Perspective

Non-noble metal photocatalysts for hydrogen production: A step ahead towards practical applications

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Introduction

Hydrogen is an attractive sustainable clean energy carrier with water the only combustion product, provided it is generated from water splitting or other renewable resources using direct sunlight. After about 150 year's exploitation and utilization of fossil fuels, their combustion products are causing the serious global problems, such as the greenhouse effect, ozone layer depletion, acid rain and environmental pollution. Hydrogen has a large specific energy density, easily convertible to electricity by fuel cells and produces more heat (122 MJ/Kg) than gasoline 44 (MJ/Kg), thus, rapidly emerging as a sustainable and the clean fuel for transportation and industrial utilities.[1]

Development of visible-light-driven photocatalysts to produce hydrogen by water splitting using solar energy is an attractive and environment friendly method, which offers a way for capturing available solar energy and converting it into hydrogen. To date, many photocatalysts have been reported capable of producing hydrogen from water in the presence of sacrificial agent, with M/SC systems where M=Pd, Au or Pt and SC=TiO_2 or CdS generally showing the best and most stable performance.[2–5] In addition, currently, g-C_3N_4 has been emerging as new support for metal loadings. Photo catalysis relies on capturing the energy of incident photons with E >E_g, via excitation of electrons from the valence band of a semiconductor into the conduction band. Electrons and holes thus produced then drive oxidation and reduction reactions on semiconductor surface. However, semiconductors alone without metal co catalyst are unable to produce hydrogen from water because of high over potential due to photogene rated charge recombination. Metal co catalyst deposited over semiconductor surface draws out the electrons from the conduction band by forming rectifying schottky barrier formation which prevent the backflow of electrons. In addition metal provides a surface for the adsorption of proton and recombination of atomic hydrogen.[6] However, noble metals are expensive with low natural abundance, hence they are not especially practical for the design and development of industrial photocatalysts for hydrogen production. The identification of alternative low cost co-catalysts that enhance the photo catalytic activity of TiO_2 for hydrogen production is a priority.

Cu and Niin metallic state or in oxide and hydroxide form when present over semiconductors are particularly promising in this regard and represent cost-effective and efficient photocatalysts systems for solar hydrogen production. For instance, Yu and co-workers deposited $Ni(OH)_2$ nanoclusters on TiO_2, CdS and g-$C_3N_4$by a simple precipitation method and observed a hydrogen production rate of 3.0 and 5.08 and 0.152 mmol g^{-1} h^{-1} under UV and visible light excitation.[7] Hydrogen evolution was attributed to the more positive redox potential of Ni^{2+}/Ni couple compared to the conduction band of TiO_2, CdS and g-C_3N_4 resulting in the photo reduction of $Ni(OH)_2$ to Ni^0 which served as active sites for the reduction of H^+ to H_2. Another group recently reported hydrogen production activity of 24.3 mmol $g^{-1}h^{-1}$ in 95% ethanol water mixture over Ni/TiO_2 system greater than many noble metal supported TiO_2 systems. Albeit a very high concentration of ethanol was used in this study but this was highest rate of hydrogen production achieved so far over Ni/TiO_2 systems. This high rate of hydrogen production was attributed to the presence of Nickel as highly dispersed and exclusively in Ni (0) state in there synthesis technique. There are numerous studies in literature validating nickel as a future non noble metal co catalyst.[8–11]

In concurrent with Ni, Cu in the form of Cu(0), Cu_2O and CuO is also emerging as excellent co catalyst for hydrogen production. Cubic Cu_2O (E_{bg}=2.1 Ev) and the monoclinic CuO (E_{bg}=1.2 Ev) for bulk CuO have broad perspectives for attractive utilization as active components in photocatalysts.[12]The redox potential for (Cu_2O/Cu) is such that it is easily reduced to Cu by photo excited electrons in TiO_2, CdS and g-C_3N_4.[13] While under the same conditions the potential of CuO/Cu is so that it remains as CuO. CuO loading is very sensitive to particle size. It is reported that with the increase of CuO particle size its conduction band potential becomes less negative than proton reduction potential and electrons flow to proton becomes unfavourable.[12] The conventional impregnation method is frequently used for the synthesis of CuO containing TiO_2 photocatalysts but it frequently results in increase of CuO particles size due to agglomerate formation during synthesis. Yu and co-workers fabricated $Cu(OH)_2$/TiO_2 photocatalysts deposition precipitation method, and reported a hydrogen production rate of 3.4 mmol g^{-1} h^{-1} under UV. Chen and co-workers fabricated highly dispersed CuO nano particles by complex precipitation method reported elsware. They ascertained that the hydrogen production activity over CuO/TiO_2 system was dependent on the nominal CuO loading, with 1.25 wt.% CuO being optimal (H_2 production rate = 20.3 mmol g^{-1} h^{-1} in 80:20 EtOH:H_2O).[12] Highly dispersed sub monolayer Cu(II) species on TiO_2 surfaces, rather than supported CuO nanoparticles, were proposed as the active site for hydrogen production. There are many reports in literature demonstrating Cu as efficient metal co catalyst for hydrogen production.[14–17] The above discussion confirmed that Cu is a promising alternative to noble metals in photo catalytic system. Considering that Ni is also an efficient co-catalyst in some photocatalysts, it can be deduced that the Cu-Ni bimetallic co catalyst might have high reactivity in photo catalytic system due to synergistic effect. Tian and co-workers synthesized Ni-

Cu co-modified TiO_2 by simple hydrothermal method and observed high hydrogen production activity (13.2 $mmolsh^{-1}g^{-1}$).[18] Very recently, we have prepared Ni-Cu co-modified TiO_2 photocatalysts by simple precipitation method and observed very high hydrogen production rate of 22.5 mmol $h^{-1}g^{-1}$ from very low glycerol concentration.[19] The work functions of Cu and Ni are 4.94 eV and 5.15eV, respectively. The work function of bimetallic Cu-Ni lies at the level intermediate between Cu and Ni. As a result, a more appropriate height of Schottky barrier is achieved than that between semiconductor and single metal.

As future perspective, the non noble metals Cu and Ni can be an excellent substitute of noble metals for semiconductor based photocatalysts, if their synthesis is properly tuned to achieve highly dispersed and catalytically active state of metal nanoparticles. Cu in the form of Cu and CuO is efficient co catalyst for hydrogen production whereas Ni is found to active when exclusively present in Ni (0) state. Although Ni in the form of NiO is also reported to produce hydrogen at good rates but not high enough to compare with other sate of art none noble metal photocatalysts.[20] Cu and Ni when co-deposited as Cu/Ni alloy due to highly synergistic electron transfer effect and optimized schottky barrier height have been emerging as strong candidate to replace noble metals in future.

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Conflict of interest

The author declares no conflict of interest.

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