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Carbon-catalyzed dye-sensitization for solar hydrogen production

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ABSTRACT

The catalytic effects of four different carbon materials (graphite, multi-walled carbon nanotubes, carbon fibers, and activated carbon) on dye-sensitized solar hydrogen production were investigated under a simulated solar light (AM 1.5G, 100 mW/cm^2). Eosin-Y (EY) and triethanolamine (TEOA) were employed as a sensitizer and electron donor, respectively. All the tested carbon materials enhanced the sensitized H_2 production, while multi-walled carbon nanotubes (CNT) exhibited the highest catalytic activity with 9- and 4-fold enhanced H_2 production and photocurrent generation, respectively. This suggests that CNT is highly effective in catalyzing charge injection and thus sensitized H_2 production. With Pt loading onto the carbon materials, the H_2 production was further improved by a maximum of 10 times. With the bare carbon materials, EY underwent simultaneous spectral shifts and decreases in absorbance presumably due to stepwise de-bromination and cleavage of chromophoric groups. With CNT/Pt, however, only the former was observed despite far higher H_2 production. This indicates that the regeneration of EY is significantly enhanced with CNT/Pt. A detailed comparison of carbon materials and the sensitized mechanism was discussed.

1. Introduction

Molecular hydrogen (H_2) produced from water via photochemical processes has received a growing attention as a renewable energy carrier [1–4]. Dye-sensitization is a simple and effective way to produce hydrogen from water in both homogeneous and heterogeneous photosystems [5–8]. It mimics the principles of natural photosynthesis in terms of sequential excitation and vectorial charge transfer [9–11]. Either homogeneous or heterogeneous dye-sensitization systems require efficient charge transfer as well as effective charge injection to achieve a high solar-to-hydrogen efficiency. Electron relays (e.g., MV^{2+}) and oxide semiconductor nanoparticles (e.g., TiO_2, ZnO, SnO_2) have often been employed for efficient charge transfer in homogeneous and heterogeneous systems [12]. For effective charge injection (catalytic reaction), on the other hand, platinum group metals (PGMs: Pt, Pd, Ru) are predominantly utilized due to their superior catalytic property for their hydrogen evolution reaction (HER) [13].

Recently, various carbon materials have been shown as effective HER catalysts in heterogeneous photocatalytic systems (e.g., TiO_2 [14–16], CdS [17,18], CdSe [19], etc.). In particular, multi-walled carbon nanotubes (CNT) have a comparable HER activity to PGMs because of their high electrical conductivity and graphic property (I_G/I_D) [17,19,20]. Surface treatments of CNT with heat and acid markedly influence the HER activity because of the change in conductivity, graphitic property, surface area, etc. [19]. More interesting is that the use of CNT can significantly reduce the use of Pt by ~50% along with maintaining the overall HER activity when they are used together in heterogeneous semiconductor photocatalysis or electrocatalysis [17,21,22].

Our primary question is if CNT can be used as an alternative to PGMs in dye-sensitized hydrogen production under solar light. To address this, we attempted to examine the applicability of CNT in dye-sensitized HER under a simulated solar light and further compare the HER activity of CNT with other carbon materials (activated carbons, carbon fibers, and graphite). As a model dye, Eosin-Y (EY) was chosen because it has been shown to efficiently produce hydrogen under visible light in the presence of an electron donor [9]. This study found that CNT is the best in catalyzing HER (Scheme 1), yet other carbon materials are also effective. When Pt was coupled to carbon materials, the hydrogen production was significantly enhanced by a factor up to a maximum of 10. Photoelectrochemical tests also showed that CNT enhances the electron transfer by around 5 times. A detailed dye-sensitized HER mechanism was discussed.

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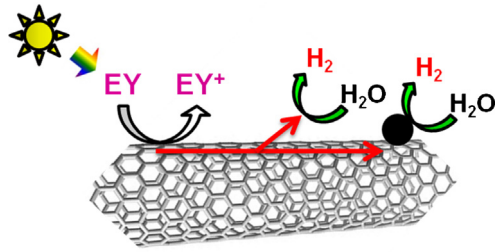

Scheme 1. Illustration of carbon nanotubes (CNT)-catalyzed dye-sensitization for solar hydrogen. Metals (e.g., Pt) can be loaded onto CNT to further improve the catalytic effect on H_2 production.

2. Experimental

2.1. Carbon materials and surface analysis

Graphite (GP: <20 μm, Sigma), multi-walled carbon nanotubes (CNT: CM-100, Hanhwa Nanotech), carbon fibers (CF: CNF-LSA, Carbon Nano Material Technology), and activated carbons (AC: Alfa Aesar) were used after acid treatment. For the treatment, the carbon materials were refluxed with 1 M hydrochloric acid and 1 M nitric acid (volumetric ratio of 3:1) for 1 h to change their physicochemical properties. Then, they were filtered with 0.45-μm PTFE filters (Millipore), washed with distilled water, and dried overnight at 80 °C [16,19]. If necessary, CNT was calcined at 500 °C for 10 min for comparison (h-CNT) [18]. The BET surface areas of GP, CNT, CF, and AC were 9, 194, 140, and 950 m^2/g, respectively, while their electrical conductivities were 1.46×10^6, 1.42×10^5, 1.89×10^4, and 1.19×10^4 S/m, respectively. Raman analysis also showed that their degrees of graphitic carbon (I_D/I_G) were 1.04, 1.79, 2.07, and 1.76, respectively (Table S1) [19]. For the Pt-loaded CNT (CNT/Pt), the CNT was dispersed in an aqueous solution (3 g/L) containing a Pt precursor ($Pt^{II}(NH_3)_4(NO_2)_2$ at 5 wt.%, which was stirred overnight to ensure the adsorption of the precursors to the CNT surfaces. Sodium borohydride ($NaBH_4$) at 2 g/L was added to the suspensions to chemically reduce the Pt^{2+}. After 3 h, the suspensions were filtered through 0.45-μm nitrocellulose membrane filters; the filtrates were rinsed with de-ionized water and subsequently dried in the oven at 80 °C for 10 min. The weight percentages of Pt deposits were determined by comparing the aqueous concentrations of Pt ions before and after the chemical reduction using inductively coupled plasma atomic emission spectrometer (Perkin-Elmer Optima 7300DV). It was found that Pt deposition changes the physicochemical properties of carbon materials by less than ca. 5% (i.e., 194–205 m^2/g, 1.42×10^5 to 1.44×10^5 S/m, and 1.79 to 1.85 for the surface area, electrical conductivity, and I_D/I_G value, respectively) (Fig. S1 and Table S1). Transmission electron microscopy (TEM, Hitachi LTD, H-7600) was employed to examine the morphology of the CNT/Pt.

2.2. Photochemical and photoelectrochemical tests

For dye-sensitized hydrogen production from water, carbon materials were suspended in water at 0.25 g/L with 1 mM Eosin-Y (2,4,5,7-tetrabromo-fluorescein disodium salt, EY) as a sensitizer and 1 M triethanolamine (TEOA) as an electron donor. The solution pH was approximately 10 because of the presence of TEOA. Prior to photolysis, a pure N_2 gas (>99.9%) was purged through the suspension for 30 min to remove dissolved oxygen. A solar simulator equipped with an AM 1.5G filter (LS-150 Xe, Abet Technologies) was used as a light source (1 Sun: 100 mW/cm^2). The reactor was sealed with ambient air during irradiation, and the head-space gases were analyzed with a gas chromatography (GC, HP6890) equipped with a Porapak-Q column and a thermal conductivity detector (TCD). No H_2 was evolved in the absence of EY or TEOA.

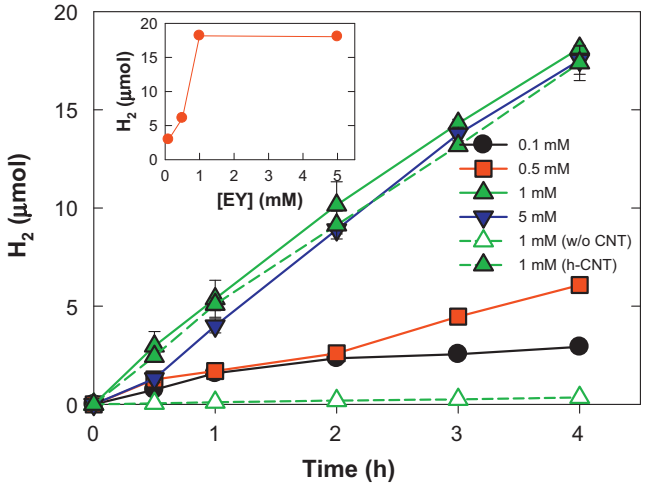

Fig. 1. EY-sensitized H_2 production in CNT suspensions as a function of EY concentration under AM1.5G irradiation (100 mW/cm^2). [CNT] = 0.25 g/L; [TEOA] = 1 M. N_2-purged for 30 min prior to photolysis.

The adsorption capability of EY on carbon materials was tested in the presence of TEOA. The suspensions were stirred for 10 h at room temperature in the dark and filtered with a 0.45 μm-PTFE filter; the concentration of the filtered EY solution (as well as the initial EY solution) was determined by recording its maximum absorbance at λ = 517 nm (UV-2450, Shimadzu) and comparing it to the concentration of the initial EY solution to estimate the adsorbed amount of EY on the carbon materials. To remove the self-aggregation effect of EY when the adsorbed amount of EY was determined, the absorbance difference value between the initial EY and the filtered EY solution was subtracted from the absorbance difference value, resulting from the self-aggregation of EY. The absorbance differences were not observed.

The EY-sensitized generation of photocurrents was also analyzed by the following typical method reported elsewhere [23,24]. Briefly, a CNT sample (0.5 g/L) was suspended in an aqueous EY solution (1 mM) with 1 M TEOA as an electron donor and 1 mM methyl viologen (MV^{2+}) as an electron mediator. The pH was adjusted to 10. A Pt wire (1.5 mm in diameter, 250 mm in length), a saturated calomel electrode (SCE), and a graphite rod were immersed in the aqueous suspension as the working, reference, and counter electrodes, respectively. N_2 gas was continuously purged through the suspension before and during irradiation (AM 1.5G; 100 mW/cm^2). Time-profiled photocurrents were collected by applying a potential (+0.4 V vs. SCE) to the working Pt electrode using a potentiostat (Ivium Compact Stat).

3. Results and discussion

3.1. Dye-sensitized hydrogen production

Fig. 1 shows the time-profiled hydrogen evolution in CNT suspensions with EY dye (sensitizer) and TEOA (electron donor) under AM 1.5G light (100 mW/cm^2). In the absence of either EY or TEOA, no H_2 was evolved. When EY and TEOA were present together, the amount of H_2 was still insignificant with ca. 0.2 μmol in 4 h at [EY] = 1 mM. This indicates that although the dye and the electron donor are essential for sensitized photolysis, the photolytic efficiency is very low in the presence of both components. The addition of CNT (0.25 g/L), on the other hand, markedly enhanced the H_2 production to ca. 18 μmol under the same photolysis condition. This