Nickel-Doped Carbon Nitride for the Photoelectrochemical Degradation of a Sunscreen-derived Organic Pollutant Found in Swimming Pool Waters

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ABSTRACT

The fabrication and consumption of sun-care products has increased exponentially the concentration of organic UV filters in the oceans and seas, which represents a threat to the marine environment. The present research project aims to explore the viability of using nickel-doped carbon nitride (Ni-CN) as a photoelectrocatalytic material to degrade 4-aminobenzoic acid (PABA), one of the most used organic UV-filters, today. For this purpose, several electrodes has been prepared by drop-casting employing Ni-CN catalysts (possessing different Ni contents), and different substrates including unmodified fluorine-doped tin oxide (FTO) coated glass, and FTO coated glass with a metallic thin films of Zn, Mn or Ni on it surface. Preliminary results indicate that all the fabricated electrodes exhibited higher current densities under irradiation of visible light, corroborating the photo-responsive nature of these CN-based materials. The catalyst prepared using the highest amount of Ni precursor salt (8X material) exhibited the highest current density during the linear sweep voltammetry experiments. In contrast, the electrode prepared using the 0X material (CN without Ni) exhibited the lowest current density, indicating that the amount Ni contained in the CN has a significant effect on the photoelectrocatalytic properties of the fabricated electrodes. Photoelectrochemical degradation experiments revealed PABA degradations about 50% when using some of fabricated the electrodes.

INTRODUCTION

Sunscreens are creams, gels, spray, or topicals that contain organic UV filters; these are applied to the skin to avoid damage from UV radiation. The high consumption of sunscreen has created a global environmental problem since the organic UV filter ends up in the oceans.[1,2] Current literature indicates that the absorption of organic UV filters by corals induces bleaching of their structures and subsequently their mortality due to viral infections.[3] In addition, reproductive organs of some fishes are being affected by these organic compounds.[4]

In order to overcome this critical issue, the present work is proposing to study the viability of using a photoelectrochemical cell to degrade one of the most common UV-filter compounds found in swimming pool waters, the 4-aminobenzoic acid, also known as PABA. More specifically, Ni-doped carbon nitride (Ni-CN) containing different Ni-compositions will be deposited on different coated substrates to fabricate electrodes, which will be integrated into a photoelectrochemical cell to degrade PABA. Visible light will be tested as a light source for the experiments.

Figure 1. Commercial sunscreens used by bathers in swimming pools & beaches.

Figure 2. Coral bleaching.[1]

OBJECTIVES

- Fabricate Ni-doped carbon nitride-based electrodes using both bared FTO and metal-coated FTO substrates.
- Study the photoelectrochemical properties of the fabricated electrodes via Linear Sweep Voltammetry (LSV).
- Quantify the PABA photoelectrochemical degradation % achieved with the fabricated electrode.

METHODOLOGY

Photoelectrocatalytic materials:

Ni-CN catalysts prepared with different amounts of precursor salts were obtained from a previous work performed at Dr. Movil research group.

Figure 3. Ni-CN prepared with different amount of nickel chloride. X = grams of the nickel chloride used in the synthesis.

Electrode fabrication process:

To fabricate the electrodes with bared FTO, suitable amount of Ni-doped carbon nitride were drop-casted onto the FTO glass substrate.

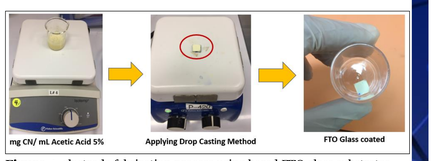

Figure 4. electrode fabrication process using bared FTO glass substrates.

METHODOLOGY (Cont.)

Electrode fabrication process (Cont.):

Ni-CN thin films were fabricated using drop casting method. A solution with the catalyst was prepared using 7.6mg of Ni-CN powder, 7.6mL of deionized (DI) water, 2.4mL isopropyl alcohol (IPA) 99%, and 40µL of Nafion 5% solution. Then, the solution was sonicated for 20min to achieve homogeneity.

Using the drop casting method, the catalytic solution was deposited on FTO substrate dropping small amounts of liquid (30µL) until completing 240µL. The substrate was heated at 80°C while the solution was dropped on the FTO substrate to facilitate the evaporation of the solvent.

FTO glass substrates were modified by electrodepositing metallic thin films (Zn, Mn, and Ni) onto its surface. The procedure used was as follows:

The experiment started with the preparation of 25 mL of a solution containing 1.0M Na_2SO_4 and a suitable concentration of the precursor salt (0.1 M Mn-Acetate or 0.1 M Zn-Acetate or 0.2M $NiCl_2$). Then, the solution was poured in an electrochemical cell consisting of three electrodes (the working electrode was a FTO glass substrate, the counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl electrode). These cyclic voltammetry experiments were carried out using a Galvanostat/Potentiostat equipment (Princeton Applied Research) at 20mV/s scan rate and a potential windows of 0V to 1V for MnAcetate and -1.8V to -1V for ZnAcetate and $NiCl_2$. The number of cycles used were 2 or 4.

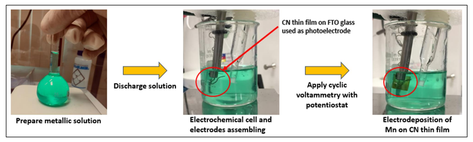

Figure 5. Metallic Electrodeposition onto FTO glass substrates using a Cyclic Voltammetry (CV) Method.

Photoelectrochemical characterization of the fabricated electrodes

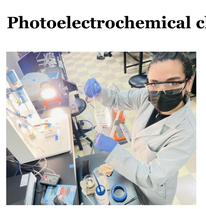

Fig. 6. Photoelectrochemical Experimental setup.

First, the quartz cell was setup with three-electrodes which were connected to the Potentiostat/Galvanostat equipment. The cell's electrodes were: The working electrode = the prepared electrodes, the counter electrode = Platinum (Pt) wire, and the Reference electrode = Hg/HgO). The electrolyte used was 0.1 M KOH aqueous solution. To carry out electrochemical measures, LSV experiments were performed under stirring at dark conditions (light-off) and under light irradiation (light-on) using an 850 W halogen lamp. The potential window and scan rate were set at 0V - 1.5V and 20mV/s, respectively.

Photoelectrochemical degradation of PABA

First, the three-electrodes the quartz cell was properly connected to the Potentiostat/Galvanostat equipment. The cell's electrodes were (1) working electrode = the prepared electrodes, (2) the counter electrode = platinum (Pt) wire, and (3) the reference electrode = Hg/HgO). The electrolyte used was 0.1 M KOH aqueous solution containing a PABA initial concentration of 7.5 E-4 M.

To carry out the photoelectrochemical degradation, The 3-electrode quartz cell was irradiated with a Halogen lights (600W) using a constant potential of -0.8 V for 2 hours. After the degradation process, samples of the solution were taken and analyzed using an evolution® 201 UV-vis equipment from Thermo Fisher Scientific. A calibration curve of absorbance versus PABA concentration was created to determine the final concentration of PABA after degradation.

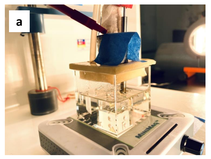

Fig 7. (a) Degradation experimental set-up and **(b)** UV-vis equipment.

RESULTS

Ni-CN Deposited onto FTO glass substrates:

Conductive side of the substrate was marked to properly deposite the Ni-CN on this side. The deposited films exhibited good mechanical stability under wet conditions

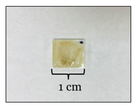

Fig 8. Example of the fabricated Ni-CN thin film onto bared FTO glass substrate.

RESULTS (Cont.)

Electrodeposited metallic thin films onto FTO glass substrates

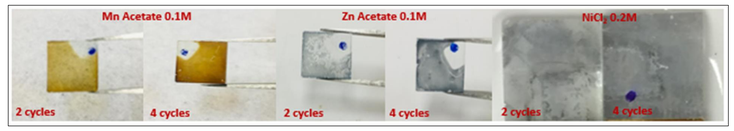

Fig 7. Metal thin films electrodeposited onto FTO bared glass substrates.

Electrochemical characterization of the electrodes fabricated by depositing Ni-CN catalysts onto bared glass substrates

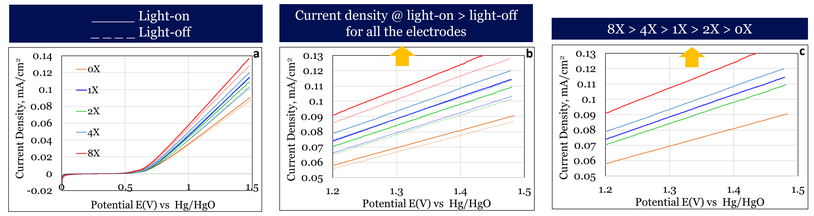

Fig 8. (a) Current density versus potential for the fabricated electrodes obtained during LSV experiments at scan rates of 20 mV/s in KOH 0.1M. The experiments were performed under light-on/off conditions. (b) zoom of fig. 8a. (c) Fig. 8b but only with the results at light-on conditions.

PABA degradation experiments

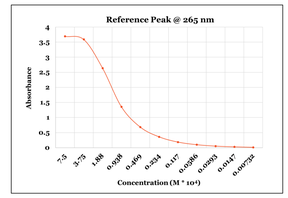

Figure . 0.1M KOH + PABA calibration curve

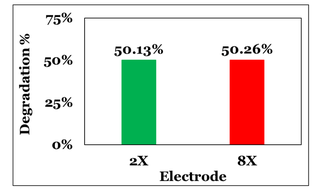

Fig. 9. PABA degradation % obtained with the electrodes 2X and 8X at -0.8 V for 2 hours.

ONGOING & FUTURE WORK

- Catalyst characterization via Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) coupled with EDAX. The last will be used to obtained the concentration of Nickel in each Ni-CN sample.
- The UV-vis for solid materials will be used to determine the catalytic material's band gap.
- Characterize via XRD the fabricated Mn, Zn, Ni thin films and evaluate their microstructures using Atomic Force Microscopy (AFM).
- Perform photoelectrochemical degradation of PABA for samples 0X, 1X, and 4X, to study the effect of Ni composition of the photoelectrocatalytic properties of the electrodes.
- Perform photoelectrochemical degradation of PABA using the fabricated electrodes at different voltages and degradation times > 2 hours.
- Perform photoelectrochemical degradation of PABA using the metal-coated FTO glass electrodes.

CONCLUSIONS

- Ni-CN-based electrodes exhibiting photoelectrochemical properties were succefully fabricated using the drop-casting technique. The catalyst films exhibited good adhesion to the FTO glass under wet conditions.
- Mn, Zn, and Ni thin films were electrodeposited onto FTO. The continuity and quality of the film increased with the number of cycles from 2 to 4.
- All the fabricated electrodes exhibited higher current densities under light-on conditions, corroborating the photo-responsive nature of Ni-CN.
- The catalyst prepared using the highest amount of Ni precursor salt (8X material) exhibited the highest current density during the LSV experiments. In contrast, the electrode prepared using the 0X material (CN without Ni) exhibited the lowest current density, indicating that the amount Ni contained in the CN has a significant effect on the photoelectrocatalytic properties of the fabricated electrodes.
- Photoelectrochemical degradation experiments revealed PABA degradations about 50% when using fabricated the electrodes containing 8X and 2X catalysts.

RECOMMENDATIONS

- Use of FTO glass substrates with large size to increase the catalytic surface area.
- Use of a solar simulator (Xenon lamp) instead of a halogen lamps to enhance the irradiation to the cell.
- Increase the surface area of the counter electrode using a Pt foil instead of a Pt wire.
- Use of electrolyte with similar characteristic to the pool waters
- Run degradation experiments at a specific wavelength using suitable light filters.
- Filter the liquid samples using filters with pores of nanometric size before analyzing them in the UV-vis equipment. This is proposed to avoid Ni-CN particulates in the sample that could affect the measurement.
- Test the effectivity of the photocatalytic materials to degrade other UV-filter organic pollutants.

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