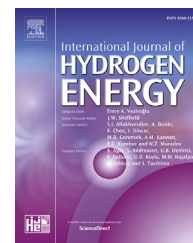




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# Co Nanoparticles@N-doped carbon coated on carbon Nanotube@Defective silica as non-noble photocathode for efficient photoelectrochemical hydrogen generation

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## ABSTRACT

The development of photoelectrodes capable of light-driven hydrogen evolution from water with non-noble metals is an important approach for the storage of solar energy in the form of a chemical energy carrier. In this study, we report Co nanoparticles@N-doped carbon coated on carbon nanotube@defective-silica (CNTs@Co@NC/D-SiO<sub>2</sub>), which are composed of Co nanoparticles@N-doped carbon as electrocatalyst, defective-silica as photocatalyst and carbon nanotube as conductive substrates. The obtained non-noble photocathode possesses the high performance for efficient photoelectrochemical hydrogen evolution reaction. When evaluated for hydrogen evolution reaction electrocatalysis, CNTs@Co@NC/D-SiO<sub>2</sub> exhibits a small onset overpotential of 104 mV ( $J = 1 \text{ mA cm}^{-2}$ ), a Tafel slope of 69.1 mV dec<sup>-1</sup> and outstanding long-term cycling stability. The P type semiconductor characteristics of CNTs@Co@NC/D-SiO<sub>2</sub> due to defective-silica with carrier concentration of  $3.53 \times 10^{19} \text{ cm}^{-3}$  is measured, which produces a significant positive shift of overpotential of 40 mV ( $J = 10 \text{ mA cm}^{-2}$ ) under 100 mW cm<sup>-2</sup> simulated sunlight irradiation. These findings provide a straightforward and effective route to produce cheap and efficient photo-electro-catalyst for water splitting.

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## Introduction

The increasing trend of energy demand and various environmental issues caused by fossil fuels have led to the urgent

study of clean energy for clean energy, such as hydrogen energy, which is considered to be the ideal sustainable energy source compared to fossil fuels. The hydrogen evolution reaction (HER) from water splitting has been widely regarded as a sustainable clean pathway for hydrogen production [1,2].

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During HER process, the catalyst plays an essential role in reducing overpotential, promoting the reaction kinetics and thus enhancing the HER catalytic efficiency. So far, platinum-based materials as the most efficient catalysts for HER, their high cost and low abundance significantly hamper their widespread applications [3–5]. Thence, the researchers have done a lot of efforts for the development of low-cost, high-activity, earth-rich hydrogen production catalyst that can replace platinum. Various electrocatalysts including transition metal dichalcogenides [6–14], metal phosphides [15–17], and metal carbides [18–21] are identified as efficient HER electrocatalysts. Among them, the active metal@carbon core-shell materials (e.g. Co, Fe, Ni, Cr, and Au) are a series of efficient hydrogen-evolving catalysts [22–28]. For example, ultrathin graphene layers coated CoNi metal nanoparticles significantly promoted the electron penetration and enhanced the catalytic activity of the HER. The catalytic activity sites are mainly on carbon atoms, and the adjacent transition-metal elements can regulate the electronic state density. The catalytic active sites are mainly located at the carbon atoms, and their electronic state density can be modulated by the adjacent transition-metal elements [29,30]. Our group also reported that evenly dispersed gold nanoparticles (ca. 20 nm) embedded in N-doped carbon (Au@NC) were derived after bioreduction of precious metals by microorganism cells, which displayed efficient HER activity with a small onset potential of only  $-54.1$  mV (vs. RHE), a Tafel slope of  $76.8$  mV  $\text{dec}^{-1}$ , a large catalytic current density, and electrochemical durability [31].

In addition, the photo-promoted water splitting, as known photoelectrochemical (PEC) HER, also reduced the overpotential of hydrogen generation. In the PEC water splitting, the type of charge carrier, such as n-type silicon (n-Si, electronic conductivity) and p-type silicon (p-Si, holes conductivity), produced the different bias voltages of positive and negative voltages, which promoted oxygen evolution reaction (OER) and HER. Silicon with a band gap of  $1.1$  eV is an earth-abundant semiconductor, which can efficiently absorb solar light [32]. Although p-Si as solar light absorption material has been widely used in PEC-HER, it was limited to silicon electrodes with plane and three-dimensional (3D) structures [33–36]. Zhang et al. reported the rational design of a novel 3D p-Si/NiCoSe<sub>x</sub> core/shell nanopillar (NP) array photocathode, which held a photocurrent density of  $-37.5$  mA  $\text{cm}^{-2}$  at 0 V (vs. RHE) under simulated  $100$  mW  $\text{cm}^{-2}$  (1 Sun) irradiation. The improvement in the production and utilization of photo-generated electrons is due to the synergistic effects of the excellent light harvesting of the Si NP array core and the good optical transparency, as well as the excellent electrocatalytic activity of the NiCoSe<sub>x</sub> shell [37]. Prof. Jin et al. reported that integrated photocathodes of CoPS on n<sup>+</sup>-p-p<sup>+</sup> silicon micro-pyramids achieved photocurrents up to  $-35$  mA  $\text{cm}^{-2}$  at 0 V (vs. RHE), onset photovoltages as high as  $450$  mV (vs. RHE), and the most efficient solar driven hydrogen generation from earth-abundant systems [38]. However, the regulation of silica nanostructure and the combination of photocatalyst and electrocatalyst have been rarely researched due to the difficulty of synthesis and the incompatible between semiconductor and catalyst interface.

Herein, we synthesized the Co nanoparticles@N-doped carbon coated on carbon nanotube@defective silica (CNTs@Co@NC/D-SiO<sub>2</sub>), which were composed of Co nanoparticles@N-doped carbon as electrocatalyst, defective silica as photocatalyst and carbon nanotube as conductive substrates. The compatible interface between semiconductor and electrocatalyst significantly improved the efficiency of photoelectric response and electrocatalytic activity. Moreover, the network structure of one-dimensional carbon nanotubes can dramatically increase the interfacial area between the electrode and the electrolyte, which can provide more catalytic sites, and facilitate transport of the reaction products. The obtained non-noble photocathode possessed the high performance for efficient PEC HER. When evaluated for HER electrocatalysis, CNTs@Co@NC/D-SiO<sub>2</sub> exhibited a small onset overpotential of  $104$  mV, a Tafel slope of  $69.1$  mV  $\text{dec}^{-1}$  and outstanding long-term cycling stability. In addition, a significant positive overpotential shift of  $40$  mV ( $J = 10$  mA  $\text{cm}^{-2}$ ) under  $100$  mW  $\text{cm}^{-2}$  simulated sunlight irradiation was produced due to the P type semiconductor characteristics of CNTs@Co@NC/D-SiO<sub>2</sub>.

## Experimental section

### Chemicals

Carbon nanotubes aqueous dispersions (~10 wt%, CNTs), anhydrous ethanol, cetyltrimethyl ammonium bromide (C<sub>19</sub>H<sub>42</sub>BrN, CTAB), sodium hydroxide (NaOH), tetraethyl silicate (SiC<sub>8</sub>H<sub>20</sub>O<sub>4</sub>, TEOS), cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), ammonium chloride (NH<sub>4</sub>Cl), ammonia (NH<sub>3</sub>·H<sub>2</sub>O, 25 wt%), dicyandiamide (C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>), nafion solution (~5 wt%), and Ar gas (≥99.99%). All reagents were used without further purification. Millipore deionized water (DI: 18.2 MΩ cm) was used to prepare all the solutions.

### Synthesis of CNTs@Co@NC/D-SiO<sub>2</sub>

200 mg carbon nanotubes dispersion (~10 wt%) and 60 mg cetyltrimethyl ammonium bromide homogeneous were dispersed in 50 mL water/ethanol solution (V:V = 3:2). After ultrasonic treatment for 1 h, 0.2 mL tetraethyl silicate was added into above solution, with magnetic stirring for 1 h. Then, 0.6 mL 0.1 M NaOH aqueous solution was put into the above dispersion. The above operations were carried out under stirring, which was continued for 12 h. The obtained product was amorphous CNTs@SiO<sub>2</sub>. After collection and washing, the mixture was dispersed to 50 mL deionized water. Subsequently, 25 mL cobalt ammonia transparent solution (Co<sup>2+</sup>, 0.3 mmol; NH<sub>4</sub>Cl, 10 mmol; NH<sub>3</sub>·H<sub>2</sub>O, 1 mL) was added into above CNTs@SiO<sub>2</sub> aqueous solution, and reacted in an oil bath pot at 90 °C for 12 h. As the reaction continued, the pink solution changed to be colourless, suggesting the reaction between Co<sup>2+</sup> and SiO<sub>2</sub> was completed. The obtained product was CNTs@Co<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. At last, 20 mg dried CNTs@Co<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> mixed with 140 mg C<sub>2</sub>H<sub>4</sub>N<sub>4</sub> were put into tube furnace and calcined at 900 °C for 2 h under Ar flow. After washing off the impurities, the obtained black powder was Co nanoparticles@N-doped carbon coated on carbon

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