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Graphical Abstract

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Graphene Oxide (GO)–catalyzed chemoselective thioacetalization of aldehydes under solvent-free conditions

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ABSTRACT

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Keywords: Aldehydes Chemoselectivity Dithioacetal Graphene oxide Thiols An efficient method for the synthesis of open chain, cyclic and unsymmetrical dithioacetals from aryl/hetero-aryl/aliphatic aldehydes is described. The reaction is performed using graphene oxide (GO) as the catalyst under solvent-free and aerobic conditions. High chemoselectivity is observed in the reaction as aryl/alkyl ketones do not give thioketals under the conditions.

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The efficiency of graphene oxide (GO) and other chemically modified graphenes (CMGs) as the carbocatalysts has raised enormous interest since the seminal papers from Bielawski and co-workers.¹ Catalytic applications of carbonaceous sustainable and easily accessible GO in diverse organic reactions is one of the recent cherished goals.² GO possesses rich chemical functionality, is slightly acidic (pH 4.5 at 0.1 mgmL⁻¹),³ and has long been recognized as having strong oxidizing properties.⁴ Accordingly, GO has been mostly employed in oxidation of different functional groups.⁵ For example, oxidation of benzyl alcohol to benzaldehyde,^{5a,b} oxidation of thiol to disulfide,^{5c} or amine to imine etc.^{5d} Because of high efficiency and metal-free catalytic activity of GO or partially reduced GO (rGO), efforts are on to develop variety of organic transformations catalyzed by these carbonaceous materials.² Although GO has been utilized as an oxidation catalyst in various organic reactions, its use as an acid catalyst has remained relatively unexplored.⁵

Generally, thioacetals are formed as the result of Brønsted and Lewis acid catalyzed condensation reaction of aldehydes and ketones with thiols or dithiols and a vast number of methods are available in the literature.⁶ Over the past decade, several heterogeneous acid catalysts such as *p*-TsOH/silicagel,^{7a} H₃PW₁₂O₄₀/SiO₂,^{7b} Montmorillonite K-10 Clay,^{7c} Amberlyst-15,^{7d} PPA/SiO₂,^{7e} Melamine trisulfonic acid (MTSA),^{7f} silicasulfuric acid (SSA),^{7g} solid-supported dithiolanylium or dithianylium tetrafluoroborate salts,^{7h} and also ionic liquids,^{7i,j} have been employed for the preparation of thioacetals. However, moisture sensitivity and reactivity of thioacetals towards acidic sources for reversible reactions pose a great limitation for their preparation in high yield and most of the methods are often unsuitable for use in large-scale applications. Moreover, while in most cases the catalyst is not recoverable, heterogeneous acid catalysts often do not find wide applicability to various substrates. We were interested to explore the feasibility and catalytic efficiency of GO in thioacetalization of aldehydes and ketones. GO has been used in the dimethylacetal formation from aldehydes using methanol.⁸ But, use of thiols in place of methanol poses the possibility of intermolecular disulfide formation.^{5c} We recently showed that GO can be used as a catalyst under controlled conditions so as to avoid the oxidation of secondary benzyl alcohols as well as minimize that of thiols.⁹

We herein report an efficient and practical method for the preparation of dithioacetal from aryl/alkyl aldehydes with the aid of catalytic amount graphene oxide (GO). The reaction is highly selective to aldehyde carbonyl groups, can be carried out under solvent-free and mild conditions, and applicable to variety of aryl and alkyl aldehydes including hetero-aryl aldehydes as well as with diverse aromatic/aliphatic thiols. As a further extension of this reaction, unsymmetrical dithioacetals have been prepared in excellent yields by using two different aliphatic thiols (Scheme 1).



Tetrahedron Letters

Scheme 1. General scheme illustrating GO-catalyzed diverse dithioacetals formation.

2

Although GO is commonly used as an oxidation catalyst,⁴ and thiols can produce disulfides via oxidative coupling in the presence of GO,^{5c} we demonstrate here that the catalytic role of GO can be diverse and tuned by changing its loading and reaction conditions.

To begin our study, we prepared GO from graphite powder according to the modified Hummers method,¹⁰ followed by exfoliation under sonication and isolation after centrifugation. The FT-IR spectrum of the resulting GO was compared with that of the reported absorption bands,^{8,11} and found fairly similar absorption bands for the functional groups (See ESI S3.1). Optimization of the GO-catalyzed thioacetalization was examined with *p*-anisaldehyde and *n*-pentanethiol (1: 2.2 ratios) as the model case and the results are shown in Table 1.

Initially, a mixture of the aldehyde and mercaptan (in 1:2.2 ratios) was gently stirred in neat at room temperature in the presence of GO (10 mg mmol⁻¹ of the aldehyde) under aerobic condition. Monitoring the reaction by tlc at intervals showed the presence of the starting aldehyde along with the desired dithioacetal even after 24 h. The reaction was stopped and after the separation of the catalyst, the residue was subjected to

column chromatography to isolate the desired dithioacetal in 51% yield (entry 1). Increasing the quantity of GO (50 mg mmol⁻¹ of the aldehyde) revealed that nearly complete conversion of the aldehyde to dithioacetal could be achieved at room temperature within 3h under aerobic condition (entry 3). Significantly, there was no detectable amount of disulfide formed in the reaction from the oxidative dimerization of pentanethiol even under the aerobic condition. A control experiment was performed in the absence of the GO under similar reaction condition, which did not produce any dithioacetal even after 24h (entry 4). In order to see any faster conversion, the reaction was also carried out at 60 [°]C. This however resulted in partial conversion of the mercaptan into the corresponding disulfide along with the desired dithioacetal in relatively lower yield (entry 5). Moreover, the same reaction at 60 °C and under a blanket of N2 did not stop the formation of disulfide (entry 6). Conducting the experiments in a solvent (THF, toluene or water) showed rather a negative effect affording the desired dithioacetal in relatively lower yields (entries 7-9). To scale up the reaction, one set of reaction was performed (in 5 mmol) using the same quantity of catalyst (GO = 50 mg). Excellent yield of the dithioacetal was realized in this case as well signifying that the minimum quantity of the catalyst can promote the reaction in a longer time (entry 10).

Table 1.	Optimization	of dithioacetal	formation from	p-anisaldeh	vde and i	<i>n</i> -pentane	thiol.4
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Entry	GO (in mg mmol-1)	Reation medium	Time (h) / Temp(°C)	Disulfide (%) ^b	Dithioacetal (%) ^b
1	10	Neat	24 / RT	Not observed	51
2	25	Neat	24 / RT	Not observed	65
3	50	Neat	3 / RT	Not observed	95
4	Nil	Neat	24 / RT	Not observed	Not observed
5	50	Neat	3 / 60	10	61
6 ^c	50	Neat	3 / 60	8	57
7	50	THF	20 / RT	trace ^d	35
8	50	PhMe	12 / RT	Not observed	68
9	50	H ₂ O	12 / RT	trace ^d	55
10 ^e	50	Neat	16 / RT	trace ^d	91

^a*p*-Anisaldehyde (1 mmol), *n*-pentanethiol (2.2 mmol).

^bIsolated yield.

^cReaction carried out under N₂.

^dDetected only on tlc, not isolated.

^e*p*-Anisaldehyde (5 mmol), pentanethiol (11 mmol).

With this mild and solvent-free optimized condition at our hand, we became interested to explore the general applicability of the reaction. Accordingly, a variety of aryl aldehydes were subjected to the reaction in the presence of thiols. The results are presented in Table 2. It can be seen that aryl aldehydes bearing different functional groups react easily with aliphatic thiols in the presence of catalytic amount of GO under solvent-free aerobic condition. The reactions were completed in 3-8 h and the products were realized in excellent yields (Table 2, entries 1-5). Higher temperature was required for α -naphthaldehyde and *p*chlorobenzaldehyde, which caused partial formation of disulfide (~5-8%) (entries 6, 7). However, the reaction with *p*nitrobenzaldehyde needed much longer time and higher temperature, and gave the dithioacetal in relatively lower yield along with disulfide (Table 2, entry 8). Trying the reaction with aromatic thiols afforded the desired dithioacetal in 80-85% yields but achieved only at higher temperature (60°C) and was associated with the formation of diaryl disulfides in 8-12% isolated yields (entries 9-11). The disulfides however could be separated easily from dithioacetal by column chromatography over silica gel. In the case of using 1,2- and 1,3-dithiol, corresponding cyclic thioacetals were obtained in excellent yields (95-98%) and the reaction was also successful with aliphatic cyclohexyl aldehyde (entries 12-15). However, there was no such formation of dithioketals from a ketone under the GO-catalyzed reaction condition (entry 16). So, there is excellent chemoselectivity observed between the aldehyde and ketocarbonyl groups.

Entry	Aldehyde	Thiol	Time (h)	Temp.	Product	Yield ^b (%)
1	CHO	<i>n</i> -C ₅ H ₁₁ -SH	3	RT	S- <i>n</i> -C₅H ₁₁	95
					S-n-C ₅ H ₁	1
	П300				H ₃ CO	
2	СНО	<i>n</i> -C ₅ H ₁₁ -SH	5	RT	S- <i>n</i> -C₅H ₁₁	91
					S- <i>n</i> -C ₅ H ₁₁	
	~					
3	H ₃ CO	<i>n</i> -C ₇ H ₁₅ -SH	5	RT	$S-n-C_7H_{15}$	95
	но				S-n-C ₇ H ₁	j
					но ∽	
4	СНО	<i>n</i> -C ₅ H ₁₁ -SH	8	RT	S- <i>n</i> -C ₅ H ₁₁	89
	СН				S- <i>n</i> -C ₅ H ₁₁	
_			_		ОН	
5	H ₃ CO	Bu ^t -SH	5	RT	S- ^t Bu	93
	HO				H ₃ CO S- ^t Bu	
					HO	
6°	СНО	<i>n</i> -C ₇ H ₁₅ -SH	3	60°C	<i>n</i> -C ₇ H ₁₅ -S ₂ S- <i>n</i> -C ₇ H ₁₅	87
7 ^c	0110	CoSH		60°C	° °	90
	CHU	Сузн		00 C		90
	CI				SCy	
3c		n-C-HSH	14	60°C	Cl S-r-C-H.	68
		11-051111 011				
	O ₂ N				O-N S- <i>h</i> -C ₅ H ₁₁	
					0211	
) ^c	СНО	C_6H_5-SH	10	60°C	s∕ ^{−C} ₆ H₅	80
	ОН				S ^{-C₆H₅}	
	0				OH	
10 ^c	СНО	C ₆ H ₅ -SH	10	60°C	C ₆ H ₅	85
K					C ₆ H ₅	
	11300				H ₂ CO	
1 1 0		(1) O (1) O (1) O (1)	10	(0)0		82
11-	H ₃ CO CHO	(H ₃ U-4)C ₆ H ₄ -SH	10	60°C	$H_{3}CO \xrightarrow{S^{C_{6}H_{4}(4-CH_{3})}} C_{6}H_{4}(4-CH_{3})$	82
	HO				HO	
12 ^d		HS SH	5	RT	S-	98
			-		, , , , , , , , , , , , , , , , , , ,	
	H ₃ CO				, j	
					H ₃ CO 💛	

3



^aAldehyde : thiol : GO (1 mmol : 2.2 mmol : 50 mg) and reactions were performed at room temperature.

^bIsolated yield.

^cCorresponding disulfides (5-12%) were formed.

^dAldehyde : thiol : GO (1 mmol : 1.1 mmol : 50 mg).

Heteroaryl compounds often exhibit promising pharmacological activities and open chain dithioacetals of heteroaryl aldehydes such as thiophene-based dithioacetals are important scaffolds for design and discovery of new medicines.¹² Since the reaction conditions are mild and solvent-free, we were interested to extend the GO-catalyzed dithioacetalization to thiophene aldehydes and also of other heteroaryl aldehydes. Indeed, 5-bromothiophene-2-carbaldehyde and furfural result in

the formation of corresponding dithioacetals with variety of aliphatic and benzenethiol without any difficulty (Table 3, entries 1-5). Other heteroaryl aldehyde indole-3-carbaldehyde also produces corresponding dithioacetals with long chain aliphatic thiols without any difficulty and in excellent yields (Table 3, entry 6). Cyclic dithioacetals of furfural and indole-3-carbaldehyde were obtained in excellent yields under mild conditions (entries 7, 8).

Table 3. GO-catalyzed thioacetalization of heteroaryl aldehydes.^a

Entry	Aldehyde	Thiol	Time (h)	Product	Yield ^b (%)
1	Вг S СНО	Bu ^t -SH	8	Br S S-tBu	89
2°	Вг СНО	C_6H_5-SH	10	Br S S-C ₆ H ₅	81
3	Вr S СНО	<i>n</i> -C ₇ H ₁₅ -SH	8	Br S S- <i>n</i> -C ₇ H ₁₅	89
4	СНО	<i>n</i> -C ₅ H ₁₁ -SH	3	$\begin{bmatrix} S - n - C_5 H_{11} \\ S - n - C_5 H_{11} \end{bmatrix}$	92
5	СНО	CySH	3	S-Cy S-Cy	88
6	CHO N H	<i>n</i> -C ₇ H ₁₅ -SH	8	n-C ₇ H ₁₅ -S-n-C ₇ H ₁₅	85
7 ^d	СНО	SH SH	3		90



^aAldehyde : thiol : GO (1 mmol : 2.2 mmol : 50 mg) and reactions were performed at room temperature.

^bIsolated yield.

^cIsolated yield of disulfide was ~ 5%.

^dAldehyde : thiol : GO (1 mmol : 1.1 mmol : 50 mg).

In order to further broaden the scope of the reaction, we attempted synthesis of unsymmetrical dithioacetal using two different thiols. Gratifyingly, the reactions of *p*-anisaldehyde or vanillin with two different aliphatic thiols (*n*-pentyl- and *n*-heptyl thiols) resulted in the formation of unsymmetrical dithioacetals as the only product in 85-88% isolated yields (Table 4, entries 1, 2). HPLC analysis of the crude product (before column chromatographic purification) showed the unsymmetrical thioether as the sole product. On the other hand, use of one aliphatic and one aromatic thiol gave rise to a mixture of all three possible products in varying proportions, as seen from the

analysis of the crude product mixture by HPLC (Table 4, entry 3). Although the exact reason for this selectivity is not known, it might be attributable to the difference in reactivity between the two thiols. Using a mixture of aliphatic or aromatic thiols, formation of the thioacetal from benzenethiol in highest quantity amongst the three possible dithioacetals also supports this rationale. Since in entry 3, all three products were obtained as a non-isolable mixture, we tried to analyze the mixture by HPLC and compared the peaks with known products, leaving the third peak likely to be for the unsymmetrical dithioacetal.

Table 4. Unsymmetrical thioacetals from aryl aldehydes using two different thiols.^a



^aThiol (A): thiol (B): GO (1.1 mmol:1.1 mmol:50 mg) for 1 mmol of aldehyde and the reaction was done at RT for entries 1 and 2.

^bIsolated yield.

^cReaction performed at 60 ^oC.

^dProduct ratios are from HPLC analysis of the crude reaction mixture (See ESI S2.3).

As regard to the plausible mechanism for the reaction, we wanted to probe the nature of active sites present in GO. In the recent years, the acidic nature of GO has been attributed mostly to the organosulfate group being originated during the oxidation of graphite using Hummers method in the presence of sulfuric acid,^{2b,8} though previous measurements of acidic pH were

attributable to the presence of surface attached carboxylic functions.³ The FT-IR spectrum of GO showed the presence of carboxyl (1719 cm⁻¹; COOH stretching) and sulphate functional groups (1052 cm⁻¹; SO₃–H stretching), which are comparable with that reported in the literature (See ESI S3.1, Figure 3).^{8,11} We measured the pH of the GO in aqueous suspension (pH = 3.9;

Tetrahedron

50 mg in 50 ml 0.5M aqueous NaCl solution), and found it in fair agreement with previous observations.³ The pH of GO remains fairly similar when measured after the reaction and also of a mixture of *n*-pentane thiol and GO in water. On the other hand, thioacetal formation is greatly retarded when the reaction is carried out in water or in other organic solvents (Table 1, entries 7, 8 and 9). GO also gave positive Carius test and Lassaigne's test signifying qualitatively the presence of S-containing functional groups. The above results suggest that GO is an acid catalyst and we tend to believe that the acidity of GO might be originating from a combination of both carboxyl and organosulfate groups, which is more pronounced in neat. Mechanistically, surface active acidic functional groups of GO facilitate activation of the aldehyde carbonyl group, more effectively in neat condition, and subsequent nucleophilic attack by the thiol results in the eventual formation of thioacetal.

The reusability of the GO as heterogeneous acid catalyst was examined with the combination of reactants: *p*-anisaldehyde and *n*-pentanethiol in 1:2.2 ratios at room temperature. The GO was recovered from the first batch of reaction by centrifugation and washed with diethyl ether, dried and reused for subsequent four batches of reactions. In all recycling experiments carried out at room temperature, appreciable conversions were achieved (Fig.1). A comparison of the FT-IR spectra of the GO before and after use does not indicate any changes of the absorption bands, signifying that the catalyst remain same after the reaction (See ESI S3.1, Figure 4)



Fig. 1 Recyclability of GO in the thioacetalization of p-anisaldehyde and n-pentanethiol

In summary, GO was found to catalyze the formation of thioacetal from a neat mixture of aldehyde and thiol under mild, solvent-free and aerobic conditions. Notable features of the methodology described herein are: operational simplicity, nil or negligible quantity of disulfide formation, applicability to a large variety of aryl/heteroaryl aldehydes, chemoselectivity, recyclability and environmental compatibility. Thus it provides a practical approach for the preparation of open chain, cyclic and unsymmetrical dithioacetals. The present method also demonstrates that controlled loading of GO in combination with reaction conditions could lead to the diversity in reaction types as well as the formation of the products, and is likely to spur more catalytic applications.

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6

Supplementary Material

Supplementary material that may be helpful in the review Accepter process has been prepared and provided as a separate electronic file in PDF.