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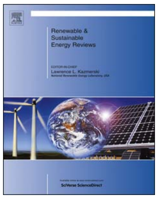

Metal clusters: New era of hydrogen production

Yasser Attia[a,*], Mohamed Samer[b,*]

[a] National Institute of Laser Enhanced Sciences (NILES), Cairo University, 12613 Giza, Egypt
[b] Department of Agricultural Engineering, Faculty of Agriculture, Cairo University, 12613 Giza, Egypt

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ABSTRACT

Clusters show intermediate properties between the isolated atoms and the bulk metals and represent the most elemental building blocks in nature (after atoms). They are characterized by their size, which establish a bridge between atomic and nanoparticle performances, with properties completely different from these two size regimes. If particle size becomes comparable to the Fermi wavelength of an electron, i.e. < 2 nm, then this is a cluster. Reducing the size from the bulk material to nanoparticles displays a scaling behavior in physical properties in the later ones, due to the large surface-to-volume portion. Through further size reduction, entering into the subnanometric cluster region, physical properties are largely affected by strong quantum confinement. These quantum size effects (HOMO-LUMO gap), the small size and the specific geometry grants subnanometric clusters with entirely novel properties, including cluster photoluminescence, enhanced catalytic activity, *etc.* In this literature review, an introduction to the physical properties of clusters is reported; the controlled synthesis methods and the catalytic properties in hydrogen evolution. Hydrogen (H_2) production by water splitting is hindered mainly by the lack of low-cost and efficient photocatalysts. Here, we show that sub-nanometric metal clusters can be used as photocatalysts for H_2 production in the presence of holes or electrons scavengers by water splitting. This illustrates the considerable potential of very small zerovalent, metallic clusters as novel atomic-level photocatalysts.

1. Introduction

Recently, fossil energy resources have depleted fast as well as serious environmental problems caused by the ever increasing carbon dioxide (CO_2) content of the atmosphere. To reduce CO_2 emissions and fulfill the ever-increasing energy demands, much research efforts have been devoted to develop sustainable and renewable energy sources, which are environmentally friendly, cost-effective and clean. In the recent years, photoelectrochemical water splitting which could produce hydrogen (H_2) using sunlight and semiconducting photoelectrodes has attracted great interest of scientists due to its cleanness and renewable characteristics. Hydrogen is a chemical fuel with high energy density, and it is an environmentally clean energy source since it does not emit greenhouse gases (GHGs) when burned. Therefore, hydrogen is recognized as a clean energy since no additional CO_2 is emitted when used. Furthermore, hydrogen can be obtained directly from water and solar radiation, both of which are the abundant, widespread, renewable resources. Therefore, hydrogen has attracted intensive interest as a promising and sustainable energy supply for replacing fossil energy resources in the future.

Investigations of H_2 production from the solar water splitting have increased in recent researches due to its environmental cleanness and unlimited utilization of solar energy and renewable characteristics in converting solar energy into chemical energy. The combustion of H_2 is not accompanied by greenhouse gases (GHGs) emission such as CO_2 and CO. Therefore, one of its enormous benefits is zero-emission of GHGs if H_2 is used as the fuel for power generation through fuel cells or turbines.

Photocatalytic system to generate hydrogen from water provides us a green and renewable way to generate hydrogen fuel. The splitting of water into hydrogen and oxygen has been studied continuously in the years following the discovery of photocatalytic water splitting using a semiconductor photoelectrode, TiO_2 in a Photoelectrochemical cell (PEC), as was demonstrated by Fujishima and Honda [1].

Clusters display intermediate properties between the isolated atoms and the bulk metals and represent the most elemental building blocks in nature (after atoms). They are characterized by their size, which set up an overpass between atomic and nanoparticle behaviors, with properties entirely different from these two size regimes. If particle size becomes comparable to the Fermi wavelength of an electron, i.e. $<$ 2 nm, then this is a cluster.

The objectives of this review are:

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* Corresponding authors.
E-mail addresses: yasserniles@niles.edu.eg (Y. Attia), msamer@agr.cu.edu.eg (M. Samer).

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1. Defining clusters and discussing their properties and role in hydrogen production.
2. Investigating the charactaristics of clusters based on their size, and the subsequent properties difference based on the size.
3. Studying the role of clusters as photocatalysts in hydrogen production by water splitting.

2. Photocatalysts and co-catalysts for H_2 production

In the twenty-first century, more and more greenhouse gas emissions from fossil fuels have caused the obvious greenhouse effect and created a serious impact on the environment. Hence, looking for alternative fuels and environmentally friendly green energy have become a major concern. Recently, H_2 energy is expected to be the ideal alternative for green energy owing to its cleanliness and high efficiency. Particularly, the photocatalytic H_2 production from water splitting using solar energy is a most potentially clean and renewable source for H_2 fuel, where Fujishima and Honda firstly reported the photo-oxidation of water on a semiconductor TiO_2 electrode [1,2].

To achieve this goal, many efforts have been devoted to the development of highly active photocatalysts, including metal oxides (Ta_2O_5 and $SiTiO_3$) [3,4], metal sulfides (CdS, PdS/CdS and $AgInZn_7S_9$) [5–7] and metal oxynitrides or oxysulfides (TaON, GaN:ZnO and $Sm_2Ti_2O_5S_2$) [8–10]. At present, the perovskite-type tantalate, $NaTaO_3$, has been widely studied because of its outstanding performance in photocatalytic water splitting into H_2 and O_2 under ultraviolet-light irradiation [11,12]. However, because of the relatively wide energy band-gap ($E_{bg} = 4.0$ eV and $\lambda < 310$ nm), as a photocatalyst the $NaTaO_3$ only absorbs the ultraviolet-light to perform the photocatalytic reaction. That is, the $NaTaO_3$ cannot be active under visible-light irradiation. Therefore, it is necessary to provide more UV-light in order to uphold higher photocatalytic hydrogen evolution activity of $NaTaO_3$. Unfortunately, ultraviolet-light only accounts for less activities than 5.0% of the solar light, which leads to the solar energy utilization rate being extremely low. In order to obtain a high solar energy utilization rate it must try to utilize the visible-light (~48%) and infrared-light (~44%) in solar light [13–16]. Recently, some research groups reported the application of the photocatalysts combined with up-conversion luminescence agents in photocatalytic degradation of organic pollutants [17–20] and photocatalytic hydrogen production from water splitting [21]. The technology combining with up-conversion luminescence agents can not only keep a high photocatalytic activity of wide bandwidth TiO_2 photocatalysts (E_{bg} = =3.2 eV and $\lambda <$ 380 nm), but also effectively uses solar light to undertake photocatalytic reaction. Accordingly, it can also be considered to combine up-conversion luminescence agent ($Er^{3+}:YAlO_3$) with $NaTaO_3$ photocatalyst ($E_{bg} = 4.0$ eV and $\lambda <$ 310 nm), which may attain the purpose of making the wide bandwidth of $NaTaO_3$ effectively utilize solar light to carry out photocatalytic reaction. In this combined photocatalyst, the $Er^{3+}:YAlO_3$, which was reported to be able to generate one high-energy photon by absorbing two or more incident low-energy photons [22], has been employed for converting infrared and visible lights to ultraviolet light that can effectively activate the $NaTaO_3$ photocatalyst.

In order to obtain the best catalytic activity of photocatalyst the use of some co-catalysts is inseparable. The co-catalysts loaded on semiconductor photocatalysts play an essential role in the production of H_2 and O_2 [23–26]. For photocatalytic reactions caused by semiconductor materials, the co-catalysts can promote the separation of photogenerated electrons (e^-) and holes (h^+). Moreover, the co-catalysts can also offer the low activation potentials for H_2 or O_2 evolution and be often served as the active sites [27–29]. Therefore, the loading of proper co-catalysts can greatly enhance the activities of photocatalysts [30–33]. In most work reported so far, mainly some noble metals (for example: Pt and Au) or metal oxides (for example: NiO and RuO_2) have been used as the co-catalysts, while some inexpensive inorganic compounds such as sulfides of transition metals can also be used as co-catalysts in photocatalytic H_2 production in recent years. Kudo et al. [34] proposed that the $NaTaO_3$ doped with 2.0 mol% La and modified by a NiO co-catalyst under UV-light can improve the efficiency of water-splitting hydrogen production. Lin et al. [35] prepared a Nb_2O_5 catalyst enclosing pure metal particles, such as Pt and Au, to investigate the photochemical hydrogen production. Xu et al. [20] reported that the MoS_2 as a co-catalyst loaded on CdS for photocatalytic H_2 production. These results showed that the addition of metal particles, metal oxides or metal sulfide into the photocatalyst materials effectively enhanced the photocatalytic activity and hydrogen production efficiency [35]. Additionally, it pointed out that the use of ultraviolet-light sources and higher concentrations of sacrificial reagents can effectively enhance the hydrogen production rate [36–38]. However, the researches on the different factors affecting co-catalyst materials in photocatalytic hydrogen production under visible-light conditions remained insufficient. Particularly, the comparison of different co-catalyst materials in hydrogen production efficiency from low-concentration methanol solution (methanol as sacrificial reagents) and even long-term hydrogen production assessments have not gotten much attention.

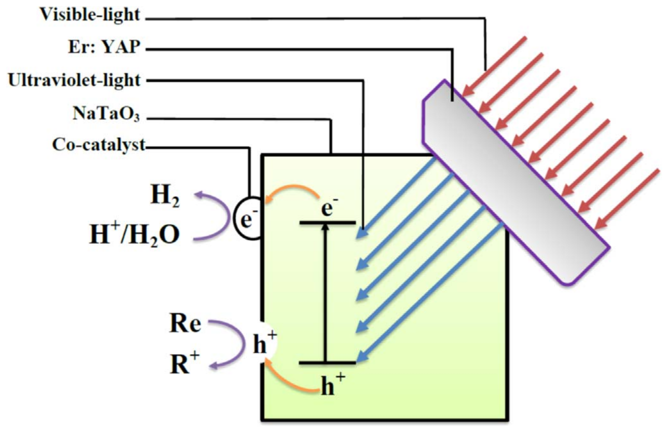

Fig. 1. Photocatalytic hydrogen production principle and process of co-catalysts under visible-light irradiation (Amended and redrawn after Lu et al. [2]).

Fig. 1 shows visible-light photocatalytic hydrogen production principle and process of co-catalysts (CuO, MoS_2 and Pt) loading $Er^{3+}:YAlO_3/NaTaO_3$ under visible-light irradiation.

3. Solar reactors for H_2 production

Thermochemical cycles are known as appropriate processes to generate hydrogen in a sustainable way, utilizing water as input and concentrated sunlight as heat source. In common two-step metal oxide based cycles, a metal oxide (MO) is reduced at high temperature liberating oxygen ($MO_{ox} = MO_{red} + \frac{1}{2}O_2$) and successively re-oxidized by water at lower temperature ($MO_{red} + H_2O = MO_{ox} + H_2$). The complete process splits water, producing hydrogen and oxygen in separate steps [39]. Numerous active chemical substrates were investigated, together with different reactor concepts [40–46], for cycles operating in the 1000–2000 °C temperature range. Such temperature levels are challenging and pose severe demands on materials and reactor design [47,48]. Varsano et al. [39] described a solar concentration facility (~1 kW), where this facility is a solar furnace, composed of one heliostat (2.2×2.0 m^2), with azimuthal and vertical sun tracking system driven by photocells, and a parabolic reflector (diameter 1.5 m, horizontal axis), which has a focal distance of 0.64 m and a concentration factor of about 600 (Fig. 2). The concentrated solar radiation is directed towards the reactor-receiver cavity, placed in the focus of the concentrating dish. A pyranometer is positioned between the heliostat and the parabolic mirror to quantify the reflected radiation from the heliostat. The incident solar radiation has been constantly monitored and recorded. Although no automatic control of the incoming solar