New Perspectives in Science Education
International Conference
NEW PERSPECTIVES in SCIENCE EDUCATION

# Photocatalytic Synthesis of Benzaldehydes in Schools

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## Abstract

*Organic chemistry forms a cornerstone of general chemistry, providing foundational knowledge for understanding chemical processes. Within this domain, aldehydes are an important precursor in numerous organic syntheses and exhibit broad application potential. Despite their significance, the synthetic pathways to aldehydes are often not deeply discussed in educational contexts, where traditional experiments such as the oxidation of primary alcohols with copper oxide, face practical limitations in school settings due to the toxicity of substances used, time-intensive and complex setups, and the low yields of products. To address these challenges, this work introduces a simple and low-cost method for the photocatalytic synthesis of benzaldehydes from benzoic acid. Central to this approach is the use of polymeric carbon nitrides, a versatile class of organic nanomaterials, as photocatalysts to drive the reaction. These materials are not only low-cost to synthesize but also highly effective in different applications as in hydrogen generation. Building on this foundation, the experiment presented expands the application of polymeric carbon nitrides to organic synthesis, showcasing their potential as innovative tools in modern chemistry. This approach bridges the gap between traditional chemistry education and cutting-edge scientific advancements by integrating sustainable materials into the classroom. By doing so, it highlights a pathway to modernize experimental chemistry and inspire further exploration of nanomaterials in education and research.*

**Keywords:** *organic chemistry, aldehydes, organic nanomaterials, photocatalysis*

## Introduction

Aldehydes are highly versatile compounds with a wide range of applications. They are commonly used as solvents and starting materials in the chemical industry and play a significant role as fragrance and flavoring agents, including benzaldehydes like vanillin. Their diversity underscores their importance in both industrial and everyday contexts.

In the chemical industry, various methods are employed to synthesize aldehydes. One prominent method is hydroformylation, also known as oxo synthesis, which involves the reaction of alkenes with carbon monoxide and hydrogen. For instance, propionaldehyde can be synthesized from propene using this process, which is also integral to the production of alcohols, plasticizers, and other industrial chemicals [1]. Another common method is the dehydrogenation of alcohols, where primary alcohols are oxidized or catalytically dehydrogenated using metal catalysts to yield aldehydes [2]. Additionally, the Wacker-Hoechst process is a key industrial technique for producing acetaldehyde, a crucial precursor and intermediate in the manufacture of acetic acid, plastics, and solvents [3].

While these methods are effective on an industrial scale, their implementation in school laboratories is limited. Hydroformylation and the Wacker-Hoechst process, for example, require high pressures, elevated temperatures, and the use of toxic chemicals, making them unsuitable for educational settings [1,3]. The dehydrogenation of alcohols offers some potential for demonstration, such as the conversion of ethanol into ethanal by heating a copper wire. However, the practicality and safety of this approach are constrained. Another experiment, involving the oxidation of ethanol to acetaldehyde using copper oxide and potassium dichromate, presents additional challenges, as potassium dichromate is hazardous and its use is only marginally acceptable in schools [4,5]. Given these limitations, this paper proposes an alternative synthesis method for aldehydes that can be safely and effectively demonstrated in educational settings. This approach aims to utilize reagents readily available in schools while ensuring both practicality and adherence to safety standards.

## Curricular Context

In school curricula, aldehydes are introduced through a structured exploration of their properties, chemical behavior, and significance. This includes understanding their general structure and physical and chemical characteristics, as well as limited experimental demonstrations to reinforce theoretical concepts [6].

The structure and properties of aldehydes are typically introduced as a foundation. Aldehydes are recognized and named based on their general formula, which includes a carbonyl group (–CHO) as the functional group. Furthermore, their physical properties, such as boiling points and solubility, are examined in relation to their molecular structure. The curriculum then transitions to the chemical properties and reactions of aldehydes, which are often demonstrated through experiments. Oxidation reactions, such as the conversion of aldehydes into carboxylic acids, and reduction reactions, leading to the formation of primary alcohols, are key focus areas. Classical tests like the Tollens' test, Fehling's solution, and the Schiff reagent are also performed, though they are more commonly applied to sugars to detect the presence of carbonyl groups. These experiments provide students with practical insights into the reactivity of aldehydes. [6]

The importance and applications of aldehydes are also covered, though the focus on industrial relevance is limited in the school context. One notable example discussed is the conversion of ethanol to ethanal within the human body, illustrating the biological and physiological relevance of these compounds.

Despite these efforts, the experimental possibilities for studying aldehydes in schools remain limited due to the constraints of available reagents and safety considerations. [6,7]

However, the topic is enriched through interdisciplinary connections, particularly with nano chemistry and is building an example for its diverse applications in the field of organic chemistry. For instance, the photochemical properties of polymeric carbon nitride nanoparticles (PCNs) are introduced to provide an innovative perspective on the catalytic applications of aldehydes, bridging foundational chemistry with advanced materials science [8]. This comprehensive approach ensures that students gain a foundational understanding of aldehydes while appreciating their broader significance in both scientific and practical contexts [7].

## Theoretic

The following experiment is based on the decarboxylative oxygenation of carbon acids, utilizing polymeric carbon nitride nanoparticles (PCN) as a photocatalyst (Figure 2). Upon irradiation with UV light (395 nm), the PCN photocatalyst is excited, promoting electrons from the valence band (VB) to the conduction band (CB), thereby generating electron-hole pairs. [9]

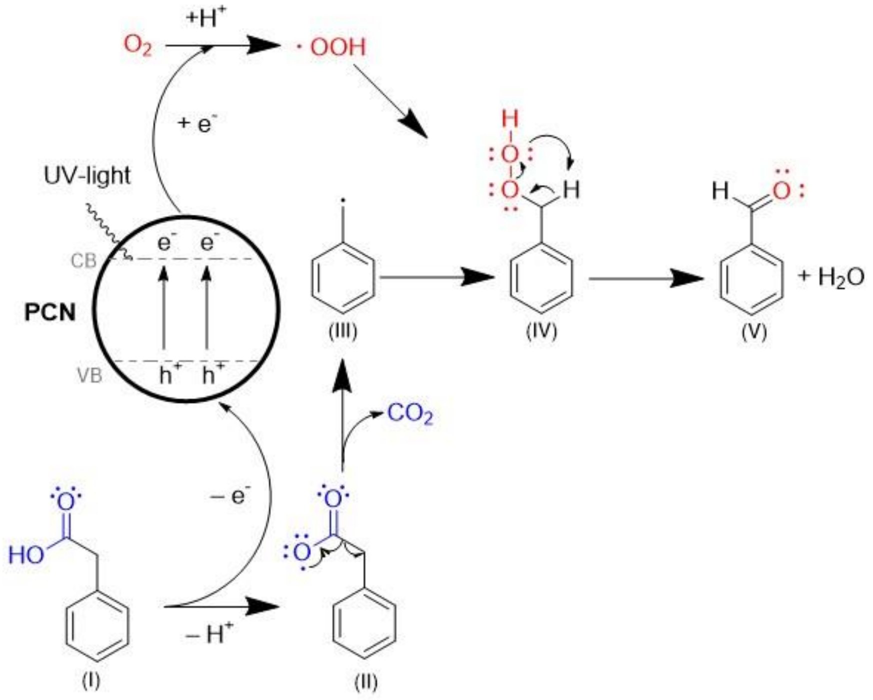

***Fig. 1.*** *Mechanism of the photocatalytic synthese of anisaldehyd. [9]*

The excited electrons participate in the reduction of molecular oxygen, leading to the formation of superoxide anions. These anions subsequently react with protons to generate hydroperoxyl radicals. Simultaneously, the oxidation process involves the transfer of an electron and the release of a proton from the carboxylic acid (I), forming a carboxyl radical (II). This radical undergoes decarboxylation, releasing carbon dioxide and yielding a benzyl radical (III). In the subsequent step, the benzyl radical reacts with hydroperoxyl radicals, leading to the formation of a transition state (IV). This intermediate can undergo further transformations, ultimately eliminating water to yield an aldehyde (V). This process is cyclic, as the PCN photocatalyst remains intact and is continuously regenerated, allowing for repeated reaction cycles. [9]

For the selective and sensitive detection of the aldehydes purpald will be used [10].

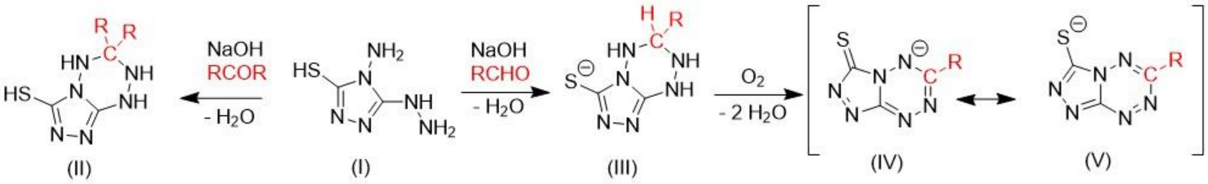

***Fig. 2.*** *Mechanism of the reaction of purpald with a keton (left) and an aldehyde (right). [11]*

Purpald, a triazole reagent (I) reacts with aldehydes and ketones to form the cyclic aminals (II, III) (Figure 2). However, only the aminal formed from aldehydes tends to oxidize readily under the influence of atmospheric oxygen. The anion of this compound forms a strongly conjugated, bicyclic system, which is responsible for the characteristic coloration (IV, V). [11]

This conjugation leads to a characteristic color change, depending on the substituent of the aldehyde used. Aliphatic aldehydes produce magenta-colored products, while aromatic aldehydes result in purple or deep red shades. Mixed aldehydes, on the other hand, can yield a brown coloration. [11]

This color spectrum not only allows for the differentiation of individual aldehydes but also offers an improved detection method in chemistry education [10]. Benedict's and Fehling's tests are unsuitable for aromatic aldehydes, while the fuchsin in Schiff's reagent is carcinogenic and so sensitive that most negative samples containing alcohols result in false positives.

## Experiment for the School

**Equipment:** 4 snap cap vials, 3 UV-flashlights (395 nm), pipette, darkening box

**Chemicals:** acetonitrile (GHS 02, 06, 07), polymeric carbon nitrides (Synthesis as described in [8]), 4-methoxyphenylacetic acid (GHS 05, 07)

**Experiment:** To investigate the photocatalytic oxidation of carboxylic acids, 4 snap-cap vials are prepared as the chart is showing.

***Table 1.*** *Preparation of the vials*

| | acetonitrile | 4-methoxyphenylacetic acid | PCN |
|---|---|---|---|
| Vial 1 | 3 mL | 40 mg | 5 mg |
| Vial 2 | 3 mL | 40 mg | 5 mg |
| Vial 3 | 3 mL | 40 mg | - |
| Vial 4 | 3 mL | - | 5 mg |

The effect of UV irradiation is assessed by exposing vial 1, vial 3, and vial 4 to UV light from a handheld flashlight, while vial 2 is placed in a lightproof box, ensuring complete darkness throughout the experiment (Figure 4). After a predetermined reaction time of 20 min, each sample is treated with 1 mL of basic 27,7 mM purpald solution.

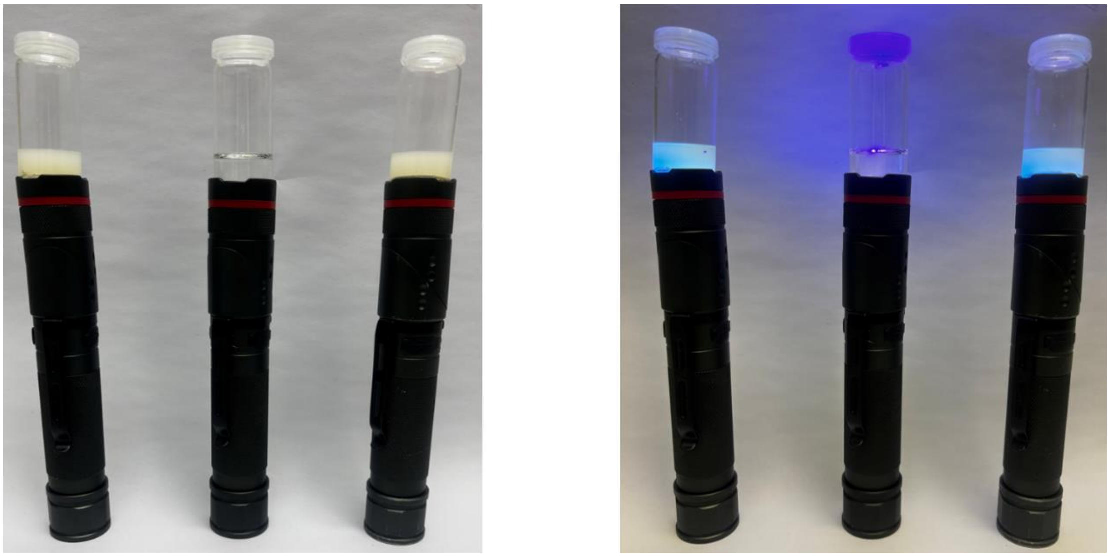

***Fig. 1.*** *Set-up and irradiation of vial 1,3 and 4*

**Observations and Results**

The results reveal the formation of two phases after adding purpald solution. As in figure 5 shown, the lower phase of vial 1 has a distinct purple coloration. Vial 2, vial 3 and vial 4 changed their colors only really light (vial 3) or not at all (vial 2, 4).

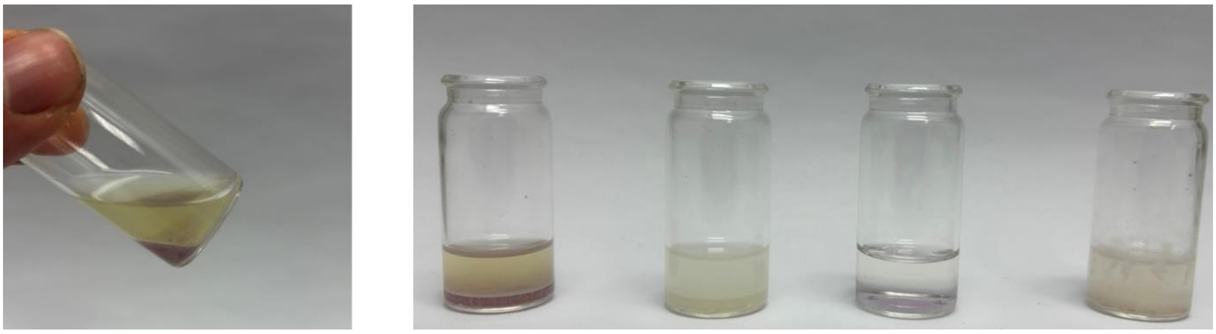

***Fig. 2.*** *Observed color after adding purpald to an irradiated (left) and comparison of all stains from vial 1 to vial 4 (right)*

This suggests that the oxidation process was light-dependent and needs PCN as a photocatalyst. The slight coloration of vial 3 indicates that the reaction occurs even in the absence of a photocatalyst, albeit to a significantly lesser extent. The presence of aldehydes was qualitatively confirmed by the purpald reagent, showing that 4-methoxyphenylacetic acid reacts to an aldehyde. The two phases can be attributed to the miscibility of acetonitrile and water or sodium hydroxide solution. Although water and acetonitrile are miscible, the solubility decreases with increasing sodium hydroxide concentration, leading to the formation of two distinct phases. Since purpald is only soluble in basic solution, only the lower aqueous phase exhibits coloration.

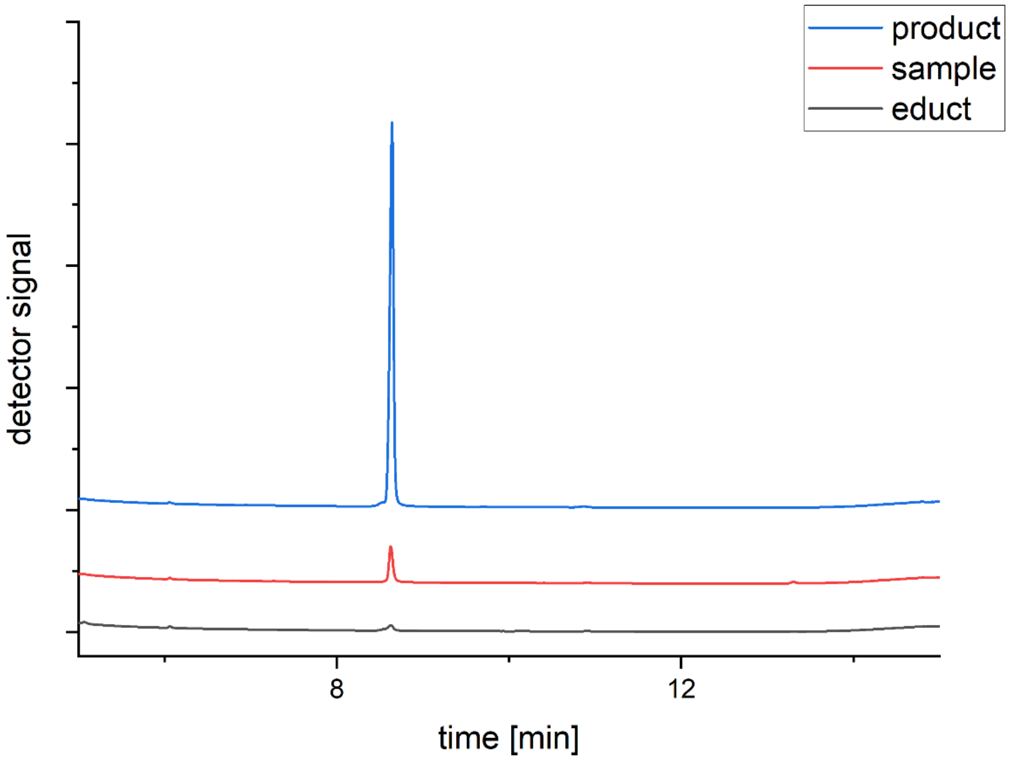

***Fig. 3.*** *gas chromatogrpahy of anisladehyd solution (blue), 4-methoxyphenylacetic acid solution (black) and the irradiated sample (red)*

The gas chromatography was performed to confirm the formation of anisaldehyde as the reaction product. For this purpose, solutions of 5 mg anisaldehyde in acetonitrile, 20 mg 4-methoxyphenylacetic acid in 3 mL acetonitrile, and the irradiated sample were analyzed. The chromatogram exhibits a characteristic peak at 8,5 minutes in both the anisaldehyde solution and the irradiated sample, which is absent in the 4-methoxyphenylacetic acid solution. This observation suggests the formation of anisaldehyde as the desired product. Furthermore, the peak intensity indicates that only a small amount of anisaldehyde was synthesized during the 20-minute irradiation period, emphasizing the high sensitivity of purpald detection. This sensitivity is particularly relevant in the context of the two-phase separation, as even low anisaldehyde concentrations result in stronger color changes than expected.

## Conclusion

In this work, an innovative and sustainable method for the synthesis and detection of aldehydes for use in school chemistry lessons was presented. By using PCN as a photocatalyst, the selective oxidation of carboxylic acids could be carried out under mild conditions. The experiments show that the reaction proceeds efficiently under UV irradiation and can be qualitatively proven by means of the color reaction with purpald. The results confirm that PCNs is not only an effective catalyst for hydrogen production [8], but also a promising material for organic syntheses in educational contexts. A particular advantage of this method is its environmental friendliness and safety compared to conventional oxidation processes, which often require hazardous reagents such as chromium(VI) compounds or high temperatures. The simple handling and the clear color change allow a demonstration in class and promote the understanding of photocatalytic processes and modern synthesis methods.

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