sub>18</sub><sup>1-</sup> reveals its electronic state of Au<sub>13</sub> core (8 electrons) protected by six [(SR)<sub>3</sub>Au<sub>2</sub>] complexes [82]. The superior stability for Au<sub>25</sub>(RS)<sub>18</sub> is achieved by structural toughness and an 8 e- shell of delocalized Au(6s) electrons for the anion. The gold nanocluster super atom model expands the jellium model [83] to explain multiple ligand-protected AuNCs with closed valence-electron shells (such as, 2, 8, 18, 20, 34, 40, etc.). The metal core is regarded as a single atom in the super atom hypothesis. The extraordinarily stability of these nanoclusters emerge from the regular closure of outer electronic shells [84]. Even if strong structural and electronic stabilization occurs for Au<sub>25</sub>(RS)<sub>18</sub>, the nature of protecting ligands affect the stability of the cluster. The role of isomer were studied using para, meta, and ortho MBA stabilized nanoclusters [85]. Figure 9 shows the isomeric effect of MBA on the stability of Au<sub>25</sub>(MBA)<sub>18</sub>NCs. The steric hindrance of the carboxylic groups plays major role. m-MBA and o-MBA ligands stabilized nanocluster shows noticeable steric hindrance at the gold core's surface, which leading to significantly lowering the binding energy required for the fragmentation of Au-S bond



**Figure 9.** a) diagram shows the synthesis protocol of different structural MBA isomers stabilized Au<sub>25</sub>(MBA)<sub>18</sub> NCs. b) ESI mass spectra Au<sub>25</sub> clusters c) collision induced dissociation breakdown curves for the 4– charge state of o/m/p-MBA stabilized. Reprinted with permission from [85] Copyright 2018 American Chemical Society.

# 2. Application of Nanoclusters in Photocatalysis

Over the course of time, research on relevance of cleaner fuels, alternate potential energy sources as well as tools to alleviate pollution, have been gainful. Research on visible light photocatalysis over the past decade draws much attention in this line. Semiconductor heterogeneous nanotechnology based photocatalysts lasted long enough and showcased their prominence in this specialty. At present, material chemists are busy preparing competent monometallic or hybrid entities by combining conventional semiconductors with suitable pre-catalyst/co-catalysts to bring about the best results in photocatalysis. Metal NCs have proved their supremacy in multiple economical and sustainable processes of photocatalysis such as photodegradation of organic pollutants, photocatalytic H<sub>2</sub> splitting, photoreduction of CO<sub>2</sub>, oxidation and hydrogenation reactions etc.,

ROS e-/h+ fast recombination of e-/h+ of semiconductors, noble metal/metallic/non-metallic moieties on semiconductors support extending photocatalytic activity towards visible range.

The following section discusses about the role of metal NCs in photocatalytic as cocatalyst as well as catalyst in various light conversion processes.

# 2.1. Photodegradation of organic pollutants

Globalization led industrialization, to satisfy the needs of world's population, has led to the steep rise in harmful pollutants in the environment at an alarming rate. The organic pollutants from textile industries majorly constitute azo dyes while inorganic pollutants hold oxidized heavy metals. These under-treated materials containing carcinogenic effluents are being dumped into the soil and water, have already created damages beyond repair to humans as well as to the aquatic flora and fauna. Initiating action plans to safely remove them without the formation of other stable secondary pollutants demanded scrutiny. Methyl Orange (MO), Rhodamine B (RB), Malachite Green (MG) and Methylene blue (MB), some of the commonly found dyes, that have been present in industrial effluents. Reactive oxygen species (ROS) such as superoxide radicals (O<sup>2</sup>.) and hydroxyl radicals (OH<sup>-</sup>) are the prime contributors and starting materials in the degradation of these toxic materials [86].

Titania (TiO<sub>2</sub>), ZnO, SiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and so on have been reported widely as a solution for pollution initiated by organic pollutants through photodegradation [87,88]. These semiconductor systems ensure photostability, low cost, mere toxicity and essential level of oxidative ability. However, the disadvantages of these semiconductors remain a barrier to photocatalytic reactions due to the large bandgap that they offer and it indeed requires UV irradiation for the electron-hole generation, this restricts their use as effective catalyst. As the research studies progressed, metal nanoparticle incorporated versions semiconductors became the focal point. Metal NCs linked to semiconductor systems as support have profoundly influenced the works in photocatalytic degradation of cationic and anionic dye pollutants as they could enable us to engineer the bandgap width [89]

Zhu and co-workers prepared AuNCs coupled with toroid structured per-6-thio- $\beta$ -cyclodextrins placed on TiO<sub>2</sub> surface (TiO<sub>2</sub>-Au NCs@ $\beta$ -CD) provided a better space for the Au cores to interact with the incoming pollutants through a host-guest interaction trap [90]. This synergistic effect between the nanocluster metallic core, peculiar ligand cavities and support system increased the photodegradation rate of methyl orange (MO) to 98% in 10 minutes. Concurrently, the integrated material's rate constant values for photodegradation (1st cycle=0.31min-1, 5th cycle= 0.15min-1) was phenomenal in comparison with TiO<sub>2</sub>(1st cycle= 0.12min<sup>-1</sup>) even after five cycles. Sharma and coworkers studied of Au-TiO<sub>2</sub> conjugated nano assembly were used as light harvester under visible light [91].

The mechanism for photocatalytic degradation of dyes using Au-TiO2 can explained by following reaction pathways

 $Au + hv \rightarrow Au \bullet$ 

 $Au \bullet + TiO_2 \rightarrow h+(Au) + e-(TiO_2)$ 

 $\text{e-(TiO_2)} + \text{O}_2 \rightarrow \text{TiO_2} + \bullet \text{O}^{2\text{-}}$ 

 $\bullet O_{2-} + H + \rightarrow HOO \bullet$ 

 $HOO \bullet + e-(TiO_2) + H+ \rightarrow H_2O_2 + TiO_2$ 

 $H_2O_2 + e_{-}(TiO_2) \rightarrow \bullet OH + OH^{-} + TiO_2$ 

 $h\text{+}(Au) + H_2O \rightarrow Au + H\text{+} + \bullet OH$ 

 $h\text{+}(Au) + OH\text{-} \rightarrow Au + \bullet OH\text{-}$ 

Organic pollutants +  $O_2$ -• or •OH-  $\rightarrow$   $CO_2$ +  $H_2O$  +....

Gowswami et.al created colloidal nanocomposite material with TiO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub> conjugated to silver NCs with captopril as ligand. They have varied the niobium loading in the incorporated product, to investigate the adhesion of the material towards cationic and anionic dyes as well as their photodegradation capability [92]. As per the analysis, the mentioned nanocomposite with 48.1% niobium loading and Ag NCs resulted in ternary junction which narrowed down the recombination rates and the surface acidity caused the Ag NCs ligands end groups to polarize COO<sup>-</sup>, thereby attracting the cationic dyes for effective 100% degradation with high photostability. Spectroscopic techniques validate the fact that Ag NCs are the reason behind absorption in visible light region and themselves act as oxidative sites, also initiates electron transfer from valence band of the NCs to conduction band of nanocomposites. Samai's group made polyethelene imine template Ag NCs incorporated with CeO<sub>2</sub> nanoparticle for degrading Acridin Red dye photocatalytically [93] (Figure 10). XPS mechanistic work and radical experiments pin down their radical pathway leading to 42% to 80% degradation in 2 hours with 1.07% and 3.10% Ag NCs loading respectively. The reduction potential and two oxidational potential vs NHE values were recorded with Cyclic Voltammogram to be -0.64V, 0.07V and 1.03V respectively (Figure 10).



**Figure 10.** Dye degradation of ZnO nanoparticle decorated with AgNCs. Reprinted with permission from [94] Copyright 2019 MDPI.

ZnO nanoparticle decorated with Ag NCs were established as a prospective candidate for Orange II (OII) dye degradation under both UV and white light by Rodriguez and coworkers [94]. Atomic Force Microscopy (AFM) confirmed the deposition of NCs moiety on ZnO rather than substitution of metallic core itself. Additionally, the optimal loading range of Ag on ZnO was found to be 1.3% w/w and it certainly ensures ample number of interaction sites for the pollutants to approach ZnO nanoparticles (Figure 11). Figure 11 shows the spectroscopic and morphological characterization of AgNC decorated ZnO nanoparticle. Vilar-Vidal et.al formulated green emitting stable closed shell electronic structured and recyclable CuNCs to degrade MB under UV and Visible

light irradiation [95]. UV-Vis data and administered multiple photoluminescence emission peaks were an indication of mixture of clusters and LDI-TOF spectrometry approves proposed structural formulas of Cu NCs: [Cu<sub>18</sub>(CH<sub>3</sub>COO)(OH)]<sup>-2</sup> and [Cu<sub>34</sub>O<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub>N(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Na]<sup>-2.</sup>



**Figure 11.** A) UV Visible B) Photoluminescence C) &D) AFM results of ZnO nanoparticle decorated with Ag NCs . . Reprinted with permission from [94] Copyright 2019 MDPI.

Light steered preparation of 3-Mercaptopropyl trimethoxy silane (MPTS) stabilized Au NCs and their performance in photodegradation of MB were examined by Zhou et.al [96]. It was observed that the nanoclusters decolorizes the dye progressively and color fades completely in 60 mins.

Man Cao and his coworkers synthesized a self-assembled silver nanocluster for photocatalytic degradation of sulphur mustard simulant (2-chloroethyl ethyl sulfide, CEES), a toxic vesicant against human proteins and DNA, can cause skin blisters, eye and respiratory system irritation, and even fatal damage. The silver cluster assembled material is prepared using a photosensitizer (5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) as the organic linker and which linked with 12-core silver chalcogenolate cluster to form [Ag<sub>12</sub>(St Bu)<sub>6</sub>(CF<sub>3</sub>COO)<sub>3</sub>(TPyP)]n, (designated as Ag<sub>12</sub>TPyP). They reported 98 % degradation of CEES with 1% loading [97,98].

Wen and co-workers developed a highly stable core-shell type catalyst for photo redox reactions. The photostability of nanocluster were improved by loading it on SiO2 sphere by utilizing multifunctional branched poly-ethylenimine (BPEI) as a surface charge modifying, reducing and stabilizing agent. Then TiO2 were coted SiO2-Au GSH clusters-BPEI to form SiO2-Au GSH clusters-BPEI@TiO2 core- shell structure further significantly improve the photocatalytic efficiency for dye degradation of organic dye (Rh B) [99].

# 2.2. Oxidation and hydrogenation processes

Application of NCs on oxidation and reduction processes are still underway. Oxidation and hydrogenation reactions in most reported cases specifically depend on their electronic structures as electron-hole separation remains the key to it. Researchers have carried out typical oxidation-reduction reactions like high selectivity styrene oxidation [100], aerobic oxidation of amines to imines [101], cyclohexane or phenol derivatives [102], water splitting [103], catalytic hydrogenation [104], pollutants treatment [105], in the presence of metal NCs, especially gold NCs (AuNCs). In 1987, Haruta and co-workers were the first to initiate oxidation of CO with few atom AuNCs along with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, NiO and Co<sub>3</sub>O<sub>4</sub> at low temperatures[106]. After two decades, mechanistic view of photocatalysis of Au<sub>25</sub> nanoclusters with TiO<sub>2</sub> as support under visible and near infrared emissions were illustrated by Kogo and co-workers [107]. They attached AuNCs to TiO<sub>2</sub> so that the excited

electrons could be transferred to the conduction band of TiO<sub>2</sub> with ease and can aid in reduction of Ag+ in the counter electrode and the generated holes (h+) could perform oxidation of donors (phenol derivatives or formic acid) in working electrode (Figure 12).



Figure 12. Photocatalytic oxidation ability. Reprinted with permission from [107] Copyright 2010 Elsevier.

Similarly, Zhu et.al did a comparative study to figure out the capabilities of a set of superatoms to oxidize styrene- Au25(SR)18, Au38(SR)24 and Au144(SR)60 with diameters of 1nm, 1.3nm and 1.6nm respectively [108]. However, their studies reassured the size and electronic structure dependence of photocatalytic abilities and Au<sub>25</sub>NCs gave the highest average of ~27 ± 1.0% as smaller the superatom, higher is the HOMO- LUMO gap (1.3eV). Later, Chen & group loaded [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SR)<sub>5</sub>Cl<sub>2</sub>] on P<sub>25</sub> to covert benzylamines to imines, TOF was recorded to be 152 2h<sup>-1</sup> for 4-methylbenzamine and other amines too showed appreciable conversions (73-99%) [101]. The attempts to learn the possible conversion route using Time Dependent Density Functional Theory (TD-DFT) calculations, Fouriertransform ion cyclotron resonance mass spectrometry (FT-IC-MS) with Electrospray ioinization (ESI) and trapping intermediates with scavengers (K2S2O8 and ammonium oxalate) confirmed the presence of +2 charge on the cluster. Hence the photocatalytically induced electron could lead to oxygen radical formation and thereby persuade conversions. Studies with organic supports too have gained momentum over the years. Gold nanocluster with organic supports (Polyvinylpyrrolidone (PVP) & Polyperoxyacetic acid (PAA)) were analyzed by H.Tsunoyama and co-workers and X-ray photoelectron spectroscopy (XPS) & X-ray absorption near edge structure (XANES) reinforced the existence of negatively charged cluster which led to the production of superoxo- or peroxo- radicals required to jump start the photocatalytic reactions [109]. Their activities and recyclability were keenly observed for CO oxidation. In addition, these set of reactions enlightened research community about the prime role of nanoclusters in oxidation and reduction reactions.

Hamoud and co-workers studied photocatalytic activity Ag NCs encapsulated into zeolite (ZX-Bi zeolite) for photooxidation of methanol under visible light. They have found that the Ag/ZX-Bi exhibits very low activity, compared to activated sample at 200 °C (Ag/ZX-Bi\_200) [110].

#### 2.3. Photocatalytic H<sub>2</sub> production

The demand for green energy sources better suited for the environment is rising due to the reduction and environmental pollution generated by conventional energy resources. While the

distinct qualities shape, Hydrogen gas as an acceptable renewable energy source for a sustainable future [111]. Ahluwalia and coworkers studied the fuel economy of Hydrogen-fuelled fuel cell (H<sub>2</sub>-FCV) vehicles and common gasoline-fuelled passenger cars in 2003 [112]. In 1972, Honda and Fujishima et al. first time discovered that water can be divided into H<sub>2</sub> and O<sub>2</sub> in presence of light. There after various photocatalyst were developed and studied for photocatalytic water splitting reaction. A. Fujishima and K. Honda, Nature, 1972, 238, [36,37].

Catalyst based on the metals such as Ti, Cobalt, Nickel, Iron, Molybdenum are widely used for as catalyse for the electrochemical H2 production [113]. Thereafter, the catalytic efficiency of metal oxides, metal nitrides were enhanced by incorporating suitable cocatalyst on these semiconducting materials. The Co-catalytic activity of metal nanoclusters was studied in the recent past due to its excellent optical, electronic and catalytic activity. The nanoclusters were incorporated into various semiconductors to enhance the catalytic activity by suppressing the electron-hole recombination rate.

Kamat et al studied the photoelectrochemical and photocatalytic production of H<sub>2</sub> using GSH stabilised AuNCs-TiO<sub>2</sub> film hybrid system under visible light irradiation [113].

Liu et al carried out a detailed investigation on the photocatalytic activity of AuNCs as cocatalyst in highly ordered nanoporous layer-covered TiO<sub>2</sub> nanotube arrays (NP-TNTAs). The photocatalytic activity of NP-TNTAs/AuNCs analysed by monitoring photodegradation of organic dyes, photocatalytic reduction of aromatic nitro compounds and photoelectrochemical water splitting [114].

The quantum confinement of MNCs enables the charge transfer, easy adsorption and desorption of intermediates and thereby fastens the photocatalytic hydrogen evolution reactions (HER) [29].

Glutathione stabilised AuNCs (Au<sub>25</sub>(SG)<sub>18</sub>) were incorporated on BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> used for photocatalytic water splitting. The catalytic activity of sub nanometer sized Au- BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> of compared with larger sized gold nanoparticle and found 2.6 times higher catalytic activity for AuNC composite [115]. Similarly, AuNCs loaded on SrTiO<sub>3</sub> were studied for HER and found the enhanced catalytic activity of SrTiO<sub>3</sub> in presence AuNCs as Cocatalyst [116]. Recently Hanieh Mousavi and Co-workers studied the photocatalytic production of H2 using AuNCs as Co-catalyst. They have prepared a nanocomposite (Au<sub>101</sub>NC-AlSrTiO<sub>3</sub> -rGO) containing AuNCs, RGO and AlSrTiO<sub>3</sub> and the composite showed enhanced photocatalytic water splitting under UV light irradiation [117].

Sub-nanosized clusters of silver adsorbed on specific sites of Gold nanorods (GNRs) disturb the growth symmetry of Au facets and leads to anisotropy [118]. In the presence of hole scavenger namely ethanol and in the absence of electron scavengers like O<sub>2</sub>, the photoelectrons accumulate in GNRs with Ag clusters. Moreover, on low UV light irradiation, Ag3 clusters at a concentration of 0.43µg within the GNRs shows high H2 production efficiency of 10%. Similarly, loading of 1 wt% of sub- nm Au clusters in CdS uplifts the photocatalytic H2 production about 35 times than the unmodified CdS under visible light [119]. The comparison of sub-nm Au loaded CdS with Pd/CdS and Rh/CdS of similar size revealed that the 3-nm sized Au/CdS as a better co-catalyst.

Likewise monolayer niobate (HTi2NbO7) nanosheets with Pt nanoclusters proved themselves as potential photocatalysts for high H2 production [120]. Monolayer niobate nanosheets enable the charge separation between photoelectron and holes and displays 5 times higher photocatalytic H2 production than that observed in its layered form. 1 wt% Pt nanoclusters loaded to niobate nanosheets via photoreduction presented increased activity due to the close contact between the HTi2NbO7 nanosheets and Pt nanocluster. On light irradiation electrons migrated to the conduction band moves to surface of nanosheets. Since Pt have a higher work function than niobate nanosheets, these electrons in the surface of nanosheets transfers to Pt and form H2.

Moreover, by monitoring nanocluster size, the photocatalytic activity of the whole system can be varied. Heiz, Feldmann and co-workers modified cadmium sulfide (CdS) nanorod with a series of Pt NCs such as Pt<sub>8</sub>NC, Pt<sub>22</sub>NC, Pt<sub>34</sub>NC, Pt<sub>46</sub>NC, Pt<sub>68</sub>NC and found that, Pt<sub>46</sub>/CdS exhibits the highest activity for photocatalytic water splitting, due to the well-known quantum confinement effect., were the bandgap increases with a decrease of the NC size [121]. Rongchao Jin and his coworkers reported a detailed review on the effect of size of nanocluster in photocatalysis [122] While Cheng and co-workers[118] revealed the effective co-catalytic effect of sub nano sized Pt-Au alloy clusters in photocatalytic H2 evolution. The synergistic effect of 0.5 wt% of both Pt and Au clusters dispersed in TiO<sub>2</sub> (Pt-Au/T) creates increased charge separation and 80.1 µmol h<sup>-1</sup> of H<sub>2</sub> is evolved with a quantum efficiency 50% at 365nm. As like HER, similar strategy have been established for enhanced efficiency for OER, by using nanocluster as cocatalyst [123]. Au<sub>25</sub> NC- CoSe<sub>2</sub> composite were studied for OER activity found enhanced OER activity in presence of Au<sub>25</sub>/CoSe<sub>2</sub> obtained current density of 10 mA cm<sup>-2</sup> at small overpotential of ~0.43 V (cf. CoSe<sub>2</sub>: ~0.52 V). The ligand and gold cluster size can also tune the catalytic performance of the composites.

The photocatalytic activity of Co-catalyst was studied by monitoring doping of heteroatom on the nanoclusters. Negishi et al. demonstrated that doping of Pt on Au<sub>25</sub> NC enhances the water splitting activity, while Pd doping reduces the water splitting activity. They proposed that the doping position plays the role in the catalytic activity. The doped Pd is located at the surface of the metalcluster cocatalyst, whereas Pt is located at the interface between the metal-cluster cocatalyst and the photocatalyst [124]. Yang et al. also illustrated the effect of heteroatom doping on the photocatalytic activity of PtAg<sub>24</sub>-loaded graphitic carbon nitride (PtAg<sub>24</sub>/g-C<sub>3</sub>N<sub>4</sub>) and found that PtAg<sub>24</sub>/g-C<sub>3</sub>N<sub>4</sub> shows higher efficiency for photocatalytic H<sub>2</sub> production than Ag<sub>25</sub>/g-C<sub>3</sub>N<sub>4</sub> alone [125]. In addition to the above studies, scientist are exploring the efficiency of photocatalytic water using composites including metal NCs with g-C<sub>3</sub>N<sub>4</sub> nanosheets,TiO<sub>2</sub>, etc [126].

# 2.4. Photocatalytic CO2 reduction

Nowadays, reducing greenhouse gas emissions from various Photovoltaic (PV) systems has become one of the scientific community's primary concerns [127]. Carbon dioxide is one of the chief greenhouse gases that influence the heat content of earth's atmosphere [1]. With a focus on reducing carbon dioxide emission, novel technologies are adopted for the production of commodity chemicals by using carbon dioxide as feedstock [128]. The conversion of carbon dioxide to value-added chemicals or to other hydrocarbon fuels such as methane, ethylene and carbon monoxide by utilizing energy from non-fossil resources such as solar energy not only increases the carbon recycling but also assists in fuel production [129,130]. Solar-driven transformation of carbon dioxide to useful products could be achieved through two major approaches such as photocatalytic and electrochemical CO2 reduction processes [131]. In 1978, M. Halmann utilized p-type semiconductors for photoelectrochemical reduction of carbon dioxide are identified as useful feedstocks [133]. The former is utilized for synthesising other hydrocarbon fuels while latter is used for Fischer–Tropsch syntheses.

CO2 is a thermodynamically stable molecule and catalysts assist the electrochemical CO2 reduction reactions and aid in achieving desired product [134]. MNCs possess ultrafine structure, electronic and optical properties [34] and function both as electrocatalyst and photocatalysts [27]. Various features of MNCs such as size, core, composition, surface ligands, charge state, geometry influences its electro and photocatalytic behaviors [27]. Colombo Jr and coworkers studied femtosecond electron-hole recombination in TiO2- nanoclusters and explained the intracluster dynamics [135]. The study demonstrates the steps involved in electron trapping, recombination and formation of long-lived species. Kauffman et. al studied the reversible weak interaction between CO<sub>2</sub> and Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>- clusters [136]. The electrochemical reduction of CO<sub>2</sub> using Au<sub>25</sub> catalyst in aqueous 0.1 M KHCO<sub>3</sub> showed maximum CO production at -1.0 V with 100% Faradaic efficiency. The electrochemical CO<sub>2</sub> reduction performance of silver nanoclusters confined in bovine serum albumin (AgNC@BSA) is enhanced via polyoxometalates [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4</sup> [137].

The presence of suitable photocatalyst possessing features such as high light absorptive power, convenient catalytic sites and low activation energy enhances the photocatalytic reduction of CO2 [138]. The small-scale size of MNCs of about 2nm, interfacial surface, energy gap, tunable chemical properties, quantum confinement are the advantages of ultrafine MNCs for CO<sub>2</sub> reduction over metal nanoparticles [139]. Titanium dioxides or titania are widely used semiconductors and have broad range of applications including photoreduction of  $CO_2$  [140]. Doping and decoration with other elements or metal ions strengthens its photocatalytic activity by reducing its band gap. In addition to these elements, attaching nanoclusters to TiO<sub>2</sub> makes it a potent visible light photocatalyst [141].

Inserting Ti3+ ions into the TiO<sub>2</sub> creates isolated states in the presence of UV and visible light. The electrons are trapped in these states and due to recombination with charge carriers' photocatalytic activity is decreased. On combining Ti<sup>3+</sup> introduced TiO<sub>2</sub> with nanoclusters of Cu (II) oxides (i.e., Cu (II)-TiO<sub>2</sub>@Ti<sup>3+</sup>), electrons from the isolated states of Ti<sup>3+</sup> moves to surface of Cu (II) nanoclusters. Hence, the photocatalytic activity of Cu (II)-TiO<sub>2</sub>@Ti<sup>3+</sup> under visible light is raised and decomposed gaseous 2-propanol (IPA) completely to yield ~18 µmol CO<sub>2</sub> generation. On UV irradiation, copper oxide (CuxO) nanoclusters incorporated in strontium titanate nanorod thin film [142] and niobate sheets [143] showed selective CO production form photocatalytic CO<sub>2</sub> reduction.

Product selectivity towards CH<sub>4</sub> and CO is shown by brookite TiO<sub>2</sub> quasi nanocubes (BTN) on surface decoration with Cu-nanoclusters (Cu-BTN) under xenon lamp irradiation [144]. XRD diffraction peaks exhibits the presence of Cu-nanoclusters only on the surface of BTN. The total consumed electron number (TCEN) is utilized for examining overall photocatalytic CO<sub>2</sub> reduction. At a 1.5 % optimum concentration of Cu-nanoclusters in BTN, maximum photoactivity with TCEN of 150.9  $\mu$ molg<sup>-1</sup>h<sup>-1</sup> and highest production rate of 4.23  $\mu$ molg<sup>-1</sup>h<sup>-1</sup> CO and 17.81  $\mu$ molg<sup>-1</sup>h<sup>-1</sup> CH<sub>4</sub> is observed (Figure 13).



**Figure 13.** CO/CH<sub>4</sub> production rates (a) and the corresponding total consumed electron numbers (TCEN) (b) for the CO<sub>2</sub> photoreduction over pristine BTN and Cu-BTN production with different Cu loading contents during the initial 2 h of irradiation. Reprinted with permission from [144] Copyright 2017 American Chemical Society.



**Figure 14.** In situ DRIFTS IR spectra of H<sub>2</sub>O (a) or CO<sub>2</sub>/H<sub>2</sub>O vapor (b) interaction with pristine BTN, 1.5% Cu-BTN, and 0.5% Cu/BTN. Reprinted with permission from [144] Copyright 2017 American Chemical Society.

In situ DRIFTS IR spectra suggested CO<sub>3</sub><sup>2-</sup> intermediate for CO formation and HCO<sub>3</sub><sup>-</sup> for CH<sub>4</sub> (Figure 14a). Cui at.el worked on the role of bridging ligand and metal ions grafted to Au nanoclusters in photocatalytic conversion of CO<sub>2</sub> to CO [145]. The functionalization of L-cysteine with glutathione protected Au nanocluster (Au-GSH NCs) helps in binding of metal cations such as Fe<sup>2+</sup> Co<sup>2+</sup> Ni<sup>2+</sup> and Cu<sup>2+</sup> and thus improves the selective CO production. Under visible light along with CO<sub>2</sub> and H<sub>2</sub>O, Co<sup>2+</sup> cation within Au nanocluster (Auc-C-Co) at optimum concentration of 4 µmol exhibited maximum CO production of 3.45 µmol.gcat<sup>-1</sup>h<sup>-1</sup>. Similarly, via 3-mercaptopropionic acid (MPA), Co<sup>2+</sup> is grafted to surface of Au nanocluster (Auc-MPA-Co) and exhibited high-rise in photocatalytic activity compared to (Au<sub>c</sub>-C-Co) through strong interlinkage between S-metal cation (Figure 15).



**Figure 15.** (a) Average production rates of CH<sub>4</sub>, CO and H<sub>2</sub> in light drven CO<sub>2</sub> reduction with H<sub>2</sub>O in the presence of TEOA, catalyzed by 10-mg Au<sub>c</sub>-MPA-Co grafted with 4  $\mu$ mol Co<sup>2+</sup> (b) The binding energy of S-Co bond in the coordination of Co with L-cys and MPA. Reprinted with permission from [145] Copyright 2018 American Chemical Society.

Zhang and co-workers [143] developed a quasi-ternary complex consisting of polymethacrylic acid stabilized Ag nanoclusters (AgNCs-PMAA), carbon monoxide dehydrogenase (CODH) and TiO<sub>2</sub> nanoparticles and under visible light CO2 reduction results generation of CO with 20 s<sup>-1</sup> turnover frequency at 25°C . Jiang, Y et. al [146] upgraded the chemical stability of gold nanoclusters (Au-NCs) by combining with metal organic framework (UiO-68) through N-Heterocyclic carbene stabilizing ligands (NHC) and denoted as AuNC@UiO-68-NHC. The photocatalytic activity AuNC@UiO-68-NHC is observed to be enhanced as a result of strong covalent bond formation between AuNCs and UiO-68 facilitated by Au-NHC bridges. This enabled easy movement of excited electrons from the Fermi levels of Au-NCs to conduction band of UiO-68-NHC and thus the recombination of photogenerated electrons and holes are reduced (Figure 16) [146].



**Figure 16.** (a) CO evolution period of photocatalytic CO<sub>2</sub> reduction using UiO-68-NHC, Au-NC@UiO-68-NHC, UiO-68-NH2 and Au/ UiO-68-NH<sub>2</sub> as photocatalysts upon AM 1.5G irradiation. (b) Time courses of photocatalytic CO<sub>2</sub> reduction on Au-NC@ UiO-68-NHC under AM 1.5 G irradiation for 12h, with evacuation every 4 h (dashed line). . Reprinted with permission from [146] Copyright 2021 Wiely.

The selective production of CO and presence of CH<sub>4</sub> and H<sub>2</sub> as side product is observed. Billo and coworkers developed effective photocatalyst with dual sites by making oxygen vacancies in Ninanoclusters loaded in black TiO<sub>2</sub> (Ni/TiO<sub>2</sub>[Vo]) [147]. Ni and oxygen defective sites acts as dual sites, lessen the C-O bond strength and supports the separation of charge carriers (Figure 17). On light irradiation from halogen lamp, Ni/TiO2[Vo] produced 10 µmol.g-cat-1 of acetaldehyde which is 18 times higher than TiO<sub>2</sub>. Thus the study refers to a different approach for enhancing photocatalytic CO<sub>2</sub> reduction by introducing active dual sites in photocatalyst.



**Figure 17.** (a) Band edge positions. (b) Schematic illustration of photocatalytic CO<sub>2</sub> reduction mechanism of Ni/TiO<sub>2</sub>[Vo]. Adapted from Ref <sup>146</sup>.

Recently, Mohamad El-Roz et al de prepared a silver nanocluster-based catalyst for the conversion of formic acid to  $CO_2$  and  $H_2$  under visible light irradiation. Here the nanocluster was incorporated into nano sized zeolite crystal <sup>145</sup>.

Table 1: Summary of Literature Reports on the use of nanocluster in Catalysis

Sl	Photocatalyst	Co catalyst	Application	Efficiency	Referenc
No					e
1	TiO <sub>2</sub>	AuNC	Photodegradation	98% degradation in	[90]
			of dyes	10 minutes	
				exposure.	
2	TiO2/Nb2O5	AgNC	Photodegradation	100% degradation	[92]
			of dyes.		
2	CaOa	A «NIC	Photodogradation	80% degradation in	[02]
5		Agive	of dves	2 hours	[93]
			of uyes.	2 110413	
4	ZnO	AgNC	Photodegradation	100% degradation	[94]
	nanoparticle		of dyes.	in 1 hr	
	CHNC	Na	Dhata da ara datian	1000/ do and do tion	[05]
5	Curve	Cocatalvet	of dyes	in 1 69hr	[93]
		Cocatalyst	of uyes.	in i onii	
6	AUNC	Ne	Photo dogra dation	100% doors dation	[06]
0	Aune	cocatalyst	of dyes	in 1 hr	[90]
		cocatalyst	of uyes.		
7	AgNC-	No	Photodegradation	98% degradation	[98]
	assembled	cocatalyst	of dyes.		
	materials				
8	TiO2 core-	SiO2-A11	Photodegradation	99.1% degradation	[90]
0	shell	GSH	of organic dyes	in 0.5 hr	[77]
	onen	clusters	or organic dyco.		

9	TiO2	Au25 NC	Oxidation of phenol derivatives and ferrocyanide and reduction of Ag+, Cu2+ and oxygen	27 ± 1.0%	[107]
10	Auzone	Catalyst	and hydrogenation of $\alpha$ , $\beta$ -unsaturated ketone	27 ± 1.0 %	[100]
11	TiO2	AuNC	Oxidation of benzylamines to imines	73-99%	[101]
12	Zeolite (ZX-Bi zeolite)	Ag NC	Photooxidation of methanol	49.60 mmol·g <sup>-1</sup> ·cm <sup>-2</sup> after 12 h of reaction	[110]
13	TiO2	AuNC	Production of H2	0.3 mmol of hydrogen/h/g	[148]
14	TiO2 nanotube arrays (NP- TNTAs).	AuNC	Photodegradation of organic dyes, photocatalytic reduction of aromatic nitro compounds and photoelectrochemic al water splitting.		[114]
15	BaLa4Ti4O15	AuNCs	Photocatalytic water splitting	190 μmol/h	[115]
16	SrTiO3	AuNC	Hydrogen evolution reaction	41.2 µmol/h of H	[116]
17	AlSrTiO₃ and rGO	AuNCs	photocatalytic production of H2, photocatalytic water splitting	385 ± 22 nmol h <sup>-1</sup>	[117]
18	Gold nanorods (GNRs)	AgNCs	Hydrogen evolution reaction	10%	[118]

19	Monolayer niobate (HTi2NbO7)	Pt NC	Higher H2 production	10 μmol h <sup>-1</sup>	[120]
20	Modified cadmium sulfide (CdS) nanorod	Pt NC	Photocatalytic water splitting	1.5‰ h <sup>-1</sup>	[121]
21	BaLa4Ti4O15	Au24Pd NCs and Au24Pt NCs	photocatalytic H2 evolution	100-150 μmolh-1	[124]
22	Graphitic carbon nitride (g-C3N4)	PtAg NC	photocatalytic H2 production	39.7 μmolh-1	[125]
23	Brookite TiO2 quasi nanocubes	CuNCS	Photocatalytic CO2 reduction	150.9 μmol g <sup>-1</sup> h <sup>-1</sup>	[144]
24	Metal cations - Fe2+, Co2+, Ni2+ and Cu2+	Au NCs	Photocatalytic CO2 reduction	3.54 µmol · <sub>gcat</sub> -1 · h <sup>-1</sup>	[145]
25	carbon monoxide dehydrogenas e (CODH) and TiO2 nanoparticles	Ag NC	Photocatalytic CO2 reduction	turnover frequency of 20 s <sup>-1</sup>	[149]
26	Au-NCs		Photocatalytic CO2 reduction	57.6 µmol g-1h-1	[146]
27	TiO2	Ni-NCs	photocatalytic CO2 reduction	10 μmol g-cat <sup>-1</sup>	[147]
28	AgNC	No Cocatalyst	reforming of formic acid to H2 and CO2	99% selectivity	[150]

# 5. Conclusion and Future Perspective

Metal NCs are an under-explored class of nanomaterials with unimaginable grade of potential. The review summarizes recent progress in the metal nanocluster based photocatalyst for various photocatalytic reactions, correlating it to their structure and properties to boost single metal, alloy hybrid system's and nanocomposite systems effectiveness. However, research on metal NCs hasn't surpassed embryonic stage yet. In particular, preventing aggregation, effective capping agents or stabilizers, optical & electronic structures, metal-support bonding, mechanistic learning, in situ

characterization techniques, structural model theories and appreciable yield yearn for more attention. Gold and AgNCs still dominate a major fraction of scientific publications in this domain, works on other transition metals could turn out to be more productive and cost-effective. Recyclability of metal NCs in photocatalysis with adequate stability after multiple cycles have to be extensively analyzed. At the same time, computer simulations could open the world of possibilities of metal NCs to us and recent additions to the software have proven their effectiveness. Of note, NCs can plausibly be the answer for low carbon fuels, a milestone to sustainable development and an affordable photocatalyst.

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