

# Carbon Materials Assisted ZnO Nanowire Array Composites for Enhanced Photoelectrochemical Water Oxidation

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## Abstract:

In an effort to enhance water oxidation kinetics, ternary structured zinc oxide nanowire (ZnO NW) array composites were investigated. ZnO NW arrays were grown via hydrothermal synthesis, electrodeposited with cobalt oxide ( $\text{Co}_3\text{O}_4$ ) as the co-catalyst, and then loaded with carbon materials to achieve hierarchical ZnO- $\text{Co}_3\text{O}_4$ -carbon NW structures to prevent electron-hole recombination and increase oxidation reaction rates. Initial PEC testing indicates that adding a co-catalyst and multi-walled carbon nanotubes (CNTs) enhances PEC water oxidation currents when compared to pristine ZnO NW photocurrents. At a potential of 0.6 V vs. Ag/AgCl (1.23 V vs. RHE), the PEC water oxidation current of ZnO- $\text{Co}_3\text{O}_4$ -CNT NW arrays measured was 1.61 mA/cm<sup>2</sup>, which is nearly double the photocurrent achieved by pristine ZnO NWs (0.8618 mA/cm<sup>2</sup>). These results demonstrate that the  $\text{Co}_3\text{O}_4$  co-catalyst in combination with CNTs promote electron-hole pair charge separation, a feature essential for water oxidation. Lastly, hierarchical graphene oxide-ZnO- $\text{Co}_3\text{O}_4$  NW array composites were fabricated to study how 1D-ZnO-2D-GO- $\text{Co}_3\text{O}_4$  influences the photoelectrochemistry of water oxidation.

## Introduction:

Achieving total photoelectrochemical (PEC) water splitting can help combat the energy crisis by providing clean alternative fuels. However, total water splitting is difficult due to the slow reaction rates of the water oxidation half reaction and rapid recombination of photogenerated electron-hole pairs in semiconductor photocatalytic materials [1]. Using the PEC approach, we can separate the total water splitting reaction into its redox half-reactions. To suppress electron-hole recombination and accelerate water oxidation kinetics, carbon materials such as CNTs and a  $\text{Co}_3\text{O}_4$  co-catalyst were hierarchically added to the ZnO semiconductor photocatalyst to achieve enhanced PEC water oxidation [2].

## Experimental Methods:

**Fabrication of Ternary Structured ZnO Nanowires.** The ZnO NWs were grown via hydrothermal synthesis [2]. As seen in Figure 1A, conductive fluorine-doped tin oxide (FTO) substrates were spin-coated five times with 0.01 M Zn acetate seed solution and then annealed at 350°C for 30 minutes. The substrates were then vertically suspended in a Teflon® autoclave, in 0.06 M  $\text{Zn}(\text{NO}_3)_2$  and HMT solution, for 24 hours at 110°C to synthesize ZnO NWs [3]. The NWs were then rinsed with deionized (DI) water and dried in air. Next, the substrates were electrodeposited with 0.06 M  $\text{CoCl}_2$  (aq) at -1 mA for 10 seconds, rinsed with DI water, and dried in air. The substrates were then soaked

in aqueous CNT solution (0.25 mg/mL, functionalized with 3:1  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture) for 20 seconds and then annealed for two hours at 300°C. Figure 1B shows the intended ZnO- $\text{Co}_3\text{O}_4$ -CNT NW structure.

**PEC Water Splitting Set Up.** Linear sweep voltammetry (current-voltage and current-time) tests were conducted to analyze and compare the photoelectrochemical activity of pristine ZnO NWs, binary ZnO- $\text{Co}_3\text{O}_4$  and ZnO-CNT NWs, and ternary structures. All experiments were conducted using AM 1.5G simulated sunlight in aqueous 0.5 M  $\text{Na}_2\text{SO}_4$  (pH of 6.8) solution, using a saturated Ag/AgCl reference electrode and platinum counter electrode. Measurements were conducted at a scan rate of 10 mV/s over a potential range of -0.3 V to 1.2 V vs. Ag/AgCl. Figure 3 shows the PEC cell testing set up in which the ZnO- $\text{Co}_3\text{O}_4$ -CNT hierarchical NWs act as the photoanode where water oxidation occurs.

## Results:

X-ray diffraction tests (Figure 2A) confirmed that the main peak at a  $2\theta$  value of 35.1° can be indexed to the <002> crystal phase, which confirms preferential <001> ZnO NW growth on the FTO substrate [2]. The effects of hierarchically adding a co-catalyst and CNTs to the ZnO NWs are clearly shown in the PEC current-time ON-OFF illumination cycle plots (see Figure 3A,B). In Figure 3B at 0.6 V

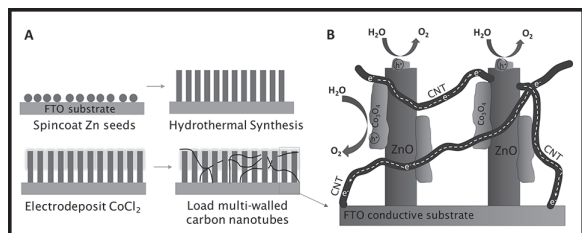


Figure 1: ZnO NW synthesis; ternary structure.

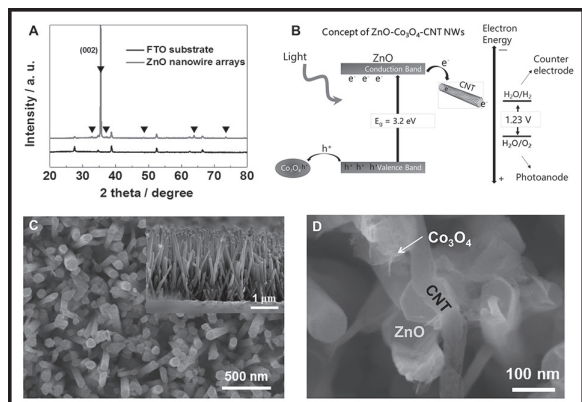


Figure 2: (A) XRD pattern. (B) Bandgap concepts. (C) ZnO NWs. (D) ZnO-Co<sub>3</sub>O<sub>4</sub>-CNT NWs.

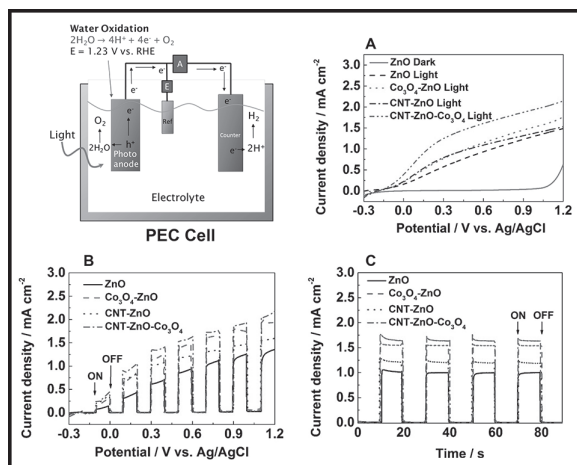


Figure 3: (A-C) PEC results.

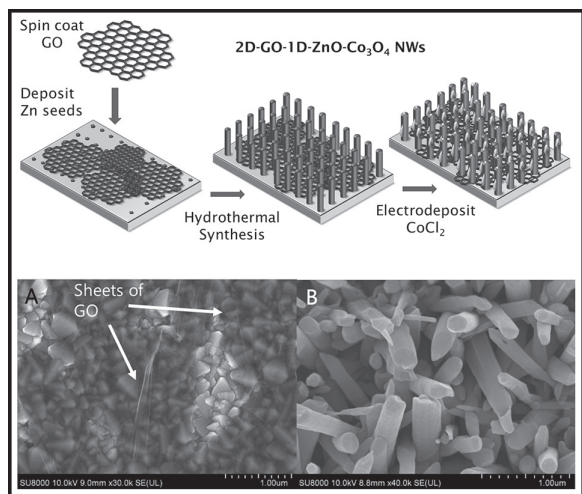


Figure 4: GO-ZnO-Co<sub>3</sub>O<sub>4</sub> NW synthesis. (A) GO on FTO. (B) ZnO on GO-FTO.

potential ( $\sim 1.23$  V vs. RHE), the PEC water oxidation current density achieved by the ternary structures is  $1.61$  mA/cm<sup>2</sup>, which is nearly double the current density achieved by pristine ZnO NWs ( $0.862$  mA/cm<sup>2</sup>).

These results also show that ZnO-Co<sub>3</sub>O<sub>4</sub>-CNT structures exhibit enhanced photoelectrochemical response, which means the Co<sub>3</sub>O<sub>4</sub> co-catalyst acts as an effective oxidation site (where holes oxidize H<sub>2</sub>O) that accelerates water oxidation kinetics, and the CNTs act as bridges for electrons to transport to the conductive substrate, thus preventing rapid electron-hole recombination. This concept (Figure 2B) explains why our photocurrent densities (ZnO-Co<sub>3</sub>O<sub>4</sub>-CNT > ZnO-Co<sub>3</sub>O<sub>4</sub> > ZnO-CNT > ZnO) are enhanced with the ZnO ternary structure.

## Conclusion and Future Work:

Ternary structured ZnO NWs were successfully fabricated in which the PEC water splitting results indicate that ZnO-Co<sub>3</sub>O<sub>4</sub>-CNT NW array composites enhance PEC water oxidation kinetics by improving photogenerated charge separation dynamics and electron transfer efficiency.

Novel ternary graphene oxide-ZnO-Co<sub>3</sub>O<sub>4</sub> NW structures were also fabricated. Similar to how the CNTs act as bridges for enhanced electron transfer to the conductive substrate, we hypothesized that adding 2D graphene oxide (GO) would facilitate improved charge transfer due to its planar geometry in combination with the ZnO NWs' 1D geometry. The 2D GO-1D ZnO-Co<sub>3</sub>O<sub>4</sub> NW array composites were fabricated by first spin coating GO onto FTO substrates (Figure 4). The samples were then spin coated with Zn acetate seed solution and annealed at  $350^\circ\text{C}$  in N<sub>2</sub> for 30 minutes to grow Zn seeds. The samples were processed via hydrothermal synthesis at the same preparation conditions as the ZnO-Co<sub>3</sub>O<sub>4</sub>-CNT NW structures. Initial SEM images (Figure 4A, B) and PEC testing indicate non-uniform GO deposition and ZnO NW growth on FTO substrates must be further investigated to synthesize stable NWs.

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