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# Gold nanoparticles supported on ionic liquid-modified cellulose as an efficient and recyclable catalyst for the oxidation of alcohols to aldehydes/ketones and reduction of nitroarenes

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Ali Pourjavadi, Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Azadi Avenue, PO Box 11365-9516, Tehran, Iran. Email: purjavad@sharif.edu A novel catalyst of gold nanoparticles supported on cellulose fibres with the ionic liquid framework (Au NPs@CL-IL) has been shown to be a highly active and recyclable catalyst for the oxidation of primary and secondary alcohols and reduction of nitroarenes in aqueous media. The reusability of this catalyst is high, and it can be reused ten times without a significant decrease in its catalytic activity. Furthermore, transmission electron micrographs of the recovered catalyst show the presence of well-distributed Au NPs on the CL-IL fibres without any aggregation.

#### KEYWORDS

cellulose, gold, ionic liquid, nanoparticle, oxidation, reduction

# **1 | INTRODUCTION**

In recent years, ionic liquids (ILs) have attracted considerable attention due to their interesting and potentially useful physicochemical properties, including high ion conductivity, non-flammability, very low vapour pressure and high chemical stability.<sup>[1]</sup> But widespread utilizations of ILs as solvents or catalysts are limited by several drawbacks such as high viscosity, homogeneity (which makes them difficult to separate) and high cost for the use of relatively large amounts of ILs.<sup>[2]</sup> Supported ionic liquid catalysis (SILC) has been developed to address these issues. SILC materials are prepared by immobilization of ILs onto a surface of a porous high-area support material. SILC combines the benefits of high activity and selectivity of homogeneous catalysts with those of the recyclability, large surface area and hydrothermal stability of heterogeneous systems.<sup>[3]</sup> Furthermore, Mehnert and co-workers have described a concept of SILC that involves the treatment of a monolayer of covalently attached IL on the surface of a silica gel with additional IL.<sup>[4]</sup> These layers serve as the reaction phase in which the homogeneous catalyst is dissolved. The active species - although the resulting material is solid - is dissolved in the IL and acts as a homogeneous catalyst.<sup>[5]</sup> Many reports of the preparation of SILC materials have been published, where the ILs were immobilized onto support materials, such as porous silica, magnetic nanoparticles, carbon nanotubes, active carbon cloth, chitosan, and polymers.<sup>[6]</sup>

It is commonly understood that cellulose (CL) is the most abundant polymer on Earth and is the main component in plants.<sup>[7]</sup> Recently, it has attracted attention in more expanded application areas such as in the fields of nanoscience, nanotechnology and functionalized materials.<sup>[8]</sup> CL as an oxygen-rich carbohydrate (polysaccharide) consists of anhydroglucose units joined by  $\beta$ -(1–4)-glycosidic linkages to form a molecular chain. The intra-chain hydrogen bonding between hydroxyl groups and oxygens of the adjoining ring molecules stabilizes the linkage and results in the linear configuration of the CL chain. It also contains microfibrils of up to 30 nm in width that are three-dimensionally connected to each other. Metal nanoparticles (NPs) can be stabilized in the cavities of these microfibrils via oxygenmetal electrostatic interaction.<sup>[8]</sup> Additionally, Abdelmouleh et al. reported the surface modification of CL fibres with silane coupling agents.<sup>[9]</sup>

The selective oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important functional group transformations in organic synthesis.<sup>[10]</sup> The corresponding aldehydes or ketones are valuable as both intermediates and high-value products for the

### 2 of 8 WILEY-Organometallic Chemistry

pharmaceutical, agrochemical and perfumery industries.<sup>[11]</sup> Traditionally, this oxidation is performed using stoichiometric amounts of oxidants, such as permanganate, chromate or bromate.<sup>[12]</sup> These methods produce a large amount of waste and are unacceptable given green chemical practices. Recently, transition metal NP-catalysed aerobic alcohol oxidations have been investigated, and many have shown high catalytic activities and good selectivities.<sup>[13]</sup> Among various transition metals, the gold has attracted significant attention due to its superior catalytic performance.<sup>[13]</sup>

Reduction of the nitro group into an amine is an important process, as the amine functionality appears in several biologically active natural products, dyes and ligands for transition-metal-catalysed reactions. Since the amino group serves as a site for further derivatization, amines are also important intermediates for the production of pharmaceutical substances, photographic materials, agrochemicals, polymers and rubber materials.<sup>[14]</sup> Perhaps the most popular methodology for accomplishing the nitro to amine transformation is transition-metal-catalysed hydrogenation. However, this often suffers from low chemoselectivity if additional reducible functionalities are present. In recent years, significant progress has been achieved in the field of nitro aromatic compound reduction under catalysis using supported gold NPs.<sup>[15,16]</sup>

Herein, we report a novel catalyst of gold NPs supported on CL with IL framework (Au NPs@CL-IL) as an efficient and highly selective catalyst for the oxidation of primary and secondary alcohols and in the reduction of nitroarenes at very low catalyst loading. Additionally, the effects of solvent polarity, reaction the temperature and recycling potential of the catalyst have all been assessed.

### 2 | EXPERIMENTAL

All chemicals were purchased from commercial suppliers. Scanning electron microscopy (SEM) of Au NPs@CL-IL was conducted using a Hitachi SU3500 electron microscope. Transmission electron microscopy (TEM) of fresh and reused of Au NPs@CL-IL was carried out using a Philips CM-30 transmission microscope with an accelerating voltage of 150 kV. The concentration of gold in Au NPs@CL-IL was estimated using a Shimadzu AA-680 flame atomic absorption spectrophotometer and an inductively coupled plasma (ICP) optical emission spectrometer (Varian Vista PRO Radial). GC was performed using a Trace GC Ultra (Thermo) equipped with a flame ionization detector and Rtx<sup>®</sup>-1 capillary column. <sup>1</sup>H NMR spectra of products were recorded with a Bruker DRX-300 and 500 AVANCE spectrometer at 300 and 500 MHz. Melting points of products were measured with an Elecrtothermal 9100 apparatus and are uncorrected. Fourier transform infrared (FT-IR) analysis was carried out using KBr discs in the range 400–4000 cm<sup>-1</sup> using an ABB Bomem MB-100 FT-IR spectrophotometer. UV–visible spectra were recorded employing an Analytik Jena Specord S600 diode array spectrometer.

### 2.1 | Preparation of IL

In a well-dried 25 ml Schlenk flask, (3-chloropropyl) trimethoxysilane (10 mmol) was added to 1-methylimidazole (10 mmol), and then the system was evacuated and purged with nitrogen three times. After being stirred at 90 °C for 48 h under the nitrogen atmosphere, the resulting mixture was allowed to cool to room temperature, was washed with dry ethyl acetate four times and dried under vacuum for 24 h at room temperature. The finally obtained IL was a kind of yellowish sticky liquid.<sup>[17]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 0.40–0.46 (m, 2H), 1.78–1.86 (m, 2H), 3.39 (s, 9H), 3.92 (s, 3H), 4.11–4.16 (m, 2H), 7.3 (s, 1H), 7.6 (s, 1H), 10.3 (s, 1H).

### 2.2 | Preparation of CL-IL

The imidazolium salt was dissolved in a mixture of ethanol–water (80:20 v/v) at a concentration of 10% (w/w) for 12 h at room temperature, and thus was hydrolysed to form reactive silanol groups. A CL suspension (10% w/w with respect to the solvent) in a mixture of ethanol–water (80:20 v/v) was added to the solution and stirred for 8 h. Subsequently, the solvent was evaporated at 40 °C for 3 h under reduced pressure. The obtained white solid thermally was treated at 110 °C for 3 h, followed by thorough washing with ethanol and drying at room temperature.

### 2.3 | Preparation of Au NPs@CL-IL

CL-IL (250 mg) was ultrasonically dissolved in 100 ml of water. After that, 1.0 ml of HAuCl<sub>4</sub> (0.25 M) was added into the solution; and the mixture was ultrasonically treated for 3 h. Finally, 10.0 ml of NaBH<sub>4</sub> (0.25 M) was gradually added at 0 °C. The resulting precipitate was collected and washed with water (5 × 10 ml) and dried at room temperature. ICP analysis gave the actual Au content as 0.87 mmol g<sup>-1</sup> for the Au NPs@CL-IL nanohybrid.

# 2.4 | General procedure for oxidation of alcohol

The reaction mixture was prepared by taking 2 mmol of alcohol, 2 mmol of  $K_2CO_3$ , 5 ml of water and 0.1 ml of dodecane as an internal standard. The mixture was stirred using a magnetic stirrer and heated in a silicon oil bath using a reflux condenser under air. The system was equipped with a thermocouple to control the temperature. The reaction

mixture was shaken vigorously for homogenization and catalyst (1 mol% of Au) was added to the mixture. In each reaction run, the mixture was heated to 90 °C under vigorous stirring. After the reaction time, the reaction mixture was analysed using GC. After completion of the reaction, the mixture was allowed to cool to room temperature, and the catalyst was successfully isolated by centrifugation and washed with EtOAc (3 × 10 ml) and dried under vacuum for 12 h. Then, the collected EtOAc phase was first washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was concentrated by evaporation under reduced pressure to give the corresponding carbonyl compounds. The recovered catalyst was used in subsequent reactions in the same manner as reported for the first run.

# **2.5** | General procedure for reduction of nitroarene

Nitroarene (30 ml, 0.12 mM) was mixed with 30 ml of a freshly prepared aqueous  $NaBH_4$  solution (0.17 M). Then the nanohybrid (1 mol% of Au) was added to the resulting solution, and the reaction was allowed to proceed until the solution became colourless. The reaction conversion was determined using UV–visible spectroscopy. After completion of the reaction the heterogeneous mixture was cooled to room

temperature and the catalyst was separated. Then the reaction mixture was extracted with ethyl acetate  $(15 \times 3 \text{ ml})$  and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

#### **3 | RESULTS AND DISCUSSION**

The synthesis CL-IL is done by silulation modification of CL. Considering the ionic nature of the IL groups in CL-IL, the material can be utilized to support anionic gold species such as  $AuCl_4^-$  via a simple ion exchange reaction. Finally, the decoration of Au NPs was performed on CL-IL by the reduction of  $AuCL_4^-$  using NaBH<sub>4</sub> (Scheme 1).

FT-IR spectra of CL, CL-IL and Au NPs@CL-IL are shown in Figure 1. The FT-IR spectra of CL-IL and Au NPs@CL-IL show a new medium absorption band at about 1550 cm<sup>-1</sup> for C=N stretching. Additionally, a new weak absorption band at about 3100 cm<sup>-1</sup> corresponds to the stretching vibration of unsaturated C–H of the imidazole ring.<sup>[17]</sup>

Thermogravimetric analysis (TGA) was used to study the composition of the Au NPs@CL-IL nanohybrid. TGA plots of CL, CL-IL and Au NPs@CL-IL are shown in Figure 2. For CL, the weight lost is about 15% at temperatures below 305 °C. In contrast, CL-IL and Au NPs@CL-IL



SCHEME 1 Synthetic methodology for Au NPs@CL-IL



FIGURE 1 FT-IR spectra of CL, CL-IL and Au NPs@CL-IL nanohybrid



FIGURE 2 TGA plots of CL, CL-IL and Au NPs@CL-IL nanohybrid

nanocomposite show good thermal stability. The temperature stability of Au NPs@CL-IL decreased markedly when compared with CL-IL. This may be attributed to the catalytic activity of Au NPs for the oxidative degradation of CL.<sup>[18]</sup>

Figure 3(a) shows a representative SEM micrograph of the morphology of Au NPs@CL-IL. The density and distribution of the imidazolium groups and Au NPs on the Au NPs@CL-IL nanohybrid were evaluated using quantitative energy-dispersive X-ray spectroscopy (EDS) mapping. As can be seen in Figure 3(b–d), rather than only being located at the edges of the CL fibres, the elements Si, N, and Au are found to be uniformly dispersed on the whole **FIGURE 3** (a) SEM image of Au NPs@CL-IL, and corresponding quantitative EDS elemental mapping of (b) Au, (c) N and (d) Si

surface of the Au NPs@CL-IL nanohybrid indicating the homogeneous distribution of the imidazolium groups and Au NPs.

A TEM micrograph of Au NPs@CL-IL is shown in Figure 4. The surface of CL-IL is covered by distributed Au NPs with an average size of 10–20 nm.

The X-ray diffraction (XRD) patterns of CL, CL-IL and Au NPs@CL-IL are shown in Figure 5. The XRD patterns of CL and CL-IL show four characteristic CL reflections at  $2\theta = 14^{\circ}$ , 16°, 22° and 34° corresponding to (110), (110), (200) and (004) crystallographic planes, respectively. In the XRD pattern of Au NPs@CL-IL, the peaks at  $2\theta = 38^{\circ}$ ,

 $44^{\circ}$ ,  $64^{\circ}$  and  $77^{\circ}$  can be assigned to the (111), (200), (220) and (311) crystal faces of Au that indicates the NPs are pure metallic face-centred cubic gold (JCPDS no. 4–0784).

After the careful characterization of the prepared Au NPs@CL-IL nanohybrid, it was employed in the oxidation alcohols to aldehydes/ketones. Aerobic oxidation of benzyl alcohol was selected as a model reaction, and the effects of solvent, temperature, base and amount of catalyst on oxidation were studied. To obtain the best solvent, CH<sub>3</sub>CN, H<sub>2</sub>O, PhCH<sub>3</sub>, EtOH and CH<sub>2</sub>Cl<sub>2</sub> were investigated. The efficiency of the catalyst in terms of yield in water is more than that in the other solvents, which is due to the hydrophilic nature of the catalyst (Table 1, entries 1–5). Various bases such as Et<sub>3</sub>N, KOH and K<sub>3</sub>PO<sub>4</sub> were also screened for their effect on the reaction in H<sub>2</sub>O as solvent at 90 °C. A superior



FIGURE 4 TEM image of Au NPs@CL-IL nanohybrid

WILEY-Organometallic 5 of 8 Chemistry

yield is obtained when  $K_2CO_3$  is used as the base (Table 1, entries 1 and 8–10).

To study the effect of the amount of catalyst, the reactions were carried out with various amounts of Au NPs@CL-IL nanohybrid ranging from 0.5 to 1 mol% of Au (Table 1, entries 2 and 11). It is found that when the amount of Au NPs@CL-IL increases from 0.5 to 1 mol%, the yields increase from 53 to 99%, respectively. It is found that 1 mol% of Au is sufficient to push this reaction forward. To optimize the reaction temperature, we also performed several experiments at 80, 90 and 100 °C in the presence of K<sub>2</sub>CO<sub>3</sub> in H<sub>2</sub>O using Au NPs@CL-IL (1.0 mol% of Au) (Table 1, entries 2, 6 and 7). The optimal reaction temperature is 90 °C (Table 1, entry 2). It is also noteworthy that, when this reaction was carried out with CL-IL (0.01 g), we failed to isolate any product (Table 1, entry 12). Additionally, in order to investigate the effect of the IL, we used Au NPs@CL in the model reaction (Table 1, entry 13). The observed yield of benzaldehyde in a case was markedly inferior. It is well known that the activity and selectivity of heterogeneous metal catalysts are increased by addition IL in the support.<sup>[3–5]</sup> Probably, for this reason, the activity of Au NPs supported on CL-IL fibres is higher than that of Au NPs supported on CL fibres without IL.

As evident from Table 2, under optimum reaction conditions, various primary and secondary aliphatic and aromatic or heteroaromatic alcohols are converted to the corresponding aldehydes and ketones in high yields.

The reusability of the Au NPs@CL-IL nanohybrid was examined in aerobic oxidation of benzyl alcohol. It is found that recovery can be successfully achieved in ten successive reaction runs (Table 3). The heterogeneous nature of the catalyst was proved using a hot filtration test and atomic absorption spectroscopy (AAS) analysis. To determine whether the catalyst is functioning in a heterogeneous manner or whether it is merely a reservoir for more active



FIGURE 5 XRD patterns of CL, CL-IL and Au NPs@CL-IL nanohybrid

#### 6 of 8 WILEY-Organometallic Chemistry

TABLE 1 Optimization of reaction conditions<sup>a</sup>

		ОН	0	
Entry	Solvent	Temp. (°C)	Base	Yield (%) <sup>b</sup>
1	CH <sub>3</sub> CN	Reflux	K <sub>2</sub> CO <sub>3</sub>	46
2	$H_2O$	90	K <sub>2</sub> CO <sub>3</sub>	99
3	PhCH <sub>3</sub>	90	K <sub>2</sub> CO <sub>3</sub>	96
4	EtOH	Reflux	K <sub>2</sub> CO <sub>3</sub>	68
5	$CH_2Cl_2$	Reflux	$K_2CO_3$	14
6	$H_2O$	80	K <sub>2</sub> CO <sub>3</sub>	76
7	$H_2O$	Reflux	K <sub>2</sub> CO <sub>3</sub>	99
8	$H_2O$	90	Et <sub>3</sub> N	61
9	$H_2O$	90	KOH	82
10	$H_2O$	90	$K_3PO_4$	72
11 <sup>c</sup>	$H_2O$	90	K <sub>2</sub> CO <sub>3</sub>	53
12 <sup>d</sup>	$H_2O$	90	K <sub>2</sub> CO <sub>3</sub>	Trace
13 <sup>e</sup>	$H_2O$	90	K <sub>2</sub> CO <sub>3</sub>	67

<sup>a</sup>Benzyl alcohol (2 mmol), base (1 eq.), solvent (5 ml), *n*-dodecane (0.1 ml) and Au NPs@CL-IL (1 mol% of Au).

<sup>b</sup>Yield determined by GC analysis.

<sup>c</sup>Au NPs@CL-IL (0.5 mol% of Au).

<sup>d</sup>CL-IL (0.01 g).

eAu NPs@CL (1 mol% of Au).

soluble gold species, we performed a hot filtration test in aerobic oxidation of benzyl alcohol after *ca* 50% of the oxidation reaction was completed. The hot filtrates were then transferred to another flask containing H<sub>2</sub>O (3 ml) at 90 °C. Upon further heating of catalyst-free solution for 4 h, no considerable reaction progress (*ca* 4% by GC analysis) was observed. Moreover, using AAS of the same reaction solution at the midpoint of completion indicated that no significant quantities of gold were lost to the reaction liquors during the process. A TEM micrograph of recycled Au NPs@CL-IL nanohybrid after ten cycles shows no change in morphology (Figure 6).

Inspired by the high activity and stability of the Au NPs@CL-IL nanohybrid, the reduction of nitroarenes was employed as another model reaction to investigate further the performance of the Au NPs@CL-IL nanohybrid. We chose the reduction of 4-nitrophenol in the presence of NaBH<sub>4</sub> as a hydrogen source in H<sub>2</sub>O as solvent at room temperature with a catalyst loading of 1 mol% of Au for 11 min. Under these conditions, we find that the reduction proceeds well, affording excellent yield (99%) of the corresponding 4-aminophenol (Table 4, entry 1).

We next examined the scope and limitation of reduction of nitroarenes (Table 4). The reduction with most substrates proceeds to good yields. Nitroarenes bearing electron-

**TABLE 2** Aerobic oxidation of alcohols catalyzed by Au NPs@CL-IL nanohybrid<sup>a</sup>

	$ \begin{array}{c}             OH \\                       $	©CL-IL (1 mol% Au)	$B^1 R^2$	
	H <sub>2</sub>	$O, K_2 C O_3, 90^{-1} C$		
Entry	Alcohol	Product	Time (h)	Yield (%) <sup>b</sup>
1	ОН	0	2	99
2	СІ	CI	3	93
3	O <sub>2</sub> N OH	0 <sub>2</sub> N	2	97
4	CI	CI	4	86
5	Me <sub>2</sub> N OH	Me <sub>2</sub> N	3	99
6	OH		4	85
7	OH		4	92
8	ОН		4	89
9	OH	°	4	78
10	HO	0~0	24	62
11	HONN	ON	4	84

 $^aReaction$  conditions: alcohol (2 mmol),  $K_2CO_3$  (2 mmol),  $H_2O$  (5 ml), at 90 °C, air.  $^bIsolated\ yield.$ 

donating and electron-withdrawing groups react well giving good yields (Table 4).

To evaluate the catalytic results, we use the turnover frequency (TOF) to determine the efficiency of our catalyst for 4-nitrophenol reduction and compare with previously

 TABLE 3
 Reusability of Au NPs@CL-IL nanohybrid in aerobic oxidation of benzyl alcohol<sup>a</sup>

Reaction cycle	1	2	3	4	5	6	7	8	9	10
Yield (%) <sup>b</sup>	99	99	99	98	98	98	98	97	97	97

<sup>a</sup>Benzyl alcohol (4 mmol), K<sub>2</sub>CO<sub>3</sub> (4 mmol), H<sub>2</sub>O (10 ml), *n*-dodecane (0.2 ml) and Au NPs@CL-IL (1 mol% of Au).

<sup>b</sup>Yield determined by GC analysis.



FIGURE 6 TEM image of reused Au NPs@CL-IL nanohybrid after ten cycles

TABLE 4	Reduction of nitroarene catalysed by Au NPs@CL-IL
nanohybrid <sup>a</sup>	

	Ar—NO <sub>2</sub> ———	$\rightarrow$ Ar—NH <sub>2</sub>	
Entry	Substrate	Time (min)	Yield (%) <sup>b</sup>
1	4-Nitrophenol	11	99
2	3-Nitrophenol	5	99
3	1-Chloro-4-nitrobenzene	60	84
4	1-methyl-4-nitrobenzene	70	82
5	1-Methoxy-4-nitrobenzene	90	76

 $^a30$  ml of  $1.20\times 10^{-4}$  M nitroarene, 30 ml of 0.17 M NaBH<sub>4</sub> and Au NPs@CL-IL nanohybrid (1 mol% with respect to Au concentration).

<sup>b</sup>Isolated yield after column chromatography.

reported gold-based heterogeneous catalysts. The TOF of the Au NPs@CL-IL nanohybrid is 4.5 min<sup>-1</sup>, calculated from the moles of 4-nitrophenol reduced per mole of gold complex per consumed time under the present reaction

**TABLE 5** Comparison of catalytic activity of gold-based catalysts for the reduction of 4-nitrophenol

Catalyst	TOF (min <sup>-1</sup> )	Catalyst amount (Mol%)	Ref.
Au NPs@CL-IL	4.5	2	This work
HAuCl <sub>4</sub> ·3H <sub>2</sub> O	0.11	46	[19]
Au-PMMA	1.23	7	[20]
Au@SiO <sub>2</sub>	0.45	7	[21]
Au NPs/SNTs	0.77	28	[22]
Au/graphene hydrogel	0.19	43	[23]

conditions. As evident from Table 5, in comparison with other gold-based catalysts, our gold catalyst shows a higher catalytic efficiency than most of the other gold-based catalysts for the reduction of 4-nitrophenol.

#### 4 | CONCLUSIONS

We have demonstrated for the first time Au NPs supported on CL fibres with IL framework. The as-prepared Au NPs@CL-IL nanohybrid exhibited a high catalytic activity for the oxidation of primary, secondary cyclic and aromatic alcohols and reduction of nitroarenes in aqueous medium. Leaching tests (hot filtration) and AAS analysis show that the catalytic reaction is mainly heterogeneous in nature. The reusability of this catalyst is high and the catalyst can be reused ten times without a significant decrease in its catalytic activity. Additionally, TEM micrographs of the recovered catalyst showed the presence of well-distributed Au NPs on the CL-IL sheets without any aggregation.

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POURJAVADI AND HABIBI

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#### SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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