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Selective charge transfer to dioxygen on KPF_6-modified carbon nitride for photocatalytic synthesis of H_2O_2 under visible light

Sujeong Kim [1], Gun-hee Moon [1], Hyejin Kim, Yeongdong Mun, Peng Zhang, Jinwoo Lee, Wonyong Choi *

Department of Chemical Engineering and Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

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ABSTRACT

Photochemical production of H_2O_2 through O_2 reduction has been proposed as an alternative method of solar energy storage. A carbon nitride (CN) photocatalyst was selected for this purpose. The incorporation of KPF_6 into the CN structure greatly enhanced the apparent quantum yield (AQY) of H_2O_2 production in the UV and visible light region. The AQY of KPF_6-modified CN was measured to be 35.9% and 24.3% under monochromatic irradiation at 370 and 420 nm, respectively, which are 8.3 and 26.1 times higher than for bare CN. The KPF_6-enhanced activity is ascribed to several factors including (i) enhanced absorption of UV and visible light, (ii) higher charge carrier density, (iii) retarded radiative recombination of charge pairs, (iv) highly selective two-electron transfer to O_2, and (v) hindered photodecomposition of in-situ generated H_2O_2. The markedly high selectivity of KPF_6-modified CN toward the two-electron reduction of O_2 (leading to H_2O_2) was demonstrated in comparision with other photoreductive conversions such as the reduction of polyoxometalate (POM → POM^-), hexavalent chromium ($Cr^{VI} \rightarrow Cr^{III}$), CCl_4 (dechlorination), and protons (H_2 production). This study developed a simple method of efficient production of H_2O_2 using visible light, which could be utilized for a variety of applications that employ H_2O_2 as a solar fuel or a green oxidant.

1. Introduction

Hydrogen peroxide (H_2O_2) is a clean oxidant that is widely used for pulp bleaching, deinking of recycled paper, chemical synthesis (e.g., the production of propylene oxide), water treatment, food industry processes, etc. [1–4]. H_2O_2 is commonly produced by the anthraquinone method, which consists of steps of (i) hydrogenation of 2-alkylanthraquinone (AQ) to anthrahydroquinone (AHQ), (ii) reoxidation of AHQ to AQ with air with concurrent production of H_2O_2, (iii) H_2O_2 extraction to aqueous solution, and (iv) purification. The yield of H_2O_2 is high, but the process needs organic solvents, high energy input, and H_2 gas, which are costly and not environmentally friendly [5]. Direct synthesis of H_2O_2 from the reaction of hydrogen and oxygen gas on metal catalysts such as Pd and Au–Pd alloy has high activity and selectivity, but it could be dangerous and demands precious metals [6,7].

Photocatalytic production of H_2O_2 is a safe and environmentally benign method since it requires water, oxygen, and light only. The in situ formation of H_2O_2 as an intermediate during various photocatalytic processes has frequently been observed, but the production of H_2O_2 as a final product has recently been in the spotlight [1,8]. H_2O_2 can be generated by sequential two-electron transfer (first step: $O_2 + e^- + H^+ \rightarrow HO_2$; second step: $HO_2 + e^- + H^+ \rightarrow H_2O_2$) or concerted two-electron transfer ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$). Proton-coupled electron transfer (PCET) and the stabilization of in situ generated H_2O_2 are desired to achieve high production efficiency. Some strategies for optimizing photocatalytic H_2O_2 production can be classified according to the modification methods: (i) metal co-catalysts loading ($AgAu/TiO_2$, Cu/TiO_2, Au/carbon nitride (CN), etc.) [9–12], (ii) hybridization with carbon nanomaterials (graphene/TiO_2, graphene/CdS, graphene/pyromellitic diimide (PDI)-modified CN, etc.) [1,13,14], (iii) surface passivation (fluoride/TiO_2, phosphate/TiO_2, etc.) [1,8,15], and (iv) chemical structural modification to control electronic and surface properties (PDI-modified CN, biphenyl diimide (BDI)-modified CN, CN with N-rich or C-vacancies, heteroelements-incorporated CN, etc.) [16–20]. For example, tri-*s*-triazine moieties on CN polymeric frameworks can facilitate photoinduced electron transfer to O_2 to produce H_2O_2, and the incorporation of earth-abundant heteroelements (K, P, and O) into the CN matrix significantly increases the production of H_2O_2 as a result of the formation of charge trapping sites and phosphate species over the surface [20]. In this study, the highest quan-

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* Corresponding author.
E-mail address: wchoi@postech.edu (W. Choi).

[1] These authors contributed equally to this work.

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tum yield (QY) for the production of H_2O_2 was achieved over the UV and visible light region by simple co-condensation of melamine and potassium hexafluorophosphate (KPF_6). Not only the incorporation of K^+ into the nitride pots of the CN framework but also the insertion of PF_6^- into the CN layers increased UV and visible light absorption and selectively promoted two-electron transfer to O_2 to yield H_2O_2 under irradiation.

2. Experimental

2.1. Chemicals and catalyst preparation

The synthesis of bare CN was done following the reported method with a slight change of calcination temperature [20]. A quantity of 4 g of melamine (99%, Aldrich) was put into a porcelain cup with a cap and calcined at 520 °C for 4 h with a ramp rate of 2.2 °C/min. Although the calcination temperature was not sufficiently high to transform melamine completely into a graphitic carbon nitride structure, it was chosen for this study because bare and modified CN samples calcined at this temperature showed the best activity in H_2O_2 production. After the heating process, the resulting product was gently ground and ultrasonicated for 3 h in an aqueous suspension (1 g/L). Then the powder was filtered, washed, and dried for further tests. KPF_6-modified CN (KPF_CN) was synthesized by a similar process of thermal polymerization. Different amounts (3, 5, 10, 15, 20 mmol) of potassium hexafluorophosphate (KPF_6, 98%, Aldrich) were mixed with melamine and ground together before the calcination process. The resulting samples were named according to the dopant amount as KPF_CN_3, KPF_CN_5, KPF_CN_10, KPF_CN_15, and KPF_CN_20, respectively.

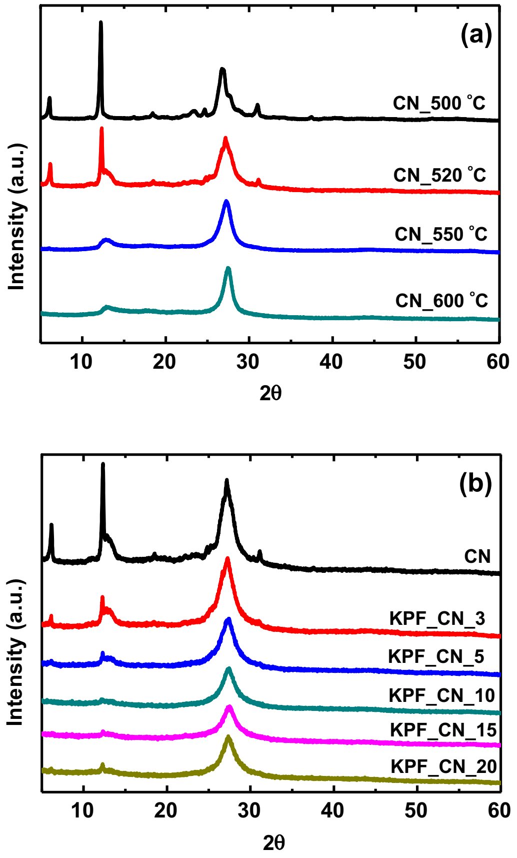

Fig. 1. XRD spectra of (a) bare CN calcined at various temperature and (b) KPF_6-modified CN calcined at 520 °C with varying KPF_6 content.

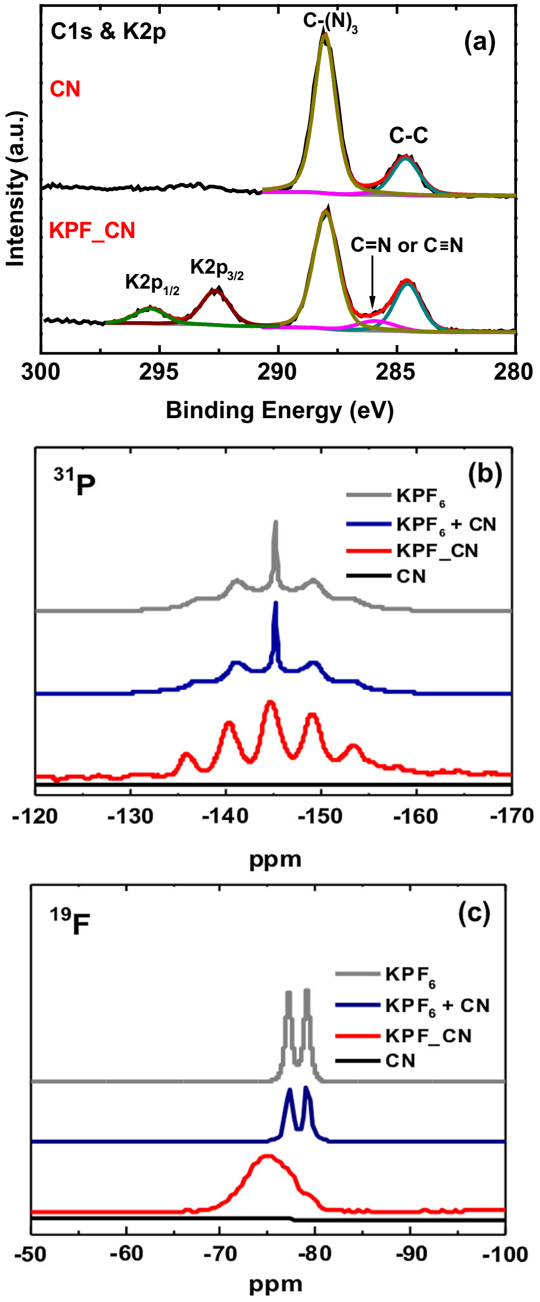

Fig. 2. (a) Deconvoluted XPS core-level spectra of C1s and K2*p* for bare CN and KPF_CN_15, (b) ^{31}P MAS NMR spectra, and (c) ^{19}F MAS NMR spectra for bare CN, KPF_CN_15, the physical mixture of KPF_6 and bare CN, and pure KPF_6. The NMR spectra of the samples (KPF_CN, KPF_6 + CN, and KPF_6) were normalized for facile comparison.

Unless otherwise mentioned, KPF_CN represents KPF_CN_15, which exhibited the optimal activity. To investigate the effect of different dopants as controls, 15 mmol of KNO_3 (99.99%, Aldrich), H_3PO_4 (85 wt%, Aldrich), NH_4F (98%, Aldrich), KF (99+%, Aldrich), K_2HPO_4 (98%, Aldrich), or NH_4PF_6 (95+%, Aldrich) was mixed with melamine (instead of KPF_6) to prepare control samples of K_CN, P_CN, F_CN, KF_CN, KP_CN, and PF_CN, respectively.

2.2. Photocatalytic activity tests

For the reductive conversion of O_2 to H_2O_2, a proper amount of catalyst (0.5 g/L) was dispersed in a mixed solution of deionized water and ethanol (10 vol%). The solution was then sonicated for