



# Alkaline modified g-C<sub>3</sub>N<sub>4</sub> photocatalyst for high selective oxide coupling of benzyl alcohol to benzoin

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## ABSTRACT

Benzoin is an important feedstock with high additional value for its extensive use in chemical industry. Benzoin condensation characterized by C–C coupling between benzaldehyde requires the use of nucleophilic catalysts including cyanide or *N*-heterocyclic carbene and is restricted to organic medium such as MeCN, diethyl ether, etc. Construction of efficient and non-toxic catalysts for benzoin synthesis still remains a challenge. Herein, highly selective (97%) benzoin synthesis from benzyl alcohol was achieved over potassium modified g-C<sub>3</sub>N<sub>4</sub> via light-driven tandem selective oxidation and C–C coupling. The outstanding performance was attributed to alkali modifications on the electronic structure and surface chemical environment of g-C<sub>3</sub>N<sub>4</sub>. K<sup>+</sup> intercalation not only facilitated the light harvesting as well as the transport of charge carriers, but also induced surface deprotonation of g-C<sub>3</sub>N<sub>4</sub> and thus remarkable nucleophilicity for prompting the C–C coupling reactions. This work sheds light on the design of earth-abundant inorganic photocatalysts for C–C coupling reactions such as the green synthesis of benzoin under ambient conditions.

## 1. Introduction

Benzoin is among the most important chemical feedstocks and high value-added downstream products, and has been used as versatile intermediates in the manufacture of various chemical additives, dyestuff, pharmaceuticals as well as the precursor of photoinitiator [1–4]. For the present, industrial benzoin synthesis from benzaldehyde coupling generally requires the catalysis of toxic cyanide (CN<sup>−</sup>) or alternative organics with strong nucleophilicity (e.g. nitroalkanes, enamines, phosphonates, malonates, etc.) [5–10]. The bottleneck of benzoin condensation lies in the sluggish C–C bond formations between two benzaldehyde molecules, that is, the homo-benzoin process. In order to achieve efficient C–C coupling, umpolung of carbonyl carbon from one benzaldehyde molecule is of crucial importance. In this regard, organic medium (MeCN, diethyl ether, etc.) is usually required to stabilize the structure of catalysts for C–C coupling reaction, greatly hindering the application of most organ-catalysts [11]. Seeking suitable catalysts for benzoin condensation at ambient conditions towards minimal toxic emissions has an important practical significance.

Semiconductor photocatalysis has been developed as a novel approach to facilitate selective activation of specific chemical bonds during organics transformation, such as oxidation, nitration, coupling,

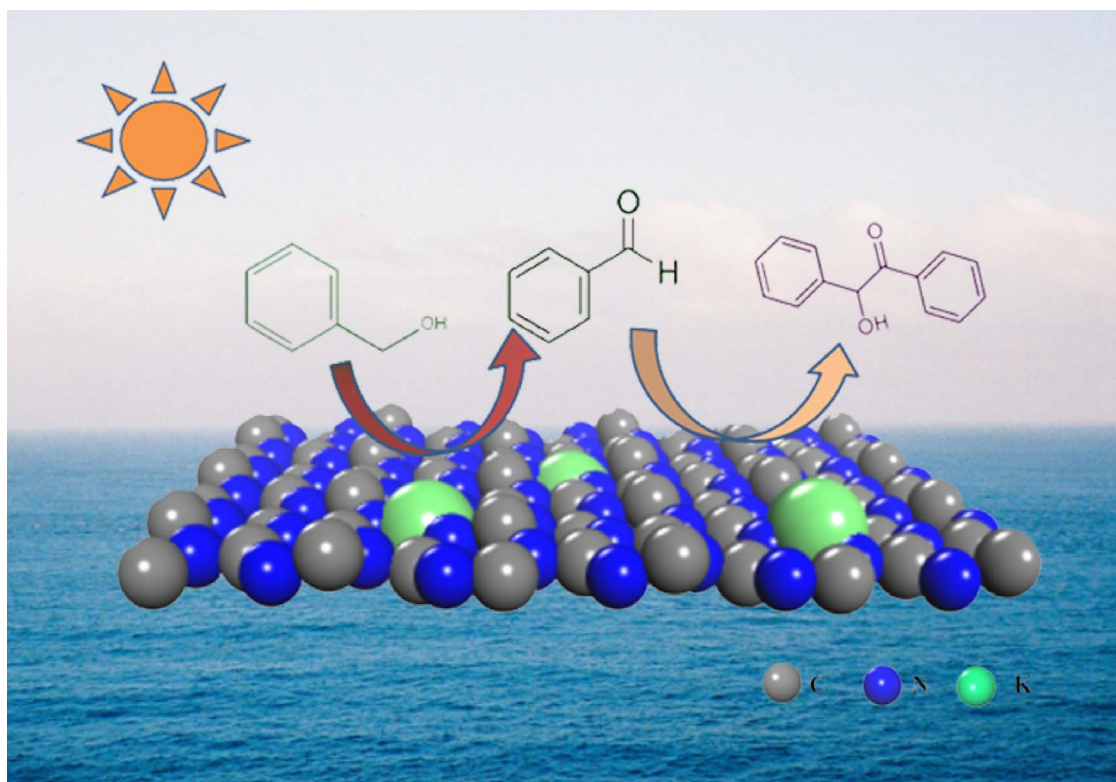
and so on [12,13]. Graphite-like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), as a non-toxic and metal-free photocatalyst, has shown its peculiar potential in selective catalysis [14,15]. However, pure g-C<sub>3</sub>N<sub>4</sub> suffers from poor performance far from satisfied for C–C coupling reaction, mainly due to the weak nucleophilicity of the active sites on g-C<sub>3</sub>N<sub>4</sub>, limited utilization of solar spectrum as well as the fast recombination of photo-induced electron-hole (e<sup>−</sup>/h<sup>+</sup>) pairs. In order to boost photocatalytic benzoin synthesis over g-C<sub>3</sub>N<sub>4</sub>, surface alkaline modification is believed to be the key [7]. On the one hand, introduced alkali atoms can increase the surface basicity of the photocatalysts as well as modify the electron structure of carbon atom in g-C<sub>3</sub>N<sub>4</sub> to show nucleophilic property [16]. On the other hand, surface alkaline modification has exhibited the potential in enhancing the light-harvesting ability via narrowing the band gap of pristine host materials [17–20]. Given above inspirations, photo-induced nucleophilicity could be further expected over alkalinized g-C<sub>3</sub>N<sub>4</sub>, favorable for the C–C bond formation in benzoin synthesis.

In this study, K<sup>+</sup> modified g-C<sub>3</sub>N<sub>4</sub> (denoted as Kn-CN, n = 1, 2, 3 n delegates the K<sup>+</sup> concentration) was synthesized via KOH solution immersing. Instead of benzaldehyde, benzyl alcohol which is economically more suitable was chosen as the starting material. Under Xe lamp irradiation at room temperature, K3-CN sample exhibited significant

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Scheme 1. C–C coupling for benzoin condensation over K–CN.

conversion (90.2%) and selectivity (97%) in transforming benzyl alcohol to benzoin, while for pristine  $g\text{-C}_3\text{N}_4$  the selectivity and conversion are only 6.3% and 4.3%, respectively. Careful studies revealed that the benzoin synthesis consists of two successive processes (Scheme 1), i.e. selective benzyl alcohol conversion to benzaldehyde, followed by benzoin formation via C–C coupling between benzaldehyde. The superior performance of K–CN is mainly attributed to the twofold enhancement of alkali modification. Firstly, K intercalation facilitates the light harvesting of K–CN as well as the transport of interlayer electrons. Secondly, after alkaline treatment K–CN turned to present much enhanced nucleophilicity on the surface, greatly enhancing the C–C coupling between benzaldehyde molecules.

## 2. Experiment section

### 2.1. Sample preparation

All the reagents were purchased from Chemical Reagents Co., Ltd (Shanghai, China), and used without further purification. In a typical synthesis procedure, Melamine (5 g) in a covered crucible (10 mL) was heated in muffle furnace at 550 °C for 3 h under static air with a ramp rate of 10 °C/min. The  $\text{K}^+$  modified  $g\text{-C}_3\text{N}_4$  prepared with different concentration of KOH solution (1%, 2% and 5%) was labeled as K1-CN, K2-CN and K3-CN, respectively. The K doped  $g\text{-C}_3\text{N}_4$  was synthesized by immersing the pristine  $g\text{-C}_3\text{N}_4$  into KOH solution of known concentration with continuously agitation at 200 °C until the complete evaporation of water. The resulted powders were collected and rinsed with ultrapure water for several times to remove the surface inclusions introduced during the synthesis.

### 2.2. Sample characterization

The X-ray diffraction patterns were recorded on a Rigaku D/MAX 2250 V diffractometer with an operating voltage of 30 kV and current of 100 mA. The morphology and microstructure of annealed samples

were investigated by transmission electron microscopy (TEM) on a JEOL JEM-2100F. The diffuse reflectance spectra (DRS) were obtained on a UV–vis spectrophotometer (Hitachi U-3010) using  $\text{BaSO}_4$  as the reference. X-Ray photoelectron spectroscopy (XPS) analysis was performed on ESCALAB 250Xi (Thermo Scientific Ltd.). The C1 s was used to correct the charge effects. The photoluminance spectra (PL) were recorded at room temperature with a fluorescence spectrophotometer (F-4600, Japan). The Zeta potential was measured via Zeta potential analyzer (Malvern Instruments Zetasizer Nano ZS90). Infrared (IR) spectroscopy was recorded using a Burkert Tensor 27 spectrometer. After accumulation of 64 scans, the spectra were collected with a resolution of 4  $\text{cm}^{-1}$ .

### 2.3. Electrochemical measurement

The electrochemical measurements were conducted with a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode system. To make a working electrode, as-prepared samples ( $g\text{-C}_3\text{N}_4$  and K–CN) were deposited on a FTO conductive support ( $1.5 \times 1.5 \text{ cm}$ ). Briefly, ethanol solution containing 30 wt% powders was ultrasonically scattered for 15 min, and then spread on the FTO substrate. After several hours air drying, as-prepared electrodes were further treated in an oven at 80 °C for 30 min before ready for tests. The photocurrent of various electrodes was recorded with a scan rate of 5 mV/s from  $-0.4 \text{ V}$  to  $1.4 \text{ V}$  (vs. SCE) in a 0.5 M  $\text{Na}_2\text{SO}_4$  solution. The Mott-Schottky curves were recorded to study the electron band structure of both  $g\text{-C}_3\text{N}_4$  and K–CN samples. The current–time ( $i\text{-t}$ ) curves were collected at 0.4 V (vs. SCE) under the irradiation of a Xe lamp. Linear sweep voltammetry (LSV) were recorded from  $+0.2 \text{ V}$  to  $-0.8 \text{ V}$  (vs SCE) with a scan rate of 50 mV/s in  $\text{O}_2$  saturated  $\text{Na}_2\text{SO}_4$  electrolyte (0.5 M). Electrochemical impedance spectroscopy (EIS) measurements were employed to study the transportation and separation of photo-generated charge carriers. A 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte containing 5 mmol of  $\text{Fe}(\text{CN})_6^{3-/4-}$  was applied.

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