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Review

Fe_2O_3/carbon spheres for efficient photo-catalytic hydrogen production from water and under visible light irradiation

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ABSTRACT

A new photo-catalyst based on Fe_2O_3 supported on carbon spheres (CSs) to improve the charge transport property of Fe_2O_3 in the photo-reduction of water under light irradiation is reported. The CSs (d ~560 nm) were prepared by a non-catalytic CVD method from C_2H_2 and characterized by XRD, UV–visible and FTIR spectroscopy, chemical analysis and TEM. Fe (10%) was added onto the CSs using a deposition precipitation method. The Fe–CS material exhibited a band gap of 1.17 eV and a hydrogen evolution rate ~370 mol/g s in Na_2SO_4 electrolyte (pH ~7). This is an improved photo-activity, relative to Fe_2O_3 mixed with CSs (179 mol/g s), Fe_2O_3 (147 mol/g s) and CSs (281 mol/g s) and the enhanced activity is attributed to the light absorption behavior of the carbon spheres, the Fe_2O_3 as well as the intimate contact between Fe_2O_3 and the CSs.

Contents

Abbreviations: SC, Semi-conductor; V_{fb}, flat band potential; e^-/h^+, electron/hole; PEC, photoelectrochemical; TEM, transmission electron microscopy; AFM, atomic force microscopy; CNTs, carbon nanotubes; CSs, carbon spheres; CFs, carbon fibers; CVD, chemical vapor deposition; DP, deposition precipitation; XRD, X-ray diffraction; FTIR, Fourier transform infrared; E_g, band gap energy; α, absorption coefficient; h, Planck constant; ν, frequency of light; VB, valence band; CB, conduction band; μ, mobility

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1. Introduction

During the last decade, considerable interest has focused on the development of materials for the conversion of solar energy into chemical energy. The conversion process entails a number of steps, ultimately involving charge transfer. This conversion process is performed in plants (photosynthesis) but inorganic materials can also be used for this purpose [1]. Photo-electrochemical and photo-catalysis studies, performed using nanostructured materials, have become a focus of interest since the light absorption and the initial charge separation can take place on a single nanometric sized particle [2]. The system responds with macroscopic output characteristics in which all the length scales used to describe such systems are considerably larger than the single particle size.

Hydrogen is considered as an ideal fuel for the future and an obvious source is water. The photo-reduction of water to hydrogen is an environmentally friendly method that can be achieved using visible light irradiation [3]. Hydrogen produced from water is regarded as a renewable energy source and is a clean fuel which does not generate CO_2 and other pollutants [4]. Several materials with different structures have been investigated for the hydrogen production by water photo-reduction. The development of a range of photo-catalysts with semi-conductor (SC) properties has attracted considerable attention in recent years. For the efficient hydrogen production by sunlight, a sufficiently negative flat band (V_{fb}) potential and good absorption in the visible region of a material is essential [5]. SCs satisfy these criteria and usually contain elements such as Fe, Co, Zn and Cu [6,7]. Metal oxides with partially filled *d*-shells typically exhibit low electron/hole (e^-/h^+) lifetimes and also suffer from low mobility [8]. Both problems could be addressed through nanoscaling, and systems with d^n orbitals have been intensively studied as photoelectrodes. For enhanced performance, nanostructuring is employed as a means to increase the surface area, doping to improve charge transport and surface modifications to increase (e^-/h^+) separation [9,10].

Much literature is available on the use of zinc oxide (ZnO) and titanium oxide (TiO_2) for photo-catalytic reactions. Both oxides are n-type semiconductors with wide band gap energies (E_g ~3.2 eV) and are usually used in conjunction with another oxide to form a hetero-system. Two examples have been reported in [11,12]. However, numerous studies using the above semi-conductors involve photo-catalytic degradation reactions (e.g. photo-oxidation of organic compounds) that are less energetically demanding than the photo-catalytic water splitting reaction.

For the sesquioxide M_2O_3, where M is a transition metal crystallizing in the corundum structure, the *3d* orbital is split by the crystal field into t_{2g} and e_g energy levels forming respectively the valence and conduction bands. The best known metal oxide of this type is iron oxide (α-Fe_2O_3), a SC with n-type conductivity [13]. α-Fe_2O_3 with a band gap of ~2 eV is one of the attractive SCs that has potential application in the field of photo-catalysis due to its chemical stability, low production cost, and ability to absorb photons in the visible spectral region [14]. Reactions that have been catalyzed by Fe_2O_3 include water splitting [15], water photo-reduction [16], degradation of organic and inorganic compounds [16–18] and the photo-Fenton process [19].

Porous aggregates of nanoparticles have emerged as one of the most important architectures for solar cells, fuel cells, batteries, and water splitting devices [20]. The complexity of these materials, as exemplified by the huge number of unique interfaces within a single nanoparticle aggregate, has frustrated attempts to identify the relationships between structure and electronic properties. Recent efforts by many research groups on Fe_2O_3 nanostructures under visible irradiation have resulted in significant advances in an understanding of the junction SC/electrolyte behavior. A preferred morphology for hematite would be one of sufficient thickness to absorb all light in the solar spectrum, but not too thick to cause light transmission problems. For example, Warren et al. succeeded in synthesizing an efficient Fe material as a photoanode based on iron nanoparticles for use in photoelectrochemical (PEC) cell devices that produce hydrogen by water splitting under sunlight irradiation [21]. The structure of this photoanode, characterized by combined DF-TEM and C-AFM (Atomic force microscopy) techniques, is suggested to be responsible for the high PEC activity of this material.

In parallel, many SCs have been developed for use in PEC conversion processes. PEC processes that occur at semi-conductor/electrolyte interfaces have been studied because of their possible applications in solar energy conversion. However, these SCs suffer from the disadvantage of a low quantum yield since they show low carrier mobilities and a small Faradic rate constant at their surface. Thus, the poor charge transport property of a SC has been a serious draw-back that reduces its efficiency in the photo-reduction of water. Therefore, the development of a new material that can satisfy these criteria and can produce hydrogen using green processes is required.

Many carbon supports with varying physical and chemical properties have been produced in the last two decades. In particular, low dimensional structures such as carbon nanotubes (CNTs), carbon spheres (CSs) and carbon fibers (CFs) are well known. These materials have excellent electrical conductivity and high stability [22].

Carbons modified with similar atoms have also been extensively studied and the added atoms have been used to modify the electrical conductivity of the carbon. Recently, new systems based on Fe_2O_3 were investigated used carbon nitride (g-C_3N_4) and carbon quantum dots in water splitting and degradation reactions, respectively [23,24]. g-C_3N_4 with a band gap around 2.7 eV was found to be an efficient photo-catalyst for H_2 production under visible light irradiation [23]. The photo-electrochemical performance of the hetero-system was due to the efficient separation of (e^-/h^+) pairs [25]. Carbon spheres have been used for their conductivity properties and the CSs have advantages such as their high purity, low cost, unique structure and they can have variable surface areas [26]. It may be possible that the modification of a semiconductor particle with CSs would improve the separation efficiency and retard the recombination of photo-generated (e^-/h^+) pairs. Various semiconductors have been attached onto CSs, such as Bi [12], Bi_2WO_6 [27], CuO [28], and TiO_2 [29].

In this contribution, we report the synthesis of Fe_2O_3 deposited on carbon spheres material and to our knowledge the first use of Fe_2O_3/CSs for the production of hydrogen via water reduction under visible light irradiation. Importantly CSs can accept electrons and are semiconductors, where the conduction can occur by electron hopping between the spheres. Our aim was to prepare an intimate hetero-system that did not entail the use of the classical SCs, TiO_2 or ZnO, for the water photo-reduction reaction. Since the photo-catalytic reaction is a difficult reaction we have used a sacrificial reagent (sulfite) to evaluate the photo-catalytic activity of the reaction [30].

2. Experimental section

2.1. Sample preparation

Carbon spheres were prepared by a non-catalytic chemical vapor deposition (CVD) method using acetylene as the carbon source [31]. A tubular quartz reactor was placed horizontally in a furnace and the acetylene was pyrolysed in the tube to generate the carbon spheres (CSs). The temperature in the reactor was first increased to 1000 °C at a N_2 flow rate of 40 mL/min. Subsequently,