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## PAPER



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# Solar and visible-light active nano Ni/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for carbon monoxide (CO) and ligand-free carbonylation reactions<sup>†</sup>

Mona Hosseini-Sarvari 😳\* and Zahra Akrami

In this study, we investigate the amino and alkoxycarbonylation reaction between various substituted aryl halides, benzyl iodides, and iodocyclohexane with different types of amines and alcohols in the absence of carbon monoxide gas and ligands. Similar reactions are carried out at high temperatures, in the presence of appropriate ligands, stoichiometric amounts of bases, and gaseous carbon monoxide, which endanger the health of organic chemists. We present a novel method that does not utilize ligands, bases, gaseous CO, and special conditions. This procedure is a redox reaction carried out by new economic nano Ni/g- $C_3N_4$  at room temperature and under visible light. Mo(CO)<sub>6</sub> was used to *in situ* generate CO, to resolve the problems caused by the use of CO gas. This protocol has the ability to be used on a gram scale by using a continuous flow reactor.

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## Introduction

The use of transition metals as catalysts for the synthesis of carbonylated organic compounds is a useful and valuable method in carbonylation reactions.<sup>1</sup> For this reason, many attempts have been made in previous decades to use transition metals as catalysts in carbonylation reactions to convert organic compounds with halide<sup>2</sup> or pseudohalide<sup>3</sup> substitutions to carboxylic acids. Nowadays, synthesized molecules containing amide and ester-based scaffolds have attracted the attention of many chemists, because they are structural units found in natural compounds and are used in the preparation of pharmaceutical, agrochemical, aromatic,<sup>4,5</sup> and biologically active compounds.<sup>6</sup> In fact, one of the most essential chemical linkages that make up the structural backbone of peptides and proteins is the amide bond. Besides, heterocyclic amides can be used as specific species in the central nervous system's active structures.<sup>7</sup> For example, as a vasoconstrictor agent, midodrine is employed in the treatment of hypotension<sup>8,9</sup> (Fig. 1 compound A), loracarbef is an antibiotic<sup>10</sup> (Fig. 1 compound B), and procainamide<sup>11</sup> is utilized as an antiarrhythmic prescription (Fig. 1 compound C). Also, the carbonylation reaction is an effective method to synthesize a wide range of aromatic esters and their derivatives.<sup>12-14</sup> Like amides, esters play a vital role in the pharmaceutical industry. For example, esters such as benzocaine and tetracaine are commonly used as pain relievers for local anesthesia or in cough drops<sup>15</sup> (Fig. 1 compounds D and E). Ethyl eicosapentaenoic acid is a drug that is used along with changes in diet to treat hypertriglyceridemia, for adults with hypertriglyceridemia  $\geq$ 150 mg dl<sup>-1</sup> (ref. 16 and 17) (Fig. 1 compound F).

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The Schmidt reaction,<sup>18</sup> Schotten–Baumann reaction<sup>19</sup> and Ugi reaction<sup>20</sup> are the conventional methods to synthesize amides and esters. Due to the importance of these compounds, various synthetic methods have been developed. However, the synthesis of carbonyl compounds *via* reactions between aryl halides and an appropriate nucleophile using a transition metal as a catalyst is an operational method. Therefore, recently, a great number of non-photochemical<sup>21-31</sup>



Fig. 1 Some biologically active amide and ester compounds.

Department of Chemistry, Shiraz University, Shiraz 7194684795, I.R. Iran. E-mail: hossaini@shirazu.ac.ir

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Fig. 2 a) UV-vis diffuse reflectance spectra of  $g-C_3N_4$  and nano Ni/g-C\_3N\_4. (b) Photoluminescence emission spectra of  $g-C_3N_4$  and nano Ni/  $g-C_3N_4$ .

and photochemical<sup>32–37</sup> techniques have been developed to synthesize amides and esters (Scheme 1).

Non-photochemical methods are limited to the use of ligands or bases and gaseous carbon monoxide (CO) and are carried out at high temperatures.<sup>21–31</sup> Coinciding with advances in radical carbonylation, particularly the light/metal





hybrid method<sup>36</sup> reported by Ryu et al.,<sup>37</sup> metal-catalyzed carbonylation as a mild experimental method replaced free radical-based methods. The use of coupling agents such as aryl halides in multicomponent radical carbonylation reactions under light irradiation has led to the synthesis of a wide range of carbonyl compounds using radical species. Recently, Xiao and Lu,32 Jacobi von Wangelin, and Gu33 groups reported the use of organic dyes causing environmental problems. Additionally, the synthesis of various functionalized carbonyl groups using carboxylic acids and aryl diazonium salts in the presence of iridium and ruthenium-based metal complexes as photocatalysts is a toxic and costly method.<sup>34-37</sup> Besides in 2018, He and co-workers reported a Pd catalyzed carbonated Suzuki reaction at 80 °C using CO from CO<sub>2</sub> photoreduction by ruthenium.<sup>38</sup> Therefore, the increasing efforts of the modern chemical industry for green and renewable reaction conditions are challenged to revise the reaction conditions. Low catalyst loading, lower reaction temperatures, separation and reutilization of the catalysts, and ligand-free catalytic systems are some of the significant targets because of environmental and economic demands. Heterogeneous semiconductors as environmentally friendly materials having the following benefits are used to replace other homogeneous catalysts: (1) separation and recovery of the catalyst by centrifugation or filtration (2) to take advantage of ligand-free catalytic systems is a cost-effective method.<sup>39</sup>



Fig. 4 EDX spectrum of nano Ni/g-C<sub>3</sub>N<sub>4</sub>.



Fig. 5 XRD patterns of  $g\mathchar`-C_3N_4$  (a) and nano Ni/g-C\_3N\_4 (b) at room temperature.



Fig. 6 SEM image of nano  $Ni/g-C_3N_4$ .

Heterogeneous photocatalyst graphitic carbon nitride (g- $C_3N_4$ ) is one of the most profitable polymers among the collection of metal-free.<sup>40</sup> Contrary to semiconductors TiO<sub>2</sub>, ZnO and WO<sub>3</sub>,  $g-C_3N_4$  materials with a lower bandgap (TiO<sub>2</sub>: 3.2 eV,<sup>41</sup> ZnO: from 3.10 eV to 3.37 eV,<sup>42</sup> WO<sub>3</sub> about 2.6 to 3.0 eV (ref. 43) versus g-C<sub>3</sub>N<sub>4</sub>: 2.7 eV) and ability to absorb visible light in the 450-460 nm region are widely considered. Due to the ease of preparation of these compounds from natural and available materials such as urea and melamine, graphitic carbon nitrides are economically viable and environmentally safe.<sup>44,45</sup> Besides, g-C<sub>3</sub>N<sub>4</sub> is a heterogeneous semiconductor, which, in addition to optical activity, has other advantages such as non-toxicity, thermal stability, chemical stability, low cost, significant electrical properties, and a large surface area. Additionally, g-C<sub>3</sub>N<sub>4</sub> has lately found a wide range of utilization in materials science, catalysis, electronic, and optical fields as a result of its particular structure and incomparable properties.46-48 The association of nitrogen atoms in the carbon architecture provides anchor sites for the immobility of active species and metal nanoparticles when g-C<sub>3</sub>N<sub>4</sub> is employed as a heterogeneous catalyst support, which in return leads to the enhancement of catalytic efficiency. Therefore, this choice is beneficial and economical compared to other semiconductors. Despite all these advantages, features such as the low specific surface area of pure  $g-C_3N_4$  and the high electron-hole



Fig. 7 a) TEM image of nano Ni/g-C $_3N_4$ . b) The distribution of nanoparticle sizes.

recombination rate have caused this compound to have relatively little photocatalytic activity.<sup>49</sup> Therefore, these problems can be solved by doping a co-catalyst on g- $C_3N_4$ nanosheets.<sup>50</sup> Nickel, like palladium,<sup>51</sup> can catalyze the crosscoupling reaction. The binding of nickel with photoredox catalysts can lead to a variety of conversions, making it a viable substitute for rare metals.<sup>52</sup> Ni is a cheap metal that is found in abundance and has high activity and good stability. Due to the effective separation of electron–hole pairs, Ni loading on g- $C_3N_4$  is an efficient method. This property is due to the change in surface band bending, which kinetically



Fig. 8 Nitrogen adsorption-desorption isotherms of nano 6 wt% Ni/g-  $C_3N_4$  and pure g-  $C_3N_4.$ 

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Table 1 BET results for nano Ni/g-C <sub>3</sub> N <sub>4</sub> and pure g-C <sub>3</sub>
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Surface area	BET surface area $(m^2 g^{-1})$ (Ni/g-C <sub>3</sub> N <sub>4</sub> )	12.884
	BJH adsorption cumulative surface area of pores $(m^2 g^{-1})$ (Ni/g-C <sub>3</sub> N <sub>4</sub> )	15.233
	BET surface area (m <sup>2</sup> g <sup>-1</sup> ) (pure g-C <sub>3</sub> N <sub>4</sub> )	4.653
	BJH adsorption cumulative surface area of pores (m <sup>2</sup> g <sup>-1</sup> ) (pure g- $C_3N_4$ )	17.241
Pore size	Mean pore diameter (nm) (Ni/g-C <sub>3</sub> N <sub>4</sub> )	35.051
	Pore size distribution (nm) (Ni/g- $C_3N_4$ )	7.98
Pore volume	Single point adsorption volume of pores (cm <sup>3</sup> g <sup>-1</sup> ) (Ni/g-C <sub>3</sub> N <sub>4</sub> )	0.1129
	BJH adsorption cumulative volume of pores $(m^2 g^{-1}) (Ni/g-C_3N_4)$	0.1147

#### Table 2 Solvent, base, and atmosphere optimization<sup>a</sup>

C0						
	t +	$MO(CO)_6 + NH_2 \text{ nano Ni/g-C}_3N_4$	(0.008g)			
	1a	2a 3a 🗹	4a			
Entry	Solvent	Base	Atmosphere	Yield (%)		
1	THF	DBU	Air	72		
2	DMF	DBU	Air	80		
3	DMSO	DBU	Air	35		
4	$CH_3CN$	DBU	Air	Trace		
5	EtOH	DBU	Air	0		
6	CHCl <sub>3</sub>	DBU	Air	0		
7	EtOAc	DBU	Air	0		
8	H <sub>2</sub> O	DBU	Air	10		
9	DMF	DABCO	Air	68		
10	DMF	Bu <sub>3</sub> N	Air	68		
11	DMF	$Et_3N$	Air	64		
12	DMF	$Cs_2CO_3$	Air	55		
13	DMF	$K_3PO_4$	Air	52		
14	DMF	$K_2CO_3$	Air	Trace		
15	DMF	КОН	Air	Trace		
16	DMF	_	Air	83		
17	DMF	_	Ar	48		
18	DMF	_	$O_2$	81		
$19^b$	DMF	—	Air	15		

<sup>*a*</sup> Reaction conditions: iodobenzene (1 mmol), aniline (1.5 mmol), Mo(CO)<sub>6</sub> (1 mmol), nano Ni/g-C<sub>3</sub>N<sub>4</sub> (0.008 g, 6 wt%), base (3.0 mmol), solvent (1.5 mL), room temperature, 11 W white LED (wavelength in the range of 400–750 nm), 24 h. <sup>*b*</sup> Without any Mo(CO)<sub>6</sub>.

#### Table 3 Amount of photocatalyst<sup>a</sup>

		×	MO(CO) <sub>6</sub>	• NH2			
		1a	2a	3a		4a	
Entry	Ni/g-C <sub>3</sub> N <sub>4</sub> (mg)		Yie	eld (%)	Entry	Ni/g-C <sub>3</sub> N <sub>4</sub> (mg)	Yield (%)
1	3		51		7 <sup>b</sup>	10	78
2	6		62		8 <sup>c</sup>	10	65
3	8		83		9	_	0
4	10		90		$10^d$	10	0
5	12		90		$11^e$	10	10
6	14		87				

<sup>*a*</sup> Reaction conditions: iodobenzene (1 mmol), aniline (1.5 mmol), Mo(CO)<sub>6</sub> (1 mmol) and photocatalyst in DMF (1.5 mL), at room temperature, 11 W white LED (wavelength in the range of 400–750 nm), air atmosphere, 24 h. <sup>*b*</sup> Nano Ni/g-C<sub>3</sub>N<sub>4</sub> (8 wt% Ni), 24 h. <sup>*c*</sup> Nano Ni/g-C<sub>3</sub>N<sub>4</sub> (4 wt% Ni), 36 h. <sup>*d*</sup> Pure g-C<sub>3</sub>N<sub>4</sub>, 36 h. <sup>*e*</sup> Pure NiCl<sub>2</sub>, 36 h.



**Fig. 9** Aminocarbonylation reaction under a) different light and b) light on and off conditions. <sup>a</sup>Isolated yield.



Fig. 10 Aminocarbonylation under natural sunlight.

increases the rate of surface reactions and causes this compound to perform better photocatalytically than unmodified  $g-C_3N_4$ .<sup>53</sup> Based on previous research into the development of inexpensive new photocatalysts that are catalytically more efficient and simpler, as well as to design more cost-effective processes, we have prepared and

characterized nano Ni/g-C3N4 as heterogeneous nanosheets. These nanosheets are biocompatible and effective photocatalysts that catalyze radical reactions between aryl halides/alkyl halides and amines/alcohols in the presence of  $Mo(CO)_6$  as a source of CO gas<sup>54</sup> to create a new method for the synthesis of amides and esters as a transformation that according to our knowledge has not previously been described. This is a simple method carried out at room temperature under the radiation of a blue LED lamp or sunlight; it does not use any base, ligand, and organometallic reagent, and it is not necessary to employ special conditions or control CO gas release. It is noted that the use of  $Mo(CO)_6$ as a harmless source of CO gas eliminated the problems caused by the use of CO gas, and made it possible to synthesize amides and esters under mild conditions and using visible light-activated catalysts. Therefore, to eliminate the hazards of carbon monoxide in the carbonylation reactions of aryl electrophiles, in the presence of a Ni photocatalyst, Mo(CO)<sub>6</sub> was used to replace CO gas, and we predicted that this redox carbonylation mechanism would attract the attention of chemists in most scientific and applied fields.

## **Results and discussion**

To achieve the aim of photocarbonylation, we first synthesized Ni/g- $C_3N_4$  nanoparticles with an approximate size of 4.6 nm using the photodeposition technique.<sup>55</sup> Since semiconductors are efficient, economical, and easy-to-use compounds, this method could be useful for gram scales. After synthesizing nano Ni/g- $C_3N_4$ , we investigated the characteristics of this nanocatalyst *via* UV-visible, PL, FT-IR, EDX, XRD, SEM, TEM, BET, and nitrogen adsorption–desorption techniques (Fig. 2–8 and Table 1).

UV-vis diffuse reflectance spectroscopy was used to determine the optical absorption of g-C<sub>3</sub>N<sub>4</sub> and 6 wt% Ni/g-C<sub>3</sub>N<sub>4</sub>. As shown in Fig. 2a, when Ni was loaded on g-C<sub>3</sub>N<sub>4</sub>, the absorption peak of modified g-C<sub>3</sub>N<sub>4</sub> gradually shifted to the more extended wavelength region. The Kubelka-Munk function<sup>56</sup> was applied to calculate the optical band-gap of both the unmodified and modified g-C<sub>3</sub>N<sub>4</sub>. As shown in Fig. 2, g-C<sub>3</sub>N<sub>4</sub> and nano Ni/g-C<sub>3</sub>N<sub>4</sub> have band-gaps of 2.76 and 2.38, respectively. This reduction in the band-gap that occurs after Ni loading is due to the increased interactions between Ni species and g-C<sub>3</sub>N<sub>4</sub> and reaffirms that Ni loading on g-C<sub>3</sub>N<sub>4</sub> regulates the electronic structure.<sup>57</sup> In addition, nano Ni/g-C<sub>3</sub>N<sub>4</sub> has stronger visible light absorption than nonmodified g-C<sub>3</sub>N<sub>4</sub>, which is in acceptable accordance with the shift of these compounds (Fig. 2a). To investigate the effect of Ni doping on the recombination performance of photocarriers, the photoluminescence emission spectra of the pure g-C3N4 and nano Ni/g-C3N4 samples were investigated. As presented in Fig. 2b, the pure g-C<sub>3</sub>N<sub>4</sub> sample shows a strong emission peak at around 450 nm, which is related to the bandgap for the recombination of photogenerated electrons-holes. The nano Ni/g-C<sub>3</sub>N<sub>4</sub> sample

 Table 4
 A broad range of synthesized aromatic and aliphatic amides<sup>a,b</sup>





<sup>a</sup> Reaction conditions: aryl halide (1 mmol), amine (1.5 mmol), Mo(CO)<sub>6</sub> (1 mmol), nano Ni/g-C<sub>3</sub>N<sub>4</sub> (10 mg, 6 wt% Ni), DMF (1.5 mL), room temperature, 11 W blue LED (wavelength in the range of 400-495 nm), air atmosphere, 48 h.<sup>b</sup> Yields refer to isolated yield.

presents a similar PL pattern, but the emission intensity is quenched together with a small redshift. The PL emission intensity of pure g-C<sub>3</sub>N<sub>4</sub> was several times higher than that of 6 wt% Ni/g-C<sub>3</sub>N<sub>4</sub>. This observation showed that the recombination of photogenerated electrons and holes was prohibited undoubtedly by Ni, which would be exactly desirable for the photocatalytic activity.

- Band gap energy  $(E) = h \times C/\lambda$
- *h* = Planck's constant =  $6.626 \times 10^{-34}$  Joules second,
- C = speed of light =  $3.0 \times 10^8$  meters per second,
- $\lambda$  = cut off wavelength nano Ni/g-C<sub>3</sub>N<sub>4</sub> = 520 × 10<sup>-9</sup> meters.
- $\lambda$  = cut off wavelength g-C<sub>3</sub>N<sub>4</sub> = 450 × 10<sup>-9</sup> meters.
- $1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joules (conversion factor)}$

The chemical functional groups of the catalyst were determined by FT-IR and Fig. 3 shows the results of g-C<sub>3</sub>N<sub>4</sub> and nano Ni/g-C<sub>3</sub>N<sub>4</sub>, respectively. The spectra showed strong IR absorption bands, which were attributed to the typical molecular structure of g-C<sub>3</sub>N<sub>4</sub>. The broad absorption at 3100-3300 cm<sup>-1</sup> belonged to the remaining N-H components and O-H bonds, corresponding to uncondensed amino groups and H<sub>2</sub>O molecules adsorbed on the surface. The broad absorption at 900 and 1800 cm<sup>-1</sup> was attributed to the polycondensation structure of g-C<sub>3</sub>N<sub>4</sub>, which was ascribed to the vibration characteristics of the s-triazine ring units and heptazine heterocyclic ring units.<sup>58</sup> In the FT-IR spectra, pure

 $g-C_3N_4$  and nano Ni/ $g-C_3N_4$  exhibited similar absorption bands. These results presented that the structure of  $g-C_3N_4$ did not change during the photodeposition of Ni.

We employed EDX analysis to detect the presence of nickel. The data obtained from the energy dispersive X-ray analysis confirmed that there was not any P element, which indicated that no phosphorus compounds were produced on the surface (Fig. 4). Furthermore, the induced coupled plasma (ICP) analysis revealed that only 6 wt% Ni in nano Ni/ $g-C_3N_4$  is present.

Fig. 5 shows the XRD patterns of pure g-C<sub>3</sub>N<sub>4</sub> and Ni/g- $C_3N_4$  nanoparticles. The small signal at  $2\theta = 13.08$  implies the interplanar length related to the interlayer packing of pure g-C<sub>3</sub>N<sub>4</sub> (Fig. 5a). The peaking signal at  $2\theta = 27.41$ indicates the specified interlayer peak related to graphitic systems. Pure g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> containing Ni exhibited a specific signal at  $2\theta = 27.41$ ; it demonstrates that the structural features of g-C3N4 were preserved well in the process of doping nickel. In addition, the signal intensity of pure g-C<sub>3</sub>N<sub>4</sub> decreased slightly when Ni was doped on it, which indicated that the surface features of g-C<sub>3</sub>N<sub>4</sub> were tuned by Ni. The weakening of this peak suggested that the Ni on the surface of g-C<sub>3</sub>N<sub>4</sub> slightly prevented the diffraction of the crystal structure of g-C<sub>3</sub>N<sub>4</sub>.<sup>54</sup> It can be observed that for Ni-loaded g-C<sub>3</sub>N<sub>4</sub>, new signals related to the (111), (200), and (220) crystal planes of Ni appear at  $2\theta = 44.5^{\circ}$ , 51.8°, and 76.4°, respectively (Fig. 5b), which are compatible with the standard data of metallic Ni (JCPDS 87-0712). The average size of nano Ni/g-C<sub>3</sub>N<sub>4</sub> was calculated using the Scherrer formula from  $2\theta$  = 27.41, and was obtained to be around 4.6 nm (see ESI† Table S2).

Fig. 6 and 7 show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images and the particle size distribution histogram of nano Ni/g-C<sub>3</sub>N<sub>4</sub>. The TEM image showed that the range of particle sizes is approximately between 5 and 9 nm, which is compatible with the data of the XRD pattern, and the particles have cubic and spherical shapes. The cubic morphology causes the increase in absorption in the visible light range.<sup>59</sup> By increasing the surface/sub-surface defect ratio, the possibility of charge-carrier separation can be elevated, which is achieved with the sub-10 nm size of the particles.<sup>60</sup> The diagram of the approximate size range of nano Ni/g-C<sub>3</sub>N<sub>4</sub> is shown in Fig. 7b.

Table 1 shows the results of the BET surface area and pore volume measurements for nano Ni/g-C<sub>3</sub>N<sub>4</sub>. The BET surface area of nano Ni/g-C<sub>3</sub>N<sub>4</sub> was obtained to be 12.884 m<sup>2</sup> g<sup>-1</sup>, and the BJH adsorption surface area of pores was 15.233 m<sup>2</sup> g<sup>-1</sup>. As shown in Table 1, the size distribution and single point adsorption volume of pores were obtained to be 7.98 nm and 0.1129 cm<sup>3</sup> g<sup>-1</sup>, respectively. Fig. 8 presents the nitrogen adsorption–desorption isotherms of nano Ni/g-C<sub>3</sub>N<sub>4</sub> and pure g-C<sub>3</sub>N<sub>4</sub>. The adsorption–desorption isotherms of all the samples exhibit typical type V curves with H3 hysteresis loops suggesting the presence of mesopores. The high-pressure hysteresis loop (*P*/*P*0 > 0.9) is related to macropores. The type

H3 hysteresis loops suggested that the slit-like pores were based on the aggregates of  $g-C_3N_4$  sheets.<sup>61</sup> It can be observed that the surface area of Ni/g-C<sub>3</sub>N<sub>4</sub> (12.884 m<sup>2</sup> g<sup>-1</sup>) is larger than that of pure  $g-C_3N_4$  (4.653 m<sup>2</sup> g<sup>-1</sup>) with the insertion of Ni. It is commonly known that a broad surface area is always desirable to the photocatalytic efficiency due to its abundant active sites. So with surface area increasing, the photocatalytic activity of Ni/g-C<sub>3</sub>N<sub>4</sub> is improved.

After the exact structure of the photocatalyst was identified and characterized, we used this catalyst in carbonylation reactions to evaluate its practical efficiency and obtain better results in the synthesis of amides from aryl and alkyl halides. Therefore, firstly we chose the reaction between iodobenzene (**1a**), molybdenum hexacarbonyl (2a), and aniline (3a) as a pattern system, and investigated different factors to optimize the reaction conditions of amide synthesis (4a). Tables 2 and 3 and Fig. 7 and 8 indicate the optimized results. We studied the effects of various factors, including the solvent, base, atmosphere, time, photocatalyst loading, and the source of light. First, we irradiated an iodobenzene solution in THF using a white LED (11 W) at room temperature and under an air atmosphere, in the presence of Ni/g-C<sub>3</sub>N<sub>4</sub> nanoparticles (0.008 g) and the DBU base. After 24 h, phenyl benzamide (4a) was obtained with a yield of 72% (Table 2, entry 1). Therefore, firstly, we studied the effects of solvents and found out that in the presence of THF or DMF, our desired product was produced with excellent yields (72% yield and 80% yield) (Table 2, entries 1 and 2). However, when we used other solvents, the yield of the product fell significantly (entries 3-9). Hence, DMF is the best solvent for this reaction. In the proposed mechanism, we explain why DMF is a better solvent for such reactions. Since we assumed that bases play an important role in this reaction, we examined several inorganic and organic bases to optimize the reaction. Table 2 includes the results of optimizing bases: DBU has the highest yield, then next are DABCO, tributylamine, and triethylamine (Table 2, entries 9-11), Cs<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> have average yields (Table 2, entries 12 and 13), and there are no products produced by K<sub>2</sub>CO<sub>3</sub> and KOH (Table 2, entries 14 and 15). We also investigated the carbonylation reaction under base free conditions and found high efficiency under base free conditions (Table 2, entry 16). Therefore, any C-N bond generated under base free conditions is proof of the existence of Ni (0) and confirms our proposed mechanism. In the next step, we investigated the effects of the atmosphere (Table 2, entries 17 and 18). In the atmosphere of oxygen and air, almost the same results were obtained, but the reaction efficiency in the atmosphere of argon decreased. These results further evidence our proposed mechanism, which will be discussed in the following. As shown in entry 19, when we removed the CO source  $(Mo(CO)_6)$ , the product was obtained with a 15% efficiency, which implies that CO could be generated by photocatalytic dissociation of DMF. This result is additional proof confirming our proposed mechanism.

 Table 5
 A broad range of synthesized aromatic and aliphatic esters<sup>a,b</sup>



<sup>*a*</sup> Reaction conditions: aryl halide (1 mmol), alcohol (1.5 mmol),  $Mo(CO)_6$  (1 mmol), nano Ni/g-C<sub>3</sub>N<sub>4</sub> (0.01 g, 6 wt% Ni), DMF (1.5 mL), at room temperature, 11 W blue LED (wavelength in the range of 400–495 nm), air atmosphere, 48 h. <sup>*b*</sup> Yields refer to isolated yield. <sup>*c*</sup> Yield of product **6p** was determined by HPLC analysis.

In addition, we optimized the photocatalyst amounts and applied an optimum of 0.01 g of  $Ni/g-C_3N_4$  nanoparticles in this research work (Table 3, entry 4). We also examined the effect of different amounts of nickel (entries 7 and 8). A study of the reaction showed a 0% conversion both in the absence of the catalyst and in the presence of pure  $g-C_3N_4$  (Table 3, entries 9 and 10). In the presence of pure NiCl<sub>2</sub>, a 10% yield of product 4a was obtained, indicating the catalytic role of Ni(II) (Table 3, entry 11).

#### Influence of light

Since the yield of the desired product depends on selective wavelengths of LEDs, we expose the reaction to different light conditions, including long and short wavelengths with the same intensity. As shown in Fig. 9a, the amide production efficiency increased to 93% when the reaction was irradiated with a blue LED (11 W). Therefore, higher frequency photons can be used to produce photoelectrons-holes, and increase the efficiency of the product. The results showed that under dark conditions, only a 10% yield of product 4a is produced, which indicates the catalytic role of nickel (0). By studying the results of the reaction in the presence of light and without light, it was found that light is an essential factor in the reaction and has a significant effect on the efficiency of the reaction. The results show that the reaction progresses as long as it is exposed to radiation, and by stopping the radiation, the reaction stops (Fig. 9b).

#### Reaction under sunlight

Besides, on a summer day, we investigated the operation of nano Ni/g-C<sub>3</sub>N<sub>4</sub> under the sun outside the laboratory. This experiment was carried out in August, in Shiraz, at a temperature of 26–37 °C and a zenith angle of 68.5°. The results showed that this photocatalyst has a high capacity to absorb sunlight (Fig. 10).

After optimizing the reaction conditions, we were able to synthesize a wide range of amides. Table 4 shows the photoaminocarbonylation reaction for a wide range of aryl halides with aliphatic and aromatic substitutions. We found that nano Ni/g-C<sub>3</sub>N<sub>4</sub> could be used to produce a wide range of different substrates with excellent efficiency. The results indicated that the amidation reaction between iodobenzene and primary amines with electron-withdrawing and electrondonating groups on the anilines, as well as secondary amines such as morpholine, piperazine, pyrrolidine, and piperidine, is well done, and the desired amides are synthesized with high efficiency (entries 4a-f). Also, Table 4 shows that both iodobenzene with electron-withdrawing groups such as -NO2 and iodobenzene with electron-donating groups such as -Me can be used in our proposed technique (entries 4g-j). Not surprisingly, aryl bromides were less reactive than aryl iodides. Thus, selective amidation of chloro-bromo or chloroiodo derivatives gives impressive results (entries 4k-n). Under optimized conditions, heteroaromatic iodides also showed favorable results. Both N-phenyl thiophene-2-carboxamide and morpholino(thiophene-2-yl)methanone were obtained from 2-iodothiophene with 95% and 89% efficiencies, respectively (entries 40-p). Similarly, *N*-(thiazol-2-yl)benzamide was obtained from thiazol-2-amine (entry 4q). In our proposed method, in addition to aromatic halides,



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Fig. 11 Recyclability of nano Ni/g-C\_ $3N_4$  in a) aminocarbonylation and b) alkoxycarbonylation reactions.

a) Amino	ocarbonylation			
Runs	Weight of the catalyst (mg)	Nickel leaching (wt%)		
1	10	0.000		
2	9.6	0.003		
3	9.3	0.005		
4	8.9	0.007		
5	8.5	0.009		
6	8.2	0.011		
b) Esteri	fication			
Runs	Weight of the catalyst (mg)	Nickel leaching (wt%)		
1	10	0.000		
2	9.5	0.004		
3	9.1	0.007		
4	8.7	0.009		
5	8.4	0.011		
6	8.0	0.014		

aliphatic halides with C-sp<sup>3</sup> also provided favorable results for synthesizing amides (entries 4r–z).

#### Synthesis of esters

The promising data from the synthesis of amide derivatives persuaded us to use the photocatalyst to form a C–O bond. To evaluate the application of the photocatalyst, we first



designed a model reaction between iodobenzene (1a), molybdenum hexacarbonyl (2a), and benzyl alcohol (5a) in the presence of nano Ni/g-C<sub>3</sub>N<sub>4</sub> as a photocatalyst, and then optimized the reaction conditions (solvent, base, atmosphere, catalyst). According to the results, the best reaction conditions for the synthesis of benzyl benzoate (6a) are very close to the optimal conditions for the preparation of amides. Therefore, we can carry out this reaction using 0.01 g of nano Ni/g-C<sub>3</sub>N<sub>4</sub>, under base-free conditions and at room temperature in the presence of DMF, and under irradiation with a blue LED (11 W), and in air. In addition, the effects of LED light and sunlight on the reaction are shown in Fig. S1-S3 (see the ESI<sup>†</sup>). This reaction is carried out in the presence of various aryl halides and aliphatic alcohols, so the yield of the obtained products is satisfactory (Table 5). By using iodobenzene and 4-nitroiodobenzene in the presence of aliphatic alcohols, various esters were obtained. In the esterification reaction, two-substituted aryl halides with chloride, bromine, or iodine could be selected, and a selective product could be obtained from its corresponding aryl halide (entries 6l and m). Finally, using our proposed method, we could obtain excellent results for synthesizing benzyl cyclohexane carboxylate, 2-nitrobenzyl cyclohexane carboxylate, and methylcyclohexane carboxylate from iodocyclohexane (entries 6n-p). The production of highefficiency carboxylic acid derivatives, using a simple method, is useful for synthesizing some beneficial compounds. This is a new pathway for the synthesis of amides and esters through photocatalytic carbonylation, in the absence of CO gas, using aliphatic and aromatic halides, and in the presence of molybdenum hexacarbonyl as the CO source.

#### Catalyst recyclability

Nano Ni/g- $C_3N_4$  can be used multiple times without a significant reduction in reaction efficiency (Fig. 11), so it can be said that nano Ni/g- $C_3N_4$  is a recyclable heterogeneous photocatalyst with useful function. At the end of each cycle, the catalyst was recovered using a centrifuge, washed with water and ethanol, and then dried in an oven at 80 °C. Even after 6 runs, no significant reduction in its catalytic activity was observed. Details about the weight of the photocatalyst



Fig. 13 The characterization of the recovered nano Ni/g-C\_3N\_4: (a) UV-vis, (b) FT-IR, (c) XRD, and (d) photoluminescence spectra.

and the wt% of the nickel leaching after each run are given in Table 6 and the results show that only trace amounts of nickel were found in the collected solution after each run (see the ESI† for more information on the leaching test). Additionally, the reaction stopped completely after hot filtration with efficiency and time of about 50% and 12 h, respectively, indicating that the reaction was performed on the surface of a heterogeneous catalyst (Fig. 12). Further, the photostability of nano Ni/g-C<sub>3</sub>N<sub>4</sub> was surveyed using XRD,



**Fig. 14** Flow reactor. L = length of the filled column,  $d_{in}$  = internal diameter of the column, F = flow rate,  $t_r$  = residence time. 5 mmol scale, 82% yield.

UV-vis, FT-IR, and PL spectra. According to Fig. 13 the XRD spectra disclosed no remarkable differences between fresh nano Ni/g- $C_3N_4$  and the recovered nano Ni/g- $C_3N_4$  affirming that the crystal structures of the photocatalyst were not changed during these recovery cycles (Fig. 13c). Also the PL emission intensity and UV-vis absorption spectra show that no significant difference was observed between fresh and recyclable nano Ni/g- $C_3N_4$  (Fig. 13a and d).

#### Scale-up of continuous flow

Features such as easy access to equipment and reactants, as well as the simple technique used, led to the investigation of large-scale reactions using a continuous-flow photoreactor. Given that in the laboratory and on a small scale, we were able to collect a significant amount of product using 0.557 ml of iodobenzene, we can use this method on a large scale. Next, we investigated the operation of this method with a continuous flow column, glass beads, silica gel, and nano Ni/ g-C<sub>3</sub>N<sub>4</sub>. As expected, a suitable and reusable continuous-flow photoreactor was obtained. By shortening the reaction time (8 h), the practical capacity of the reaction was determined (Fig. 14). As a result, a continuous-flow photoreactor is a viable option for large-scale use. To do this, 50 mg of Ni/g- $C_3N_4$  nanoparticles and 4 g of silica gel (particle size 70–230 µm) were gently ground in an agate mortar for 5 minutes. An 80 cm long glass tube (with an inner diameter of 1 cm) was fitted with a cotton filter at an outlet to keep the solid mixture in the reactor. The tube was filled with 8 g of glass beads (d = 0.5 cm) and a pre-prepared mixture of nano Ni/g-C<sub>3</sub>N<sub>4</sub> and silica gel. DMF was added for rinsing. Blue LED wires were wrapped outwards. Iodobenzene (0.557 ml, 5 mmol), aniline (0.684 ml, 7.5 mmol), and  $Mo(CO)_6$  (1320 mg, 5 mmol) were dissolved in DMF (40 ml), and the resulting solution was gradually added to the tube. The flow rate was 1 mL h<sup>-1</sup>, controlled using a plunger with a residence time of  $t_r$ 

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Table 7 Comparison of using Mo(CO)<sub>6</sub> instead of CO gas for the synthesis of some compounds similar to compounds 4c, 6d and 6i

Catalyst Compds.		Conditions	Yield (%)	Ref.
Nano Ni/g-C <sub>3</sub> N <sub>4</sub>	6d	Mo(CO) <sub>6</sub> /visible light	95	This work
Eosin Y	6d	Gaseous CO/visible light	86	33
Nano Ni/g-C <sub>3</sub> N <sub>4</sub>	6i	Mo(CO) <sub>6</sub> /visible light	88	This work
Eosin Y	6i	Gaseous CO/visible light	57	33
Nano Ni/g-C <sub>3</sub> N <sub>4</sub>	4 <b>c</b>	Mo(CO) <sub>6</sub>	95	This work
Pd/SiO <sub>2</sub>	4 <b>c</b>	Gaseous CO/heat	77	22

= 8 h. During operation, the reactor was irradiated with an air-cooled LED module. After 8 hours, we collected the product in the outlet. Upon completion of the reaction, the solvent was evaporated at room temperature. The crude product was obtained as a powder and purified by column chromatography to give the desired product (82%).

Finally, a comparative study of using  $Mo(CO)_6$  instead of CO gas with other photochemical and non-photochemical reported catalysts for the synthesis of some compounds similar to compounds **4c**, **6d** and **6i** was made, which revealed that  $Mo(CO)_6$  is an efficient alternative to CO gas (Table 7).

#### Control experiments and mechanism suggestion

To increase our insight into this mechanism, some additional studies were made, as shown in Fig. 15. Tetramethylpiperidinyl-1-oxy (TEMPO·) is a stable nitroxide radical which acts as an electron-trapping agent for semiconductors.<sup>62,63</sup> When 2 mmol of TEMPO was added to the reaction mixture, the yield of the target molecule was severely decreased. It could trap electrons from the CB of

g- $C_3N_4$  and also it could capture the  $O_2$ <sup>--</sup> radicals acquired from the CB of g- $C_3N_4$ .

Besides, according to Table 2 entry 17, the reaction did not progress under the Ar atmosphere as well as only a trace amount of the target product was obtained without the use of the photocatalyst (Table 3 entry 9). For this reason, light, activated oxygen ( $O_2$ , ), and a photocatalyst are required to process this reaction. Also, in a new test, triethanolamine (TEA), methanol, and ethylenediaminetetraacetic acid were added as hole scavengers, and it was again observed that the desired product was obtained in trace amounts. These observations confirmed the possibility that the reaction took place through a radical pathway. In addition, the fact that the product does not form under dark conditions confirms that visible light stimulates the carbonylation reaction.

According to previously reported articles<sup>64–67</sup> and our experimental results, the proposed mechanism for amino and alkoxycarbonylation is shown in Fig. 16. By light irradiation, charge separation occurs, and electron/hole pairs (e–/h+) are generated on the g-C<sub>3</sub>N<sub>4</sub> surface. The electron in the CB of g-C<sub>3</sub>N<sub>4</sub> is effective for the generation of superoxide radical anion O<sub>2</sub><sup>--</sup>. This superoxide radical anion reacted with amines or alcohols (3 or 5) by abstracting proton generated HX and molecular O<sub>2</sub>. The corresponding RY anion is trapped by Ni(II) species II generating organometallic adduct III. In the catalytic cycle of nickel, the oxidative addition of



Fig. 15 Control experiments: a) aminocarbonylation, b) alkoxycarbonylation.



Fig. 16 Proposed mechanism of carbonylation.

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nickel (0) (which exists on the catalyst surface and has been proven by characterizing the photocatalyst and other experimental results) to aryl halide 1 resulted in the production of intermediate I. These nickel(II) species yield intermediate II through the insertion of CO that is released from  $Mo(CO)_6$ . Finally, products 4 or 6 were obtained by reductive elimination of intermediate III, and Ni (0) was regenerated for the next catalytic cycle. According to Table 2, the results of optimizing solvents showed that DMF provides the best efficiency. Based on the reports published by Feng and Li, C-N bond cleavage in DMF may occur through electron transfer to the hole. As a result, CO gas and dimethylamine are produced.68 Dimethylamine can serve as a base to balance the HX produced from RYH and  $O_2^{-}$ . That is why it is possible to obtain 15% of the desired product without using any Mo(CO)<sub>6</sub>. DMF is a suitable species for electron transfer to the hole (Table 2, entry 19).

## Experimental section

Chemicals materials were acquired from Fluka, Aldrich, Acros, and Merck, and all solvents were obtained from commercial sources and dried employing standard procedures.

#### **Catalyst preparation**

**Preparation of g-C<sub>3</sub>N<sub>4</sub>.** g-C<sub>3</sub>N<sub>4</sub> was prepared according to the procedure reported by Li.<sup>69</sup> Typically, a Coors highalumina crucible was charged with 10 g of melamine powder, and then placed in a 673 in<sup>3</sup> muffle furnace (115 V/14 Amps) at a heating rate of 20 °C min<sup>-1</sup> to 500 °C in 2 h. For formation of a better structure, it was put at 520 °C for 2 h.

**Preparation of nano** Ni/g-C<sub>3</sub>N<sub>4</sub>. Nano Ni/g-C<sub>3</sub>N<sub>4</sub> was prepared by an altered photodeposition procedure.<sup>51</sup> 10 mg g-C<sub>3</sub>N<sub>4</sub>, 3 mL triethanolamine (TEOA), 250  $\mu$ L NiCl<sub>2</sub> (0.1 M) solution, 2 mL NaH<sub>2</sub>PO<sub>2</sub> (0.1 M) aqueous solution, and 4.9 mL H<sub>2</sub>O were blended in a round bottom flask at room temperature. The system was stirred for 40 min under a nitrogen atmosphere. Then, the mixed solution was irradiated under UV-vis light (300 W Xe lamp) for 30 min. The final step involved washing collected precipitates with distilled water to remove the residues of reactants.

General procedure for aminocarbonylation in the presence of the nano Ni/g-C<sub>3</sub>N<sub>4</sub> photocatalyst. To a Pyrex roundbottom flask set with a magnetic stir bar, aryl iodide (1 mmol), amine (1.5 mmol), Mo(CO)<sub>6</sub> (1 mmol), nano Ni/g-C<sub>3</sub>N<sub>4</sub> (0.01 g, 6 wt%) and DMF (1.5 mL) were added and the reactant mixture was irradiated with an 11 W blue LED lamp ( $\lambda > 440$  nm, distance 3.0 cm) in an air atmosphere at room temperature. The reaction was stirred for a suitable time at room temperature (25 °C) and checked using TLC. After the termination of the reaction, ethyl acetate (2 mL) was added to the reaction mixture and heterogeneous nano Ni/g-C<sub>3</sub>N<sub>4</sub> was entirely isolated applying centrifugation, then, the organic phases were dehydrated over MgSO<sub>4</sub> and the solvent was vaporized under reduced pressure to acquire the crude. Ultimate product purification was done by silica gel column chromatography utilizing petroleum ether/ethyl acetate.



General procedure for alkoxycarbonylation in the presence of the nano Ni/g-C3N4 photocatalyst. To a Pyrex roundbottom flask set with a magnetic stir bar, aryl iodide (1 mmol), alcohol (1.5 mmol), Mo(CO)<sub>6</sub> (1 mmol), nano Ni/g-C<sub>3</sub>N<sub>4</sub> (0.01 g, 6 wt%) and DMF (1.5 mL) were added and the reactant mixture was irradiated with an 11 W blue LED lamp  $(\lambda > 440 \text{ nm}, \text{distance 3.0 cm})$  under air conditions at normal temperature. The reaction was stirred for a suitable time at room temperature (25 °C) and checked using TLC. After the termination of the reaction, ethyl acetate (2 mL) was added to the reaction mixture and heterogeneous nano Ni/g-C<sub>3</sub>N<sub>4</sub> was entirely isolated applying centrifugation, then, the organic phases were dried and dehydrated over MgSO4 and the solvent was vaporized under reduced pressure to acquire the crude. Ultimate product purification was done by silica gel column chromatography utilizing petroleum ether/ethyl acetate.

General procedure for using TEMPO in the presence of the nano Ni/g-C<sub>3</sub>N<sub>4</sub> photocatalyst. To a Pyrex round-bottom flask set with a magnetic stir bar, aryl iodide (1 mmol), amine or alcohol (1.5 mmol), Mo(CO)<sub>6</sub> (1 mmol), nano Ni/g-C<sub>3</sub>N<sub>4</sub> (0.01 g, 6 wt%), TEMPO (2 mmol), and DMF (1.5 mL) were added and the reactant mixture was irradiated with an 11 W blue LED lamp ( $\lambda > 440$  nm, distance 3.0 cm) in an air atmosphere at room temperature. The reaction was stirred for a suitable time (24 h) at room temperature (25 °C) and checked using TLC and GC. As expected, a trace amount of the target product was obtained in the presence of TEMPO.

## Conclusion

semiconductors Heterogeneous are eco-friendly an replacement for photocatalyst reactions and sewage treatment. A class of extracted metal-free polymers from inexpensive natural resources like graphitic carbon nitrides are heterogeneous semiconductors with great potential for organic photosynthesis. In this study, we demonstrated that graphitic carbon nitrides grafted with a nickel catalyst can induce selective C-N and C-O cross-coupling of alkyl halides and aryl halides with amines and alcohols, by using Mo(CO)<sub>6</sub> as the source of CO gas under visible light that alkoxycarbonylation has not been reported so far. This makes it possible to operate carbon monoxide coupling reactions under benign and safe conditions, without the presence of

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## Conflicts of interest

There are no conflicts to declare.

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