

A Novel One-step Photocatalytic Synthesis of Benzo[*d*]oxazol-2(3*H*)-one with C-doped TiO₂ Nanoparticle

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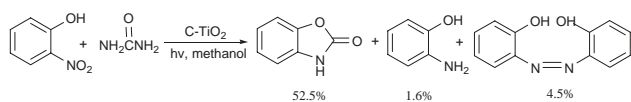
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A novel approach was proposed to synthesize benzo[*d*]oxazol-2(3*H*)-one by photoreduction of *o*-nitrophenol and cyclization with urea using C-doped TiO₂ nanoparticles as photocatalyst which was prepared by a modified sol-gel method using glucose as carbon source.

Wide attention has recently been devoted to photocatalytic applications for organic synthetic chemistry, such as oxidation,¹ reduction,² addition,³ polymerization,⁴ amino acid,⁵ alkylation,⁶ and cyclization⁷ reactions. Benzo[*d*]oxazol-2(3*H*)-ones have attracted considerable attention as a result of their medicinal properties and some interesting efficacy of antiviral, analgesic, anti-inflammatory, chemo-preventive, anticancerous, antibacterial, anti-mycotic, and antiprotozoal,⁸ have been reported. Benzo[*d*]oxazol-2(3*H*)-one and its derivatives have been synthesized by many methods,⁹ many of which show several limitations including long reaction time, harsh reaction conditions, poisonous reagents, and generating dangerous pollutants for the environment. We recently discovered a mild and one-pot synthesis of benzo[*d*]oxazol-2(3*H*)-one during a successful attempt based on new active-TiO₂ catalytic systems. Compared to the corresponding TiO₂, the use of C-doped TiO₂ nanoparticles has shown that their photocatalytic activity is superior and has also received considerable attention.¹⁰

The anatase TiO₂ and C-TiO₂ particles were prepared by a simple modified sol-gel process with glucose as carbon source and tetrabutyltitanate as a precursor respectively. Tetrabutyltitanate (8.4 mL) and glacial acetic acid (1.2 mL), which prevents the precipitation of oxides and stabilizes the solutions, were dissolved in 30 mL of ethanol. After 1 h, nitric acid was added to adjust the pH 3. During the hydrolysis process, the mole ratio of H₂O, C₂H₅OH, and C₆H₁₂O₆·H₂O was maintained at 13:21:1. Then the process consisted of evaporation of the solvent, drying at 100 °C for 8 h and finally calcination at 350 °C for 4 h. The photocatalytic synthesis of benzo[*d*]oxazol-2(3*H*)-one was carried out in a self-designing reactor of 250 mL capacity with a refluxing device. The suspending solution, which was composed of an ratio (1:1.2) of *o*-nitrophenol (1 mmol) and urea and 500 mg of C-TiO₂ along with 20 mL of methanol solvent in the photoreactor was irradiated using a 500-W high-pressure mercury lamp (356 nm) under magnetic stirring at refluxing temperature in Scheme 1. After irradiation for 7.5 min, nitric acid



Scheme 1. Synthesis of benzo[*d*]oxazol-2(3*H*)-one with nanoparticle C-TiO₂ in methanol.

was added to the solution. The reaction mixture was centrifuged at 20 min after irradiation to separate the catalyst and the compound benzo[*d*]oxazol-2(3*H*)-one was isolated as the major product. HPLC measurement was performed by Agilent 1100 liquid chromatography equipped with a UV detector and an auto-sampler with MeOH/H₂O/THF (38/10/18 in volume) as eluent to detect the product. The product was isolated and purified. Further analysis was performed by FT-IR and ¹H NMR spectra measurement.¹²

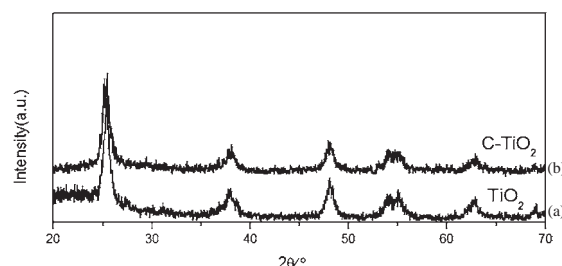


Figure 1. XRD patterns of (a) as-synthesized TiO₂ and (b) C-TiO₂ samples prepared using sol-gel method.

Shown in Figure 1 are X-ray powder diffraction (XRD) patterns of TiO₂ and C-TiO₂ powder samples prepared, collected using a Model D/Max 2550V and Cu anticathode radiation. From the intensity ratios between the diffraction appearing at $2\theta = 25.5^\circ$ (anatase 101) one may conclude that the TiO₂ deposited at 350 °C consists almost completely of the anatase phase and no other crystal phase can be detected. The average crystalline size of C-TiO₂ was calculated using the Scherrer equation. Pure TiO₂ had a particle size of 10.3 nm; doped TiO₂, about 6.8 nm. Crystalline of C-doped TiO₂ showed smaller size than undoped-TiO₂ at the same calcinations temperature.

Shown in Figure 2 are XPS spectra of the as-synthesized C-TiO₂ sample. The XPS survey spectra analysis indicated the presence of Ti, O, and C on the surface of C-modified TiO₂. It can be seen from Figure 2 that the C 1s peaks fitted to two different peaks are found at 284.6, 287.99, and 294.15 eV. The first signal at 284.6 eV is assigned to the C 1s peaks related to the C-C or C-H bonds. The other signal can be attributed to C-O and C=O bonds. According to the literature,¹¹ the XPS peak at 288.6 eV indicated the presence of C-O bonds and carbon might substitute for some of the lattice titanium atoms and form a Ti-O-C structure. The characteristic doublet Ti 2p_{3/2} and Ti 2p_{1/2} are at 461.8 and 467.5 eV, respectively. All of these values indicate that TiO₂ is the main constituent of the as-deposited C-modified TiO₂. The O 1s peak of XPS spectra presented in Figure 2 can be decomposed into two contributions. The main peaks at 530.25 eV and a shoulder at 533.21 eV were assigned

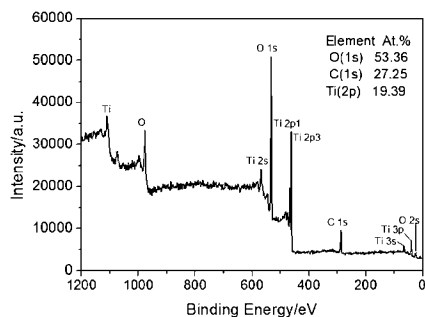


Figure 2. XPS spectra of C-TiO₂ prepared by the sol-gel method.

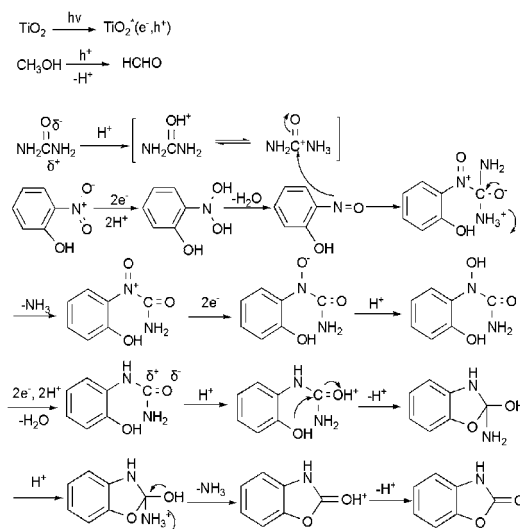
Table 1. Reaction performance of catalytic synthesis of benzo[*d*]oxazol-2(3*H*)-one using C-TiO₂ in methanol

Catalyst	Reaction time /min	Surface area /m ² g ⁻¹	Selectivity /%	Yield/%
None	20	—	0	0
P25	20	50	32	4.7
TiO ₂	20	64.8	40	10.3
C-TiO ₂	20	165.2	90	52.5

to bulk O²⁻ from TiO₂ and OH⁻, respectively. Based on the above XPS analysis, the C 1s feature and the of Ti 2p peaks in this work indicated the TiO_{2-x}C_x structure was formed.

The progress of the reaction was monitored by TLC and yields reported were estimated on the basis of isolated yields. Parallel experiments were also carried out using pure nano TiO₂ and C-TiO₂ to compare the photocatalytic activity. Listed in Table 1 were the reaction performance data for three catalysts and a non-catalytic case in methanol. Obviously, the reaction was not carried out without the catalyst. The yield (52.5%) on C-TiO₂ was higher than that (10.3%) on pure TiO₂. Concerning the role of the catalyst, it was inferred that the doped catalyst might improve the efficiency of the synthesis, resulting in the enhanced conversion. One reason was that C dopant decreased the particle size, and the other reason was that C dopant caused a decrease in oxygen vacancies and minimized the electron-hole recombination.

Further experiments were carried out to confirm whether the reaction was photocatalytic or not and it was observed that no product was formed in the absence of C-TiO₂ catalyst. Thus irradiation in the presence of photocatalyst when carried out without nitric acids also did not yield the product. The acidity medium and photocatalyst seems to commonly influence the reaction mechanism. For the photocatalytic reaction mechanism in methanol solution, it is suggested that carbonylation of *o*-nitrophenol can occur to form benzo[*d*]oxazol-2(3*H*)-one. Scheme 2 shows a plausible reaction mechanism. First a pair of electron and hole (e⁻, h⁺) would be generated by the band gap photo-excitation of C-TiO₂. Most of the pairs are lost by recombination, but the Schottky barrier at the C-TiO₂ interface would assist the charge separation. The methanol solution serves as hole-remover was oxidized by a portion of positive holes. Generally, the main by-product of the reaction was formaldehyde. Few azo compounds and amine were formed. The proposed mechanism for reduction of *o*-nitrophenol is enhanced photo-generated elec-



Scheme 2. Proposed reaction mechanism for the formation of benzo[*d*]oxazol-2(3*H*)-one.

trons at the surface of the C-TiO₂ particles. And nitrosoarene formed as an intermediate carried out an addition reaction with urea in the presence of hydrogen ion to give the product.

It is worth stressing that the photocatalytic reaction is a useful one-step alternative to only a few methods designed for the synthesis of benzo[*d*]oxazol-2(3*H*)-one and most interestingly the C-TiO₂ as photocatalyst is stable with the photoirradiation and reusable in repeated experiments.

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References and Notes

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