



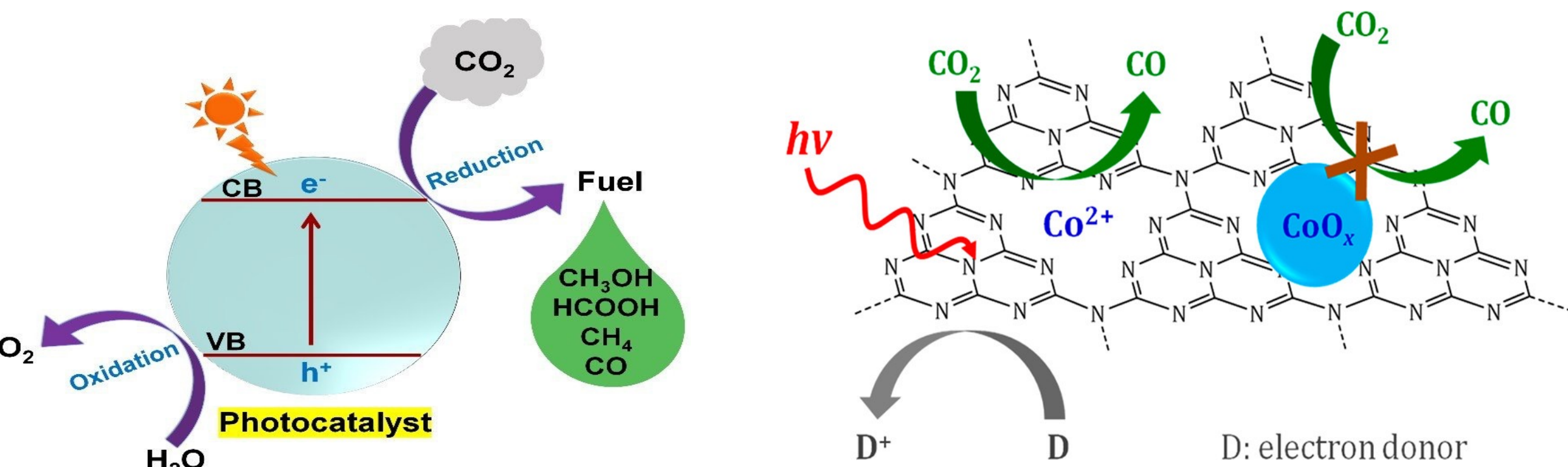
Molecular Doping of g-C₃N₄ for Enhanced Solar CO₂ Reduction on Single Atom Catalysts

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Introduction

Energy demand continues to rise, intensifying the need for clean, sustainable energy sources. **Photocatalytic CO₂ reduction** uses solar energy to convert CO₂ into useful fuels and stores solar energy in the form of chemical bonds, helping close the carbon cycle and reduce reliance on fossil resources.¹



Graphitic carbon nitride (g-C₃N₄) is an attractive reduction platform

- Metal-free semiconductor with visible light activity: 2.7 eV band gap²
- Limited by rapid electron-hole recombination and weak CO₂ adsorption³

Incorporating **Co single atom catalysts** into the g-C₃N₄ lattice introduces highly active Co-N_x sites that enhance photocatalytic performance and are selective towards CO formation.⁴⁻⁵

Molecular doping provides a strategy to tune the electronic structure of g-C₃N₄ by introducing extended π-systems into the framework.⁶ Effective dopants should:

- enhance charge separation
- increase CO₂ adsorption strength
- modulate the electronic environment around Co-N_x sites
- promote selective CO₂ reduction

Research Objectives

- Explore new dopant compounds that may be advantageous for photocatalysis
- Synthesize doped g-C₃N₄ materials for use in photocatalysis
- Correlate photocatalysis results with dopant structures

Methodology

Synthesis of g-C₃N₄ via Pyrolysis

- Pristine g-C₃N₄: 20 g urea calcined at 600°C for 4hrs
- Doped g-C₃N₄: 20 g urea and 20 mg of dopant calcined at 600°C for 4hrs

Cobalt Loading onto g-C₃N₄

- 10 mg CoCl₂ dissolved in 20 mL acetonitrile. 500 μL of the solution diluted with 7.5 mL ACN and added to 100 mg g-C₃N₄
- Sonicated for 5 min and stirred for 30 min. 65 μL triethylamine added and stirred for additional 30 min. Stirred for 12 hrs at room temperature
- Solids washed twice with chloroform, methanol, and acetonitrile, and dried overnight at room temperature

Photocatalysis and Characterization

- Prepared 4:1 acetonitrile/triethanolamine solution, dispersing 5 mg catalyst in 5 mL and sonicated at room temperature
- 1 mL aliquot added to 3 mL solution and bubbled with CO₂ for 20 min.
- Irradiated with 200 mW/cm² halogen lamp and sampled every 30 min over 2 hr for product analysis (see **Figure 4** on the right)
- Characterization was carried out on various instruments

Materials Characterization

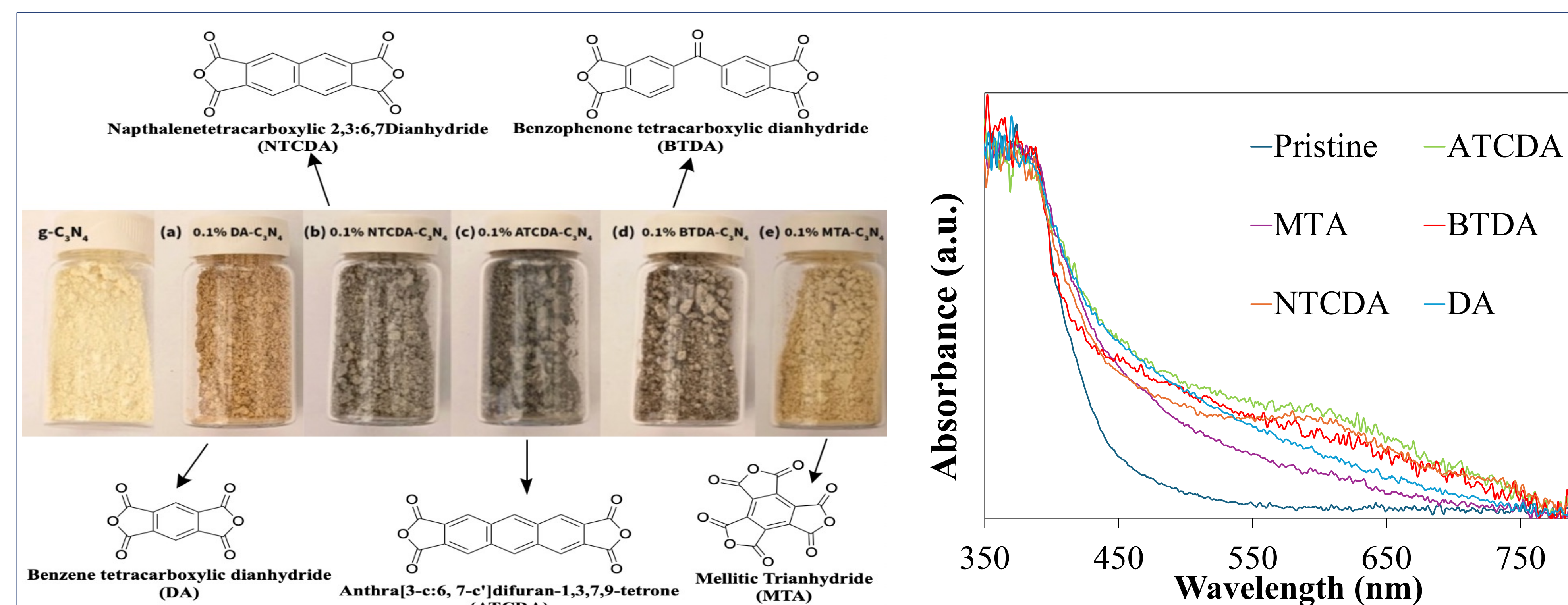


Figure 1. Visual comparison of pristine and doped g-C₃N₄, with corresponding dopant structures shown for each material.

Figure 2. Diffuse reflectance UV-Visible spectra of synthesized g-C₃N₄ samples.

Photocatalytic Performance

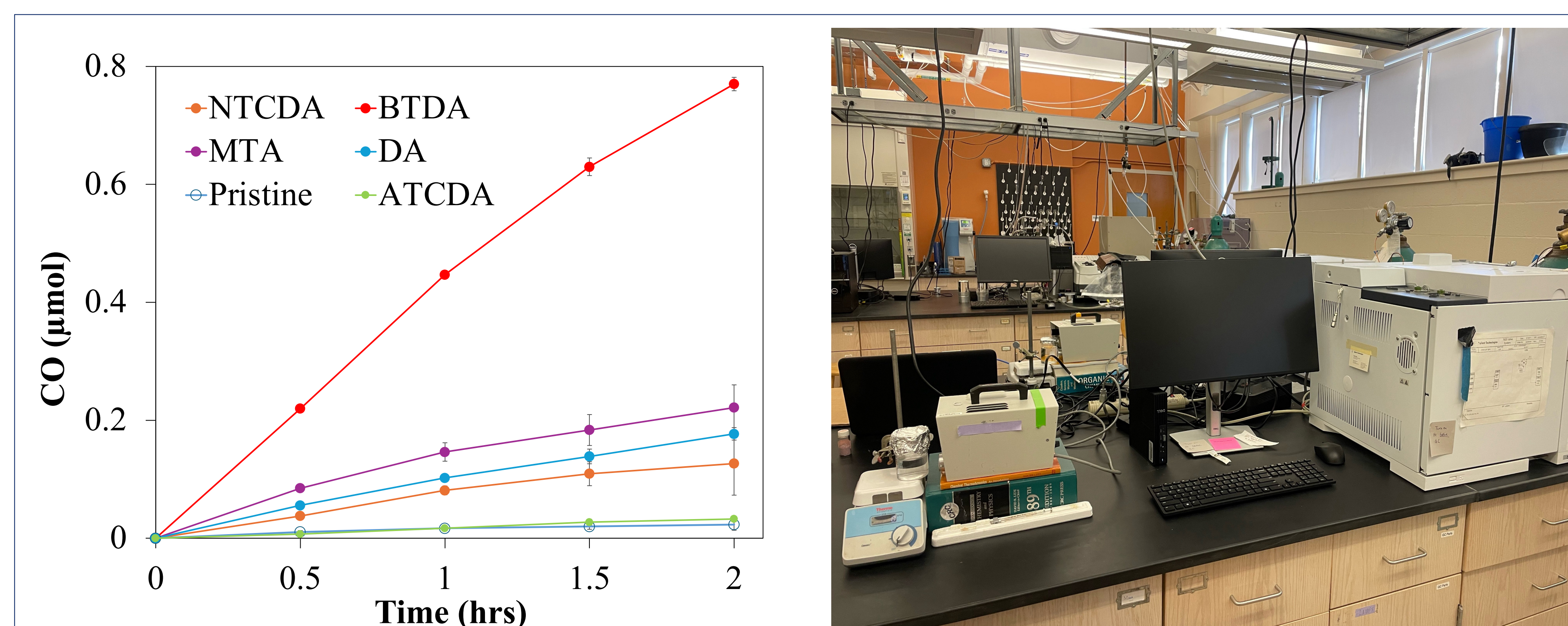


Figure 3. CO evolution in photocatalytic CO₂ reduction using Co SACs on pristine and doped g-C₃N₄ under visible-light irradiation.

Figure 4. Photocatalysis set up with a halogen lamp as the light source and an Agilent 7820 GC for CO formation analysis

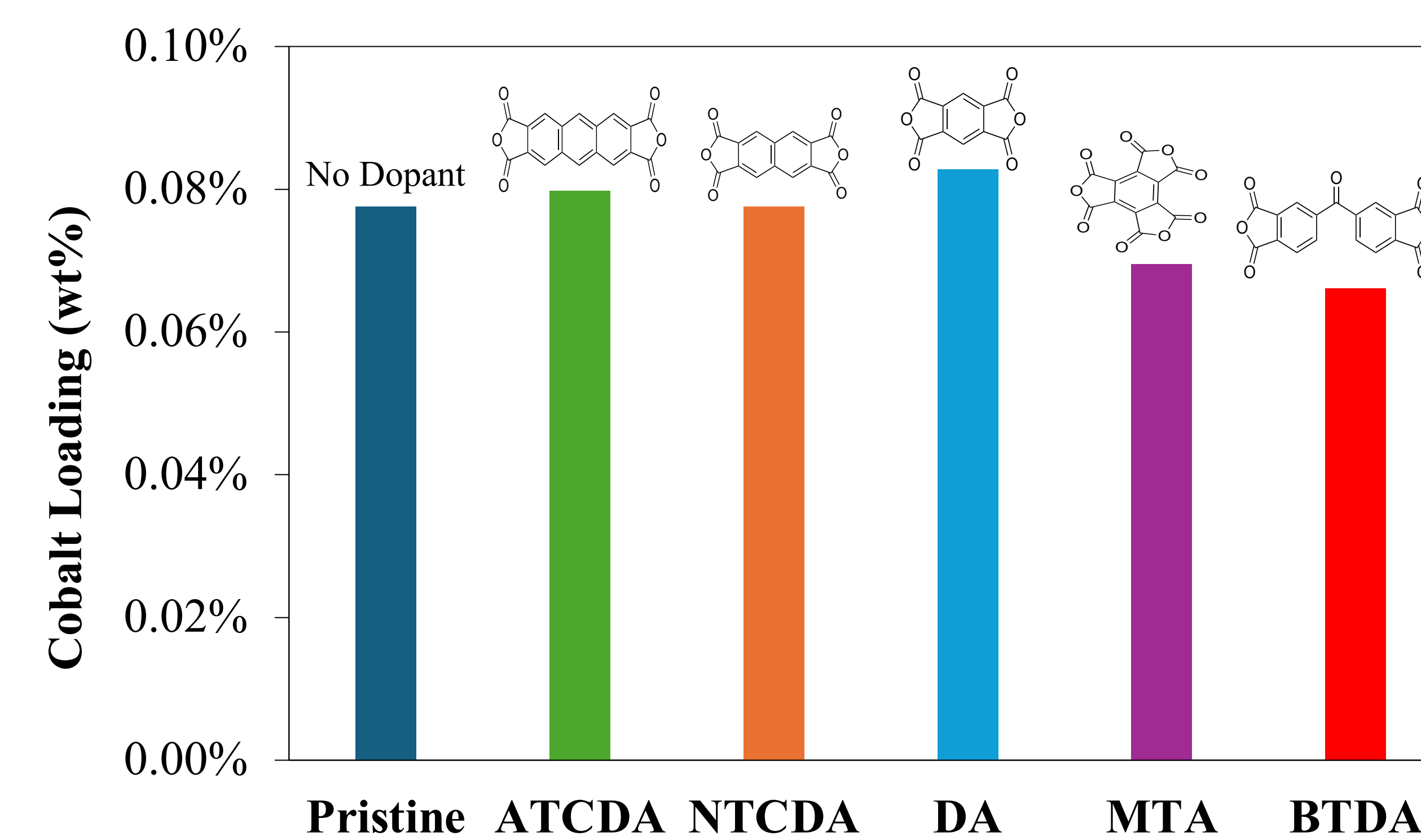


Figure 5. Cobalt loadings (wt%) in g-C₃N₄ samples quantified using elemental analysis

- Molecular doping with anhydride molecules changed the color of g-C₃N₄ (**Figures 1 and 2**)
- Co SAC on BTDA-doped g-C₃N₄ delivers the highest photocatalytic activity compared to g-C₃N₄ doped with other anhydride compounds (**Figure 3**)
- The difference in activity could be due to difference in light absorbing ability and charge separation kinetics.
- Co SACs synthesized by the stirring method led to similar Co²⁺ loadings across all samples (**Figure 5**)

Catalytic TONs

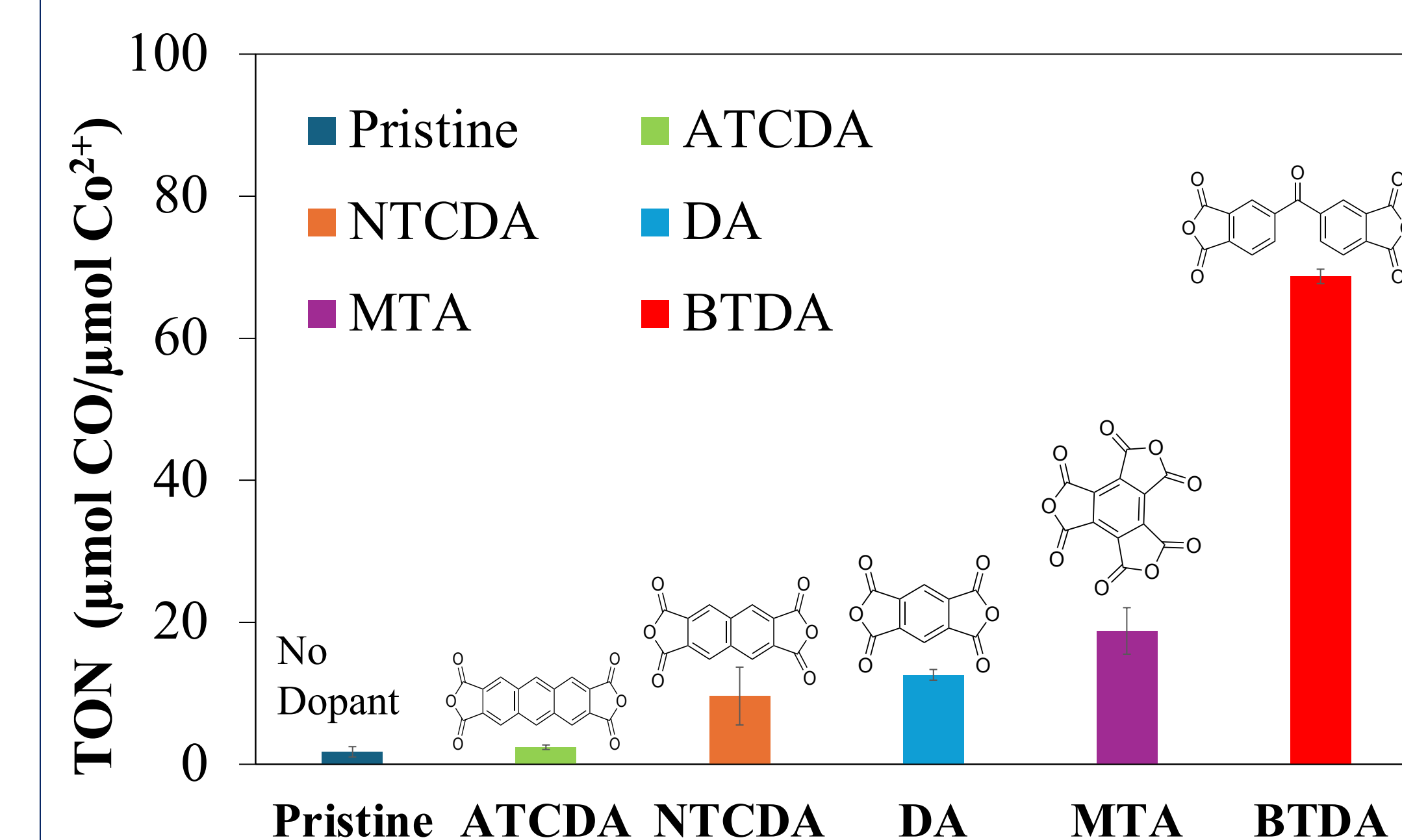


Figure 6. Effect of molecular dopants on photocatalytic activities indicated by turnover numbers (TONs). Though all dopants share a dianhydride framework and enhance TONs, BTDA delivers the highest TON amongst all compounds.

Future Work

- Synthesize Co SACs on doped g-C₃N₄ using a microwave-assisted method to potentially enhance photocatalytic performance
- Characterize the synthesized materials using photoluminescence spectroscopy, microscopy, surface area analysis and X-ray photoelectron spectroscopy to evaluate dopant-induced changes in structural and charge separation properties
- Explore more flexible anhydride-containing dopants to probe how specific molecular features affect efficient photocatalysis

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