



Short communication

Highly active Ru-g-C₃N₄ photocatalyst for visible light assisted selective hydrogen transfer reaction using hydrazine at room temperature

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ABSTRACT

The present study describes the highly efficient heterogeneous photoactive catalyst Ru-g-C₃N₄ screened for selective transfer hydrogenation of nitroarenes and olefins. Photoactive catalyst Ru-g-C₃N₄ exhibits excellent reactivity in visible light under very mild reaction conditions via using hydrazine hydrate as a source of hydrogen with high turnover number. The easily separable heterogeneous photoactive Ru-g-C₃N₄ catalyst is straightforward to handle in visible light (LED lamp), non-toxic, environmentally friendly and at the same time eliminates the use of high pressure hydrogenation reactors without the need for external sources of energy.

1. Introduction

The reduction of nitroarenes to the corresponding amines is an important key transformation in organic synthesis as well as in the chemical industry for the preparation of various chemicals, medicinal, printing dye and polymers based printing industry [1–3]. Numerous catalysts were reported for the nitroarenes hydrogenation, including molecular hydrogen, homogenous catalyst, or supported catalysts on different support [4–7]. Literature shows some of these catalysts are not commercially efficient in the several cases due to harsh reaction conditions, expensive catalysts, reagents, multi-step synthetic procedures, and the need for special facilities for generation, storage & transportation of hydrogen gas. Frequently hazardous wastes were generated in these processes [8–10]. In view of the above basic points the need to develop safe, greener, sustainable synthesis, low cost, non-toxic, visible light-assisted protocol is highly desired.

Solar energy offers a great potential usage as a clean and economical energy source for organic transformations due to high abundance, inexpensive and thus rapidly growing worldwide during the last two decades [11–13]. In the same context, recently metal free semiconductors polymeric carbon nitride exhibits significant attention in recent years, due to unique photochemical properties like; visible light energy storage, semiconductor properties (~2.7 eV band gap), high stability, nontoxic, metal free organocatalyst, environmentally benign photo catalysts and easy synthesis from cheap raw material without any additional support [14,15]. Whereas at the same time with doping of metals like Cu [16], Fe [17], Pd [18], Ag [19,20], Pt [21], V [22] and single Atom (Pd/Pt) Supported [23] graphitic carbon nitride (g-C₃N₄)

increases its photo catalytic activity due to two dimensional (2D) polymer consisting of interconnected tri-s-triazine units via tertiary amines. However the regular arrangement of nitrogen atoms in g-C₃N₄ creates mobile electrons and holes after visible light absorption; which results in enhancement of its electronic and catalytic properties [24,25]. Precisely, g-C₃N₄ material in photo catalysis has been extensively studied for various organic transformations in environmental and economic perspectives [26,27].

Very recently, our research group reported an efficient, simple protocol; which has been developed for the hydrogen transfer reaction of the carbonyl functional group (> C=O) using a heterogeneous photoactive catalyst Ru-g-C₃N₄, the reaction occurs efficiently at room temperature in the presence of visible light using different alcohols as a hydrogen source [28]. In continuation of our ongoing research of novel photo catalysts, herein we report for the first time Ru-g-C₃N₄ as a high performance photo catalyst for the reduction of nitroarenes to the corresponding amines at room temperature under visible light irradiation (Scheme 1) using hydrazine monohydrate as hydrogen source (SI S5).

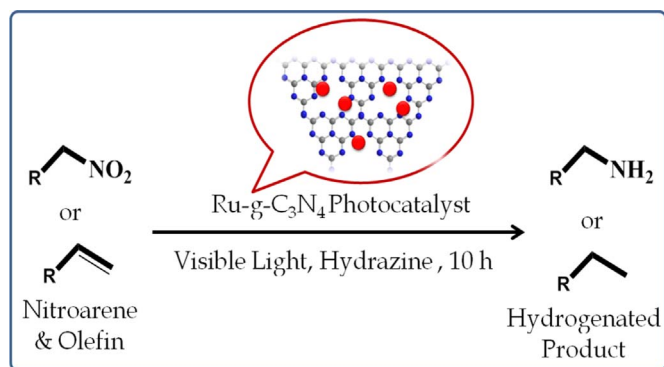
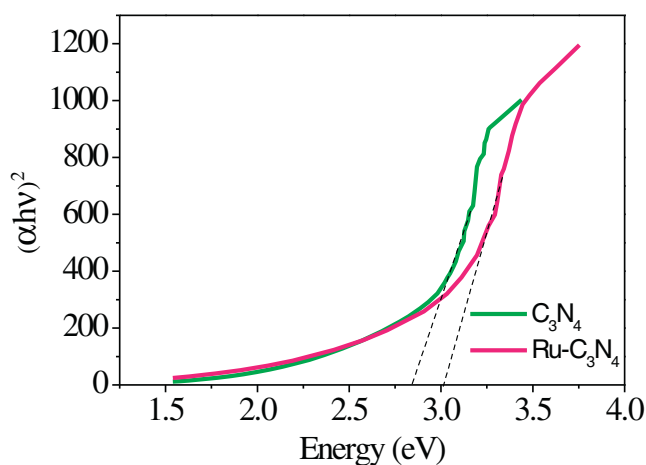
2. Experimental

2.1. Materials

The material used in the experiments such as Urea, Alcohols, Ruthenium chloride, Deionized water, Nitro arenes, Olefins, Hydrazine (hydrogen source) chemicals were purchased from commercial firms (Sigma Aldrich and reliable resources) and used without further

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Scheme 1. Photoactive Ru-g-C₃N₄ catalyzed transfer hydrogenation.Fig. 1. Tauc plots, (a) g-C₃N₄, (b) Ru-g-C₃N₄.Table 1
Reaction parameters optimization for photocatalytic hydrogenation reaction.

Entry	Reaction condition	Time (h)	Yield (%)
1.	RuCl ₃ (no light)	12	< 5
2.	RuCl ₃ (visible light)	12	< 5
3.	g-C ₃ N ₄ (no light)	12	0
4.	g-C ₃ N ₄ (visible light)	12	0
5.	Ru-g-C ₃ N ₄ (no light)	24	< 9
6.	Ru-g-C ₃ N ₄ (visible light)	10	99
7.	No catalyst (blank reaction)	24	00

Reaction conditions: Ru-g-C₃N₄ (30 mg), nitroarene (1 mmol), NH₂NH₂·H₂O (10 mmol), Isolated yields, visible light irradiation > 420 nm (9 W LED domestic ceiling lamp), room temperature, Conversion based on GC analysis.

purification. LED lamp (9 W domestic ceiling down light Epistar LED ceiling lamp) used as a visible light source. GC analyses were performed using Focus GC from Thermo Electron Corporation, equipped with low polarity ZB-5 column. GC analyses were performed using Trace 1300 Gas Chromatograph model from Thermo Scientific, equipped with the Rxi-1ms (cross bond 100% dimethyl polysiloxane) column. Conversion based on GC area. The ruthenium (Ru) content of catalyst was determined by an Inductively Coupled Plasma Mass Spectrometry (ICPMS) spectrometer (Agilent 7500 cx).

2.2. Semiconductor graphitic carbon nitride (g-C₃N₄), Photocatalyst Ru-g-C₃N₄ synthesis

Graphitic carbon nitride (g-C₃N₄) and Ru-g-C₃N₄ was fabricated by following our group earlier reported procedure [28]. Photocatalyst Ru-g-C₃N₄ is prepared by stirring with 1 g of g-C₃N₄ with 8% by weight

loading of ruthenium chloride (RuCl₃) for 6 h in ethanol solution at 50 °C temperature followed by till dryness.

2.3. General protocol for the photocatalytic hydrogen transfer reaction via Ru-g-C₃N₄ catalyst

The photocatalytic hydrogenation was carried out in a 25 mL oven dried, R.B. (round bottom flask), under visible light (9 W LED domestic ceiling lamp) with high magnetic stirring ~800 rpm at room temperature. In catalysis run, substrate (1 mmol), photocatalyst Ru-g-C₃N₄ (30 mg), ethanol solvent (10 mL), Hydrazine (10 mmol) were allowed to stir (800 rpm). The reaction samples were taken periodically time to time with fixed intervals and analyzed by gas chromatography. The samples were added with DCM (dichloromethane) solvent for dilution and filtered by Whatman paper before injection into a gas chromatograph (Scheme 1) (SI S9).

2.4. Characterization

XRD measurements were performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Sollers slits, and 0.2 mm receiving slit. A low background quartz sample holder was carefully filled with the powder samples. XRD patterns from 5° to 85° 2θ were recorded at room temperature using Cu Kα radiation (λ = 0.15418 nm) with the following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step scan mode with a step size 0.02° 2θ and counting time of 1 s per step for preliminary study and 12 s per step for structural refinement. The instrumental broadening was determined using LaB6 powder (NIST-660a). XPS analysis was conducted using XPS Kratos AXIs Ultra (Kratos Analytical Ltd., UK) high resolution photoelectron spectroscopy instrument. FTIR spectra were collected by a Bruker (Alpha-T). Sample morphology was observed by extra High-Resolution Scanning Electron Microscopy (Magellan™ 400 L). X-ray diffraction patterns were collected by using a Bruker AXS D8 Advance. UV/Vis absorption spectra were monitored by Carry 100 Bio and Diffuse Reflectance analysis was carried out by an Integrating Sphere (JASCOV-650 Series ISV-722). FTIR spectra were collected by a Bruker (Alpha-T).

3. Results and discussion

Graphitic semiconductor support g-C₃N₄ and Ru-g-C₃N₄ photocatalyst were fabricated via our recently reported procedure [28]. Heterogeneous photoactive catalyst Ru-g-C₃N₄ was fabricated by simple stirring ruthenium chloride (RuCl₃) salt with graphitic g-C₃N₄ in ethanol solvent in round bottom flask at 50 °C till dry in 6 h. The synthesized photo catalyst Ru-g-C₃N₄ is well characterized by various characterization techniques.

Transformation of urea into g-C₃N₄ after calcinations at 550 °C for 3 h exhibits clearly with intense emergence peak at 27.20 in the typical X-ray diffraction (XRD) pattern. In case of g-C₃N₄, and Ru-g-C₃N₄ the two distinct diffraction peaks at 13.20 and 27.20 do match well with the reported procedure that corresponding to (100) and (002) diffraction plane of the graphitic g-C₃N₄ materials, respectively with the disappearance of urea characteristics background peaks (Fig. S1) [29]. Most apparently due to partial loading of ruthenium salt, Ru-g-C₃N₄ diffraction of (002) plane shows less intense comparatively to the g-C₃N₄ material (Fig. S1).

Conducted FT-IR characterization analysis confirms synthesis of g-C₃N₄ from urea and ruthenium loaded Ru-g-C₃N₄ fabrication (Fig. S2) systematically. The absorption bands at 3430, 3345, 1454, 1582 cm⁻¹ are the typical absorption bands of urea (raw material) and vanished after transformation into g-C₃N₄ in calcinations process. The sharp absorption at 1248 cm⁻¹ and 1624 cm⁻¹ shows the C–N and C=N stretching vibrations, respectively [30,31]. Furthermore, the

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