Solar Photochemical Reduction and Oxidation of Water and Related Aspects

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Conversion of solar energy to useful chemicals has become necessary for finding solutions to energy and environmental issues. One of the means is to use of solar energy for the reduction of water to generate hydrogen or for the reduction of CO₂ to useful chemicals. In spite of substantial effort, the discovery of stable and efficient photocatalysts remains a challenge, although some encouraging results have been reported. In this article, we provide a brief perspective of the current status of solar water splitting and reduction of CO₂.

Keywords: Artificial Photosynthesis; Hydrogen Generation; Oxygen Evolution; Photocatalysis; Reduction of CO₂; Water Splitting.

1. INTRODUCTION

Use of solar energy to produce sustainable chemical fuels is an important means of solving the serious energy problem. These chemical fuels include production of high energy density hydrogen, carbon monoxide, methanol, methane, etc. This objective is achievable by mimicking natural photosynthesis artificially in the laboratory, generally referred to as artificial photosynthesis¹. Artificial photosynthesis is a fascinating topic of research wherein hydrogen is produced from water by photochemical or photoelectrochemical means². Besides generation of hydrogen by using solar irradiation, photochemical reduction of CO₂ to useful chemicals is equally important, since elimination of CO₂ or decrease of its concentration in the atmosphere is a burning problem facing mankind.

In photocatalytic splitting of water, solar energy is stored in the form chemical bonds in hydrogen associated with a Gibbs free energy change of +237 kJ/mol. Akin to natural photosynthesis, it is an uphill reaction. In this article, we present the basics and recent developments in photochemical water splitting and also discuss recent progress in the reduction of CO₂.

2. NATURAL VERSUS ARTIFICIAL PHOTOSYNTHESIS

2.1. Natural photosynthesis

Solar energy is stored in the form of chemical bonds in the process of natural photosynthesis. In natural photosynthesis, two pigments, P700 and P680 play a crucial role in the light absorption and in the cascade of electron-relay channels assisting the spatial separation of charges with an efficiency of near unity. This process is also known as the Z-scheme. Holes confined to photosystem II are efficiently utilized by the water oxidation complex (WOC) for the oxidation of water whereas the electrons confined to photosystem I are efficiently utilized for the reduction of NADP⁺ to NADPH. NADPH is used for the reduction of CO₂ to carbohydrates in subsequent dark reactions.

2.2. Artificial photosynthesis

The principles of natural photosynthesis are successfully adopted and embedded in artificial systems based on the use of advanced materials^{3,4}. The design and processing of photocatalysts has resulted in the discovery of several

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promising photocatalysts for the splitting of water to hydrogen and oxygen. Half-reactions of the reduction and oxidation of water are as follows:

The entire process of photocatalytic water splitting is divided into three steps (**Figure 1**). They are,

- (i) Absorption of photons of sufficient energy by the photocatalyst
- (ii) Generation, separation and migration of charge carriers to the active sites
- (iii) Reduction of water and oxidation of water at respective reaction sites

One can choose suitable photocatalysts for the splitting of water based on their band edge positions relative to the reduction potentials of water reduction and oxidation. As shown in **Figure 1**, a semiconductor with a negative conduction band (CB) and positive valence band (VB) relative to the water reduction and oxidation potentials, respectively, is thermodynamically suitable for splitting water. The process can be either one-step or two-step depending on the process

involved (**Figure 2**). Generation of one electron and one hole, requires one photon in a one-step process whereas it requires two photons in a two-step process. The physical and chemical processes involved in photocatalytic water splitting have different time scales. Generally, the time scales of surface redox reactions (water reduction and oxidation) are longer compared to either recombination or relaxation. Therefore, finding suitable means to prolong the life-times of charge carriers is essential.

3. WATER SPLITTING

Producing hydrogen and oxygen from water in a ratio of 2:1 is known as water splitting. Photocatalysts employed for water splitting range from wide bandgap to narrow bandgap semiconductors. Generally, narrow band gap materials are preferred for the solar energy conversion process owing to their capacity to absorb maximum fraction of sunlight. It is common practice to modify the electronic band structure of wide band gap materials by doping or forming solid solutions for the efficient sunlight harvesting. To evaluate the activity of water reduction and oxidation independently, it is customary to use sacrificial agents. For the reduction of water, the sacrificial electron donors such as Na_2S - Na_2SO_3 , methanol, benzyl alcohol are used. Scavenger quickly consumes holes and leaves behind the excited electrons. These electrons possess longer life-time and can be efficiently utilized. Similarly,

Figure 1. Schematic representation of (a) the steps involved and (b) relative energy levels of photocatalytic water splitting. (c) Comparison of band positions of semiconductors relative to the redox potentials of water. Reproduced with permission from Ref. 3. Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

electron acceptors such as AgNO_3 and $\text{Na}_2\text{S}_2\text{O}_8$ are used for the oxidation of water.

3.1. Overall water splitting

Of the photocatalysts that have been discovered, several of the materials contain the metal ions with d^0 or d^{10} configuration⁵. These include metal oxides such as TiO_2 , ZrO_2 , Ta_2O_5 , Nb_2O_5 , etc. In these oxides O 2p states form the VB and it exists deep down in energy therefore the VB is sufficiently positive relative to water oxidation potential. Their CB is slightly negative relative to the water reduction potential. However, they possess wide band gaps and are less promising for the solar absorption. Wide band gap metal nitrides such as $\beta\text{-Ge}_3\text{N}_4$ and GaN and sulphides such as ZnS have also been employed. In nitrides and sulphides, the VB consists of states originating from N 2p and S 3p respectively. Photocatalytic activity of the wide band gap materials can be improved by various means. For example, doping of metals such as Rh, V, Mo, etc. or doping of non-metals such as C, N, B, S, etc. in TiO_2 ⁶. Photocatalytic activity of substituted TiO_2 is greatly influenced by the ability of the dopant to trap and transfer the charges depending on the distribution and electronic configuration of the dopant ions⁶. Doping of anions such as N, S and P alters the VB. Doping of F^- , Cl^- and Br^- ions also cause

an increase in hydrogen evolution activity although their impact on electronic structure is marginal. Substitution of N in place of O elevates the VB due to mixing of O 2p and N 2p orbitals causing a decrease in energy gap.

Substitution of N alone in place of O in an oxide results in charge imbalance and increases the number of anion vacancies. However co-substitution of N with F in place of O would not cause any change, due to balance of charges. This also significantly changes the electronic structure rendering visible absorption of the material. It causes a decrease in band gap from 3.2 to 2.4 eV with a reduction in band gap of 0.6 eV in the case of ZnO ⁷. Similarly, a red-shift in absorption onset in the case of TiO_2 is observed with N and F cosubstitution⁸. It also exhibits hydrogen evolution of $60 \mu\text{mol h}^{-1}\text{g}^{-1}$ under visible-light irradiation in the presence of $\text{Na}_2\text{S-Na}_2\text{SO}_3$.

Combinations of metal oxides with metals have been well explored. Often Pt, Au, Ru, Rh, Pd and Ag are used as cocatalysts for water reduction⁶. The activity obtained with Pt is generally superior due its low over potential and high work function. Au and Ag nanoparticles also serve as visible-light responsive materials due to their surface plasmon resonance band in the visible region. The excited electrons in the metal nanoparticles are injected into the CB of the oxides. It has been

found recently that activity of such materials depends on the shape, size and other factors. For example, Janus structures of Au- TiO_2 exhibit superior activity ($\sim 46 \text{ mL h}^{-1}$) over core-shell Au- TiO_2 ($\sim 26 \text{ mL h}^{-1}$) whereas amorphous TiO_2 and bare Au show negligible hydrogen evolution yields (Figure 3)⁹.

Solid solutions of semiconductors are interesting due to their unique optical and photocatalytic properties. For example, solid solutions of ZnO and GaN such as $\text{Zn}_{1-x}\text{Ga}_x\text{O}_{1-x}\text{N}_x$ exhibit remarkable lowering of the band gap¹⁰. This results in photocatalytic activity under irradiation of visible-light alone. $\text{Zn}_{1-x}\text{Ga}_x\text{O}_{1-x}\text{N}_x$ exhibits hydrogen evolution of $320 \mu\text{mol h}^{-1}$ and oxygen evolution of $160 \mu\text{mol h}^{-1}$ simultaneously under visible-light irradiation from water in acidic medium. It should be noted that both the parent materials, ZnO and GaN, are inactive for water splitting under visible-light irradiation. Here, RuO_2 is employed as hydrogen evolution cocatalyst. The ratio of H_2 and O_2 is 2:1 as expected for an ideal water splitting reaction. Quantum yield (QY) values depicted in the Figure 4 match with the optical absorption spectrum and the photocatalyst is inactive under irradiation of long wavelength photons. The photocatalytic activity however, extends from UV to visible region and is found to be consistent over several cycles.

Figure 3. TEM images of (a) Janus and (b) core-shell Au-TiO₂ nanostructures. (c) Hydrogen generated under visible-light irradiation using Janus and core-shell Au-TiO₂ nanostructures and related compounds. Reproduced with permission from Ref. 9.

Figure 4. (a) Comparison of quantum efficiencies with the absorption spectrum of ZnO:GaN. (b) Rate of evolution of H₂ and O₂ with ZnO:GaN. Reproduced with permission from Ref. 10. Copyright 2005, American Chemical Society.

3.2. Reduction of water (hydrogen generation)

In metal chalcogenides, ZnS is a wide band gap material and CdSe possesses unsuitable band positions. On the other hand, CdS has gained importance due to its optimum band gap and suitable band positions¹¹. Unfortunately, CdS undergoes photocorrosion under photocatalytic conditions and requires electron donors. Multicomponent heterostructures of type CdSe/CdS/Pt exhibit good hydrogen evolution yields ($40 \text{ mmol h}^{-1}\text{g}^{-1}$)¹². This superior activity is attributed to the effective spatial separation of charges¹². Subjecting CdS to form type II heterostructures with ZnO and TiO_2 results in charge carriers with longer life times.

We have recently investigated the photocatalytic properties ZnO/Pt/CdS heterostructures¹³. Interestingly, these heterostructures exhibit excellent hydrogen evolution activity due to its rational design, synthetic procedure employed and the relative configuration of the components. In this heterostructures, electrons and holes generated upon photoexcitation are confined to ZnO and CdS respectively due to their type II relative band alignment (**Figure 5**). Holes are consumed by using sacrificial scavengers such as Na_2S - Na_2SO_3 . Presence of Pt on

ZnO enhances the activity nearly 7 times yielding a hydrogen evolution activity of $17.4 \text{ mmol h}^{-1}\text{g}^{-1}$. Here replacing inorganic sacrificial with benzyl alcohol improves the photocatalytic activity in addition to oxidation products with an activity of $35 \text{ mmol h}^{-1}\text{g}^{-1}$ (AQY 50%). These heterostructures yield negligible hydrogen evolution in the higher wavelength region. The activity increases with increase in absorption of the CdS and the activity is attributed to the absorption of CdS. NiO in place of Pt in these heterostructures also yields activities comparable to Pt¹⁴. Similarly, $\text{TiO}_2/\text{NiO}/\text{CdS}$ exhibits superior activity compared to $\text{TiO}_2/\text{Pt}/\text{CdS}$ heterostructures¹⁵.

Role of morphology and surface area of the oxide nanostructures on the hydrogen evolution activity in $\text{ZnO}(\text{TiO}_2)/\text{Pt}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructures has been investigated. Photocatalytic activity increases with increase in surface area. Highest photocatalytic activities obtained with nanotubes in the case of TiO_2 and nanorods in the case of ZnO ¹⁶.

Hydrogen evolution activity of $\text{ZnO}/\text{Pt}/\text{Cd}_{1-y}\text{Zn}_y\text{S}$ ($y = 0.0, 0.2$) heterostructures has been improved by cosubstitution of N and F in place of O in ZnO ⁷. It has been shown that optical properties of ZnO and CdS are significantly altered by

Figure 5. (a) Comparison of hydrogen evolution activity of ZnO/CdS and ZnO/Pt/dS. (b) Comparison of AQY with electronic absorption spectrum of ZnO/Pt/Cd_{0.8}Zn_{0.2}S. (c) Comparison of activity obtained with Na_2S - Na_2SO_3 with benzyl alcohol and (d) schematic representation of process of hydrogen evolution on ZnO/Pt/Cd_{0.8}Zn_{0.2}S. Reproduced with permission from Ref. 13.

Figure 6. (a) Comparison of electronic absorption spectra of ZnO_{1-x}(N,F)_x nanostructures and ZnO and (b) comparison of effect of co-doping of N and F in ZnO on hydrogen evolution of ZnO/Pt/CdS using Na₂S and Na₂SO₃ or benzyl alcohol-acetic acid mixture under visible light irradiation. Reproduced with permission from Ref. 7.

Figure 7. (a) Band edge positions obtained from first-principles calculations relative to water reduction and oxidation potentials and (b) variation of hydrogen evolution activity with NaOH concentration on Cd₄P₂Cl₃. Reproduced with permission from Ref. 19.

cosubstitution of a trivalent anion along with a monovalent anion. As shown in **Figure 6**, the optical band gap of the material changes from 3.2 to 2.4 eV up on N and F cosubstitution. Hydrogen evolution increases to 43 mmol h⁻¹g⁻¹ upon N and F cosubstitution. Similarly, N and Cl cosubstitution also causes a decrease in the band gap from 3.2 to 2.0 eV and enhances the photocatalytic activity¹⁷. P and Cl substitution in place of S has been carried out in CdS and ZnS¹⁸. States originating from P³⁻ ions cause a decrease in the band gap giving rise to improved photocatalytic activity. Progressive substitution of P and Cl in place of S in CdS finally results in the formation of Cd₂P₂Cl₂. Roy *et al.*¹⁹ have investigated properties of Cd₄P₂Cl₃. Cd₄P₂Cl₃ is a semiconductor with a band gap of 2.36 eV which is close to that of CdS. It also possesses

suitable band positions for splitting of water. Interestingly Cd₄P₂Cl₃ exhibits hydrogen evolution in the absence of any sacrificial hole scavenger unlike CdS (**Figure 7**). It is resistant to photocorrosion and has the potential to replace CdS. N and C codoping in ZnS red-shifts the visible light onset resulting in absorption activity for organic pollutant degradation. P and Cl cosubstitution in ZnS lowers the energy gap as predicted from theoretical calculations¹⁸.

Complete substitution of O in ZnO with N and F results in the formation of Zn₂NF²⁰. It has a slightly narrow band gap (2.8 eV) compared to ZnO. Therefore, Zn₂NF/Pt exhibits visible-light induced hydrogen evolution in the presence of Na₂S-Na₂SO₃. The band gap of the material varies with progressive substitution of N and F in ZnO. It is a function of N

Figure 8. (a) Schematic representation of summary of the dark hydrogen evolution process. (b) Photographs of the “blue radical” (left) and its color reversal after the dark hydrogen evolution (right). (c) Plot representing the process of dark hydrogen evolution as a function of time. (d) Wavelength dependence of dark hydrogen evolved. Reproduced with permission from Ref. 21.

content with the least band gap of 2.0 eV for the composition $\text{ZnO}_{0.6}\text{N}_{0.2}\text{F}_{0.2}$.

Recently explored cyanamide-functionalized heptazine-based polymer (NCN-CN_x) shows a time-delayed hydrogen evolution in dark similar to dark reactions in natural photosynthesis²¹. In this study, upon irradiation of light on NCN-CN_x in the presence of electron donor (4-MBA) results in the formation of long-lived blue radicals (Figure 8). It produces hydrogen upon addition of the HER cocatalyst and material color reverted back to original color. The cyanamide moiety in NCN-CN_x is crucial for the formation of the radical. The blue radical is not obtained in the presence of electron acceptors.

Layered materials have gained importance after the discovery of graphene. Although graphene is not active as a photocatalyst, it serves as an electron transport channel in several systems²². Among graphene analogues MoS₂ is excellent as a cocatalyst since edge sites of MoS₂ are active for the reduction of water²³. The 1T form of MoS₂ with an activity of 30 mmol h⁻¹g⁻¹ is more active compared to the stable 2H form (Figure 9). Here, the vacant d orbitals on MoS₂ receive electrons and are utilized in the reduction of water.

3.3. Oxidation of water (oxygen evolution)

In the oxidation of water, holes get used for the oxidation of water to yield oxygen whereas electrons are used by

sacrificial electron scavengers such as AgNO₃ and Na₂S₂O₈. The electron scavengers get consumed in the process. In natural photosynthesis the WOC containing the Mn₄O₅Ca cluster catalyzes the oxidation of water. It has a cubane structure in the intermediate form and upon donation of four electrons to PSII, it restores back to its resting state by releasing oxygen and four protons²⁴. It is important to note that turnover frequency of this PSII-WOC is very high ($5 \times 10^2 \text{ s}^{-1}$) and life times of nearly 30 minutes. The metal-oxocubane structure was believed to be critical for the activity and therefore research was focused on developing such systems. It has, however, been found recently that the electron configuration of Mn or Co ions is more important than structural factors²⁵. In Mn³⁺ and Co³⁺ containing compounds presence of one *e_g* electron is found to be crucial for the oxidation of water. In Mn₂O₃ and LaMnO₃, Mn³⁺ has the *t_{2g}³e_g¹* configuration whereas Co³⁺ in the intermediate spin state has the *t_{2g}⁵e_g¹* configuration. These are best for the photocatalytic oxidation of water. As shown in Figure 10, increase in Li content in Li_xCo₂O₄ decreases the relative charge on Co and resulting in the formation of Co³⁺ with *x* = 2 i.e. Li₂Co₂O₄. Similarly, LaCoO₃ wherein Co exists in trivalent state exhibit good oxygen evolution activity with TOF of $1.4 \times 10^{-3} \text{ s}^{-1}$. Co³⁺ containing compounds shows superior activity over Mn³⁺ containing compounds.

Figure 9. (a) Electronic configuration of 2H-MoS₂ and 1T-MoS₂ induced by the crystal-field splitting and proposed mechanism of hydrogen evolution on 1T-MoS₂. (b) Time course of H₂ evolved by 1T-MoS₂. Reproduced with permission from Ref. 23. Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 10. (a) Comparison of amount of O₂ evolved by Li_xCo₂O₄ with different amount of Li. (○) Li₂Co₂O₄ and (□) Li_{1.1}Co₂O₄. (b) Comparison of amount of O₂ evolved in (i) LaCoO₃, (ii) Li₂Co₂O₄, (iii) Mn₂O₃, and (iv) LaMnO₃. Reproduced with permission from Ref. 25.

Semiconductor-based photocatalysts such BiVO₄, WO₃, Fe₃O₄ are suitable for water oxidation, we shall discuss BiVO₄-Pt-MnO_x system here (Figure 11)²⁶. In BiVO₄ the electrons migrate to the (010) facet and the holes migrate to the (110) facet due to the difference in their relative energies. Photodeposition of both the cocatalysts (Pt, MnO_x) results in selective deposition Pt on the (010) and MnO_x on the (110) facet. Selective deposition of photocatalysts shows 2 orders of superior photocatalytic activity over random deposition.

Random deposition MnO_x causes a decrease photocatalytic activity. N and F cosubstituted TiO₂ exhibits an oxygen evolution activity of 500 μmol h⁻¹ g⁻¹ under visible light irradiation.

4. CO₂ REDUCTION

Solar energy can be used to address the problem associated with increase in CO₂ levels. CO₂ can be converted to other chemicals using solar energy. Thus, CO₂ can be photochemically

Figure 11. (a) SEM images of BiVO₄-Pt-MnO_x (b) Schematic representation of mechanism of water splitting on BiVO₄-Pt-MnO_x (c) Comparison of photocatalytic activity of BiVO₄-Pt-MnO_x with the activities of other related photocatalysts. Reproduced with permission from Ref. 26. Copyright 2013, Macmillan Publishers Limited.

reduced in the presence of solar irradiation to form CO and organic products (HCHO, HCOOH, CH₃OH, CH₄, etc). It is a sustainable process since it only uses CO₂, H₂O and solar energy. Since CO₂ is a stable compound ($\Delta G_f^\circ = 394.4 \text{ kJ mol}^{-1}$), it is difficult to reduce directly. Mechanism of CO₂ reduction has been discussed in detail in the literature^{27,28}.

The process of photocatalytic CO₂ reduction on a semiconductor photocatalyst is illustrated in Figure 12²⁹. Photogenerated electrons are utilized in the reduction of CO₂ and holes are utilized for the oxidation of water. Single electron transfer to CO₂ to form CO₂^{•-} is associated with a highly negative reduction potential (-1.85 V vs. SHE) due to the change in hybridization of C from sp² to sp³²⁷. It undergoes proton-coupled electron transfer (PCET) wherein electron transfer to CO₂ is coupled with a proton transfer. Reduction of water always competes

with the reduction of CO₂ since the reduction potentials for PCET reactions are close to the water reduction potential.

CO₂ reduction is usually carried out in gaseous phase with humidified CO₂ and in the liquid phase with CO₂ saturated aqueous NaOH or bicarbonate solution. TiO₂ has been extensively studied for purpose of photocatalytic reduction of CO₂. Cation as well anion doped TiO₂ materials have also been employed for CO₂ reduction. Anion doped (N) TiO₂ as well as cation-doped (Ce) TiO₂ exhibit superior activity compared to undoped TiO₂, anion doping being more favorable²⁷. Deposition of Pt, Au, Pd, Ag, Cu, etc. on the photocatalysts enhances the activity of photochemical reduction of CO₂. Pt mostly favors the reduction of water and is poisoned by CO. Ag exhibits superior CO₂ reduction activity owing to weak binding with the CO²⁷.

Zinc germanium oxynitride obtained by nitridation of Zn₂GeO₄ has a band gap 2.7 eV and exhibit production rate of 2.7 ppm g⁻¹h⁻¹ of CH₄ from CO₂ under visible light irradiation³⁰. Zn₂AlO₄-modified ZnGaNO also exhibit 9.2 μmol h⁻¹g⁻¹ of CH₄ under visible-light irradiation³¹. In both these materials the visible light activity is due to the narrow band gaps compared to the parent oxides. Type II heterostructures such as TiO₂/CdSe with Pt effectively drives the reduction of CO₂ producing methane (48 ppm h⁻¹g⁻¹)³². In these structures, visible-light is absorbed by the CdS and the interface between CdSe and TiO₂ causes charge separation. In a recent study, we have employed bimetallic alloys containing heterostructures for the CO₂ reduction in the presence of 2-propanol³³. Ag_{1-x}Cu_x alloys found to be superior to Ag_{1-x}Au_x

Figure 12. Schematic representation of process of photocatalytic reduction of CO₂. Reproduced with permission from Ref. 29.

Au, Ag and Pt for catalysis. These heterostructures exhibit CO₂ reduction activity in the absence of a hole-scavenger in gas-phase under direct sunlight.

5. CONCLUDING REMARKS

There has been extensive research on developing photocatalysts for water splitting, hydrogen as well as oxygen evolution and reduction of CO₂. Visible-light responsive materials have received greater attention. Nanomaterials with narrow band gaps also show good photocatalytic activity. Heterostructures of type II are particularly effective in solar conversion. They provide charge carriers with longer life-times due to their relative band positions. Interfaces between the components in the heterostructures play a crucial role. For the purpose of reducing the band gap of wide band gap materials, aliovalent anion cosubstitution is found to be effective. Thus cosubstitution of trivalent anions (N³⁻, P³⁻) and monovalent anions (F⁻, Cl⁻) in place of divalent anions (O²⁻, S²⁻) reduces the band gaps due to states originating from trivalent anions. Graphene acts as a channel for charge transport in Z-scheme photocatalysts. MoS₂ catalyzes the reduction of water due to its unique edge sites.

The activity of photocatalysts is limited by either poor light absorption or charge separation. Presence of defects decreases the life-times of charge carriers and it is therefore important to have fewer defects. Developing multicomponent structures to simultaneously produce hydrogen and oxygen from water is important to avoid sacrificial scavengers. These catalysts should be based on earth abundant elements to make the process practicable. Photocatalytic reduction of CO₂ has been carried out by using on several systems including doped oxides, oxynitrides and heterostructures. Heterostructures containing bimetallic alloys such as Ag_{1-x}Cu_x are also effective for the reduction of CO₂. Selectivity of the products and suppression of the competing water reduction are crucial for developing photocatalysts for the reduction of CO₂.

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