Metal (Fe, Co, Ni or Cu) oxides supported on carbon nanotubes photocatalysts for the reduction of carbon dioxide.

Giovanni Saboia1,\*, Gustavo Chacón2, Lucas Bonan Gomes3, Maria do Carmo Rangel1

1Intituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil

2Instiuto de Tecnologia Química, Valencia, Espanha.

3Instituto de Geologia, Universidade Federal do Rio Grande do Sul. Porto Alegre, Brasil.

e-mail: giovanni@gsaboia.com.br

Resumo/Abstract

RESUMO - O consumo de fontes não renováveis de energia resulta em aumento nos gases de efeito estufa, especialmente CO2, levando a mudanças climáticas. A busca por soluções para reduzir o CO2 tem impulsionado a fotossíntese artificial, tecnologia capaz de converter CO2 em insumos industriais. No entanto, a recombinação de cargas nos semicondutores durante a fotocatálise limita a eficiência. Nanotubos de carbono (CNT) surgem como suportes promissores, devido à sua área superficial específica, condutividade e estabilidade. Neste estudo, foram usados CNT de paredes múltiplas, sem tratamento e funcionalizados, sobre os quais foram depositados óxidos metálicos (Fe, Co, Ni, Cu). A funcionalização aumentou os grupos oxigenados na superfície. Foram obtidos os óxidos Fe2O3, Co3O4, NiO e CuO, observando-se um aumento da área superficial de catalisadores, exceto naquele contendo CuO. O intervalo de banda de todos os catalisadores foi de 1,9 ± 0,1 eV. Os catalisadores produziram CO e CH4 (0,9 e 0,3 µmol.g-1) após 180 min de reação. O agente de sacrifício trietanolamina ativou o catalisador, obtendo-se H2 (7,8 µmol.g-1), CO (3,0 µmol.g-1) e CH4 (1,3 µmol.g-1). Os óxidos de Fe e Cu foram mais estáveis sobre CNT funcionalizados. NiO tornou o catalisador mais lábil, enquanto o Co3O4 não afetou o catalisador.

*Palavras-chave: fotocatálise, dióxido de carbono, nanotubos de carbono, óxidos metálicos, fotorredução*

ABSTRACT - The consumption of non-renewable energy sources results in an increase in greenhouse gases, especially CO2, leading to climate changes. The search for solutions to reduce CO2 has driven artificial photosynthesis, a technology capable of converting CO2 into industrial feedstock. However, the charge recombination in semiconductors during photocatalysis limits the reaction efficiency. Carbon nanotubes (CNT) emerge as promising supports due to their specific surface area, conductivity, and stability. In this study, multi-walled CNTs were used, both untreated and functionalized, with deposited metal oxides (Fe, Co, Ni, Cu). Functionalization increased the oxygenated groups on the surface. Fe2O3, Co3O4, NiO, and CuO oxides were obtained, the specific surface area of the catalysts increasing, except for CuO. The bandgap was 1.9 ± 0.1 eV for all catalysts. They produced CO and CH4 (0.9 and 0.3 µmol.g-1) after 180 min. Triethanolamine as a sacrificial agent activated the catalyst, producing H2 (7.8 µmol.g-1), CO (3.0 µmol.g-1), and CH4 (1.3 µmol.g-1). Fe and Cu oxides were more stable on functionalized CNTs. NiO made the catalyst more labile, while Co3O4 dis not affect it.

*Keywords: photocatalysis, carbon dioxide, carbon nanotube, metal oxides, photoreduction*

## Introduction

The surging energy demand starting in the 19th century led to the intensive consumption of fossil fuels, coal initially and later oil, spurring rapid progress but releasing greenhouse gases even more rapidly. As Earth's climate stability hinges on atmospheric balance, the increase in atmospheric CO2 leads to an enhanced greenhouse effect, causing global warming and climate changes (1).

Under mounting pressure, photocatalytic CO2 reduction emerge as a tool against global warming, valuing CO2. However, the charge recombination in semiconductors during photocatalysis limits the reaction efficiency (2). To overcome this drawback, carbon nanotubes (CNT) emerge as promising supports due to their specific surface areas, conductivity, and stability. Thus, we propose to support Fe, Ni, Cu and Co oxides over CNT for getting active and stable catalysts to improve the CO2 photoreduction (3, 4).

## Experimental

*Catalysts preparation and characterization*

Commercial CNT (NT) underwent surface modifications using an acid oxidation functionalization method to produce the nNT samples. Metal-supported catalysts on carbon nanotubes were prepared through wet impregnation methods. Iron nitrate, cobalt nitrate, nickel nitrate and copper nitrate were used as metal precursor. The catalysts were then calcined and the samples were labeled as MMNT or MMnNT, MM representing the metal (Fe, Co, Ni, and Cu). The catalysts were characterized by nitrogen physisorption, XRD, FAAS, XPS and DRS

*Photocatalysis evaluation*

The photocatalytic reduction was performed in a jacketed quartz reactor with water circulation at 25 °C. In this setup, 10 mg of catalyst were mixed with 10 mL of ultrapure water, then subjected to a quick ultrasonic bath to disperse the catalyst. Afterward, carbon dioxide was bubbled through for 20 min to purge other gases and saturate with it. The reactor was illuminated using a 300W xenon lamp for 180 min. The gas phase analysis was performed using GC-TCD-FID. The leaching of metal oxides from carbon nanotube catalysts into the liquid phase was evaluated by FAAS.



Table 1. Production of H2, CO, and CH4 obtained through photocatalytic reduction of CO2 using TEOA and the NinNT catalyst.

## Results and Discussion

The metal load on the catalysts was around 10% w/w. Fe2O3, Co3O4, NiO, and CuO oxides were detected for the catalysts. The specific surface area of the catalysts increased after the incorporation of metal oxides, except for the copper catalysts. The acid functionalization led to an increased amount of oxygen on the surface of the carbon nanotubos. The catalysts bandgap was 1.9 ± 0.1 eV, the functionalization and the metal addition not changing this value.

The desired products, carbon monoxide and methane were obtained in quantities below 1 µmol.g-1 under the evaluated conditions In this work, this behavior might be attributed to the ability of CNTs to absorb incident photons or insufficient photon supply during the reaction. Thus, the formation of excited states and catalyst activation necessary for CO2 reduction are mitigated by carbon nanotubes. Triethanolamine (TEOA) was evaluated as a sacrificial agent to favor CO2 photoreduction. In this case, a 9:1 mixture of water and sacrificial agent was used, maintaining other initial conditions unchanged. TEOA favored CO and CH4 production and facilitated H2 formation (Table 1), a product not observed without the sacrificial agent. The production of H2 indicates competition between the CO2 reduction and the water splitting reaction.

All metals were leached during reaction. Iron, cobalt, and copper catalysts exhibited low leaching (~5%), except for the FenNT catalyst for which the leaching was negligible (0.36%). The leaching of iron and copper oxides was lower in functionalized catalysts, indicating better stabilization of the oxides on the surface. Cobalt oxide stabilization seems unaffected by functional groups. Furthermore, higher leaching intensity was observed forn nickel catalysts. The 21.70% nickel leaching in the functionalized catalyst indicated that the incorporation of functional groups did not stabilize nickel oxide.

## Conclusion

Functionalization modifies the structure of CNTs by introducing oxygenated functional groups, but it does not affect the specific surface area. Catalysts with supported Fe, Co, or Ni oxides on CNTs exhibited nanoparticles below 10 nm and higher specific surface areas than the support. On the other hand, copper oxide nanoparticles are larger, and the specific surface area of the catalyst remains unchanged. The incorporation of metal oxides (Fe, Co, Ni, and Cu) on the surface of commercial carbon nanotubes, whether functionalized or not, also widens the band gap of the catalysts by approximately 0.1 eV. Functionalization of the support also produces this effect. Metal oxide catalysts (Fe, Co, Ni, and Cu) supported on carbon nanotubes exhibit low production of CO and CH4 (<1 µmol.g-1) in the photocatalytic reduction of carbon dioxide. Furthermore, the production of short-chain organic compounds in the aqueous phase was not observed. The use of TEOA as a sacrificial agent promoted the photocatalytic reduction of CO2, enabling the formation of hydrogen and increasing the production of CO and CH4 in the presence of metal oxide catalysts (Fe, Co, Ni, and Cu) supported on carbon nanotubes. All metal oxides (Fe, Co, Ni, and Cu) supported on CNTs are leached during the reaction. However, iron and copper oxides are better stabilized on functionalized carbon nanotubes. Nickel oxide becomes more labile, and cobalt oxide is unaffected by functionalization.

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