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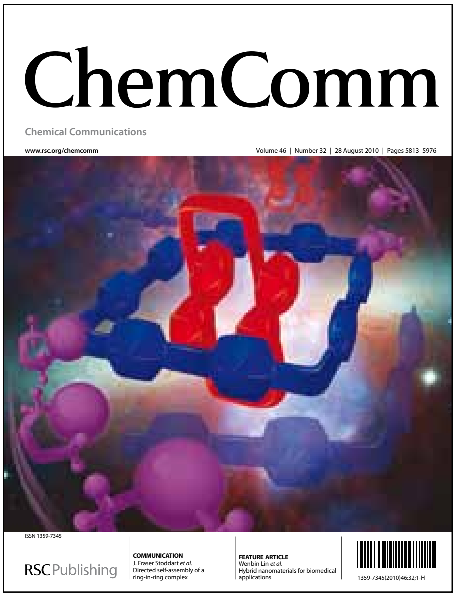

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ARTICLE TYPE

Graphene oxide as a recyclable phase transfer catalyst†

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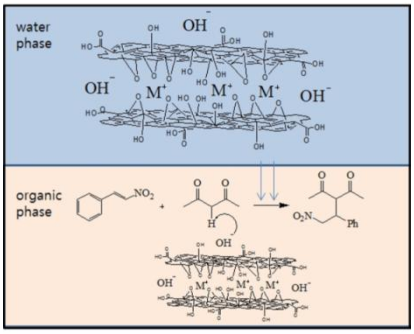
We demonstrated simple and green chemical method to obtain Michael adduct and its derivatives by using GO as a phase transfer catalyst with different kinds of bases in water and dichloromathane, and we also used GO multiple cycles with almost without reduction of reaction yields.

Graphene and its derivatives have great promise for diverse electronic applications,[1] and have also attracted great interest for use in composite materials and catalysts[2-4] due to their remarkable physical,[5] chemical[6] and electrical properties,[7] including their very high specific surface area.[8] As part of wider trends to develop green chemistry and to mimic nature, recent efforts have been made to develop aqueous organocatalytic reactions,[9] and innovative synthetic approaches involving the use of chemicals that reduce the risks to humans and the environment have gained interest.[10] To this end, the development and use of catalysts that can be easily recovered and repeatedly recycled in a heterogeneous organic reaction system is of tremendous importance.[11]

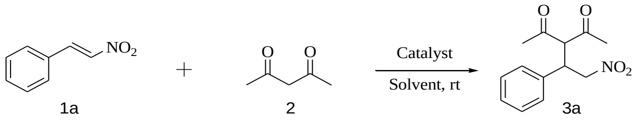
Herein, we report a novel graphene oxide (GO) as a recyclable phase transfer catalyst (PTC) for the Michael addition. The Michael addition is one of the most useful and representative methods for the mild formation of new C-C bonds.[12] The formation of new C-C bonds via Michael addition is an important transformation in organic chemistry, and is used extensively in the synthesis of a variety of molecules, including biologically active natural products and antibiotics. For the Michael addition, we selected trans-β-nitrostyrene and 2,4-pentanedione derivatives as reactants, GO as a PTC, potassium hydroxide as a base, and water-dichloromethane as an aqueous-organic co-solvent system. We anticipated that the performance of the GO PTC in the Michael addition would exceed that of the best-known crown ether (CE), because GO has a large surface area with many oxygen functional groups, including epoxide, alcohol, phenol, carbonyl, carboxyl, lactone and quinone groups. These functional groups are expected to easily hold the metal cations by forming a metal-centered intercalated structure like GO-metal-GO layers. We also expected that this intercalated structure would accommodate alkali cations of any size, including Na^+, K^+ and Cs^+, because GO carries many oxygen functional groups throughout its surface layer. However, the most commonly used CE, 18-crown-6, carries only the K^+ cation well in the Michael addition (when KOH is used as the base). Furthermore, we expected that the Michael addition using GO PTC should be faster and give higher yield than that of the CE catalyst due to GO's unique characteristics. As expected, GO does not dissolve in water or organic solvents such as methylene chloride (MC), but rather is possible to disperse in aqueous solvent and MC as



M^+ = Na^+ or K^+ or Cs^+

Scheme 1 GO Phase-transfer catalyst in the Michael addition reaction.

Table 1 Michael addition reaction of trans-β-nitrostyrene and 2,4-pentanedione[a]

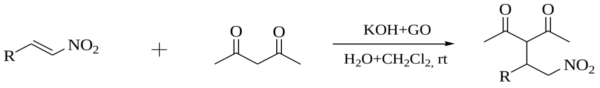


Entry	Catalyst	Solvent	Time [min]	Yield [%][b]	Recyclable
1	KOH	CH_2Cl_2	40	55	No
2	KOH	2MTHF[c]	38	53	No
3	KOH	H_2O	—	ND[d]	—
4	KOH	H_2O+CH_2Cl_2	60	25	No
5	GO	CH_2Cl_2	—	ND	—
6	GO	H_2O	—	ND	—
7	GO	H_2O+CH_2Cl_2	—	ND	—
8	KOH+GO	CH_2Cl_2	37	59	Yes
9	KOH+GO	H_2O	—	ND	Yes
10	KOH+GO	H_2O+CH_2Cl_2	10	83	Yes
11	KOH+GO	H_2O+2MTHF	10	82	Yes
12	KOH+CE[e]	H_2O+CH_2Cl_2	30	76	No
13	NaOH	CH_2Cl_2	45	45	No
14	NaOH	H_2O	—	ND	—
15	NaOH	H_2O+CH_2Cl_2	60	15	No
16	NaOH+GO	H_2O+CH_2Cl_2	15	75	Yes
17	NaOH+CE	H_2O+CH_2Cl_2	45	41	No
18	CsOH	CH_2Cl_2	30	60	No
19	CsOH	H_2O	—	ND	—
20	CsOH	H_2O+CH_2Cl_2	60	23	No
21	CsOH+GO	H_2O+CH_2Cl_2	10	80	Yes
22	CsOH+CE	H_2O+CH_2Cl_2	30	55	No

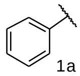
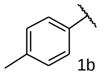
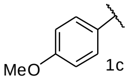
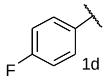
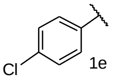
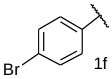
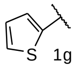
[a] Reactions were carried out with **1a** (25 mg, 0.1676 mmol), **2** (1.5 equiv.), base (1.1 equiv.), 0.5 mg ml^{-1} GO aqueous (0.5 ml) and catalyst 18-crown-6 ether (1.1 equiv.). [b] Isolated yield. [c] 2-methyl tetrahydrofuran. [d] Almost no product was detected. [e] CE = 18-crown-6 ether.

well. The insolubility of GO has been a serious drawback in other applications, but GO as a PTC is expected to have a strong advantage, which will be a superior to the conventional CE catalyst. After the reaction is completed, the GO can be collected simply by filtering, washing and drying the GO-metal composites. This character of GO is superior to CE, which can carry the potassium cation from the aqueous phase to the organic phase,[13] and can also be easily dissolved in organic solvents like MC. And due to high solubility of CE it is difficult to recover CE after the reaction is over. For the experiment, GO was prepared from graphite powder (Bay carbon, SP-2) using a modified Hummers method and was purified as previously reported.[14] Abundant oxygen functional groups are present at both edges and at defects in the plane of the GO sheet.[15] The abundant oxygen functional groups of GO should be the key elements to act as a cation holder which makes base, hydroxide anion, stronger and also make the reaction related to the high surface areas faster to enhance the activities. The possible reaction process is illustrated in Scheme 1. For efficient catalytic performance, GO nanosheets need to be fully dispersed in the reaction medium in order to maximize the number of catalytic sites provided by various oxygen functional groups, especially epoxy and hydroxyl groups. XPS, Raman and AFM analysis were used to characterize the GO (see ESI† Figure S1, S2, S3 and S4). As-made GO was first dispersed in water to create an aqueous solution. The electrostatic repulsion among negatively charged carboxylate groups on the edges of the GO sheets prevented aggregation and stabilized the dispersion. In this way, most of the surface area of each single-layer GO sheet was available to provide catalytic reaction sites. After the GO solution was prepared, we dissolved one of three alkali bases for each individual experiment. We then added each solution to a reaction mixture of trans-β-nitrostyrene and 2,4-pentanedione in MC solvent or other derivative systems. All experiments were carried out at RT and reactions were vigorously stirred. To evaluate the GO catalyst in the Michael addition, we used 2,4-pentanedione as a nucleophile and trans-β-nitrostyrene as an electrophile, using 0.5 ml of aqueous solution containing 0.5 mg ml^{-1} GO catalyst and 1 ml of MC solvent at RT (Table 1). The catalytic properties of GO were studied under various conditions including the use of different solvents and bases (Table 1). Same reactions using 18-crown-6 ether were also carried out for comparison. Control experiments included single-phase organic reactions using bases of differently sized metal ions without a PTC (Table 1, entries 1, 2, 13 and 18), single-phase aqueous reactions without a PTC (entries 3, 14 and 19), and two-phase reactions without a PTC (entries 4, 15 and 20). No product were observed in the aqueous-only systems (entries 3, 6, 9, 14 and 19), and also in absence of bases (entries 5, 6 and 7).

Table 2 Trans-β-nitroolefins as Michael acceptors[a]

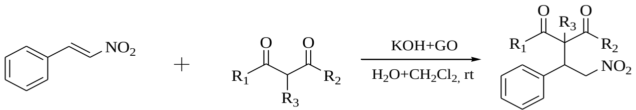


1a-g 2 3a-g

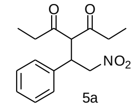
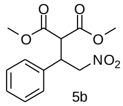
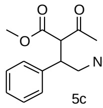
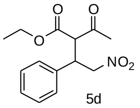
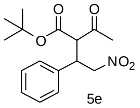
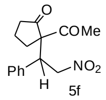
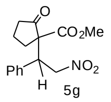
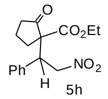
Entry	R	Time [min]	Yield [%][b]
1	 1a	10	83
2	 1b	16	80
3	 1c	16	77
4	 1d	30	69
5	 1e	23	79
6	 1f	25	75
7	 1g	20	78

[a] Reactions were carried out with 1a-g (0.1676 mmol), 2 (1.5 equiv.), KOH (1.1 equiv.), and 0.5 mg ml^{-1} GO aqueous (0.5 ml) in MC (1 mL). [b] Isolated yields.

Table 3 1,3-dicarbonyl compounds as Michael donors[a]



1a 4a-h 5a-h

Entry	Product	Time [min]	Yield [%][b]
1	 5a	35	80
2	 5b	2880	50
3	 5c	25	79
4	 5d	20	80
5	 5e	15	83
6	 5f	60	66
7	 5g	15	82
8	 5h	25	81

[a] Reactions were carried out with **1a** (25 mg, 0.1676 mmol), **4a-h** (1.5 equiv.), KOH (1.1 equiv.), and 0.5 mg ml^{-1} GO aqueous (0.5 mL) in MC (1mL). [b] Isolated yields.

But in the two-phase system in the absence of a PTC, yield was poor, presumably owing to the poor transfer of OH^- ion into the organic phase. For the control experiments using only one solvent system, the reaction of KOH+GO in only water did not produce any product. On the other hand, the reaction of KOH+GO in only MC (Table 1, Entry 8) was a slightly faster and produced 4% higher yield than that of KOH in only MC (Table 1, Entry 1), but much lower than that of KOH+GO in water and MC two phase system (Table 1, Entry 10). As a result, two-phase solvent system gives better yield and shorter reaction time than that of one-phase system (entry 8, 9 and 10).The ability of GO to bind cations of various sizes was tested through a series of reactions using KOH, NaOH, and CsOH (entries 10, 16, and 21); these were mirrored by experiments using 18-crown-16 ether (CE) as a comparison PTC (entries 12, 17 and 22). When aqueous GO solution (0.5 ml) was loaded with potassium cations using KOH, the reaction in MC (1 ml) was completed within 10 min, affording the Michael adduct in up to 83% yield (entry 10). The comparison reaction with CE was more than 3 times longer (30 min) and gave poorer yield (76%, entry 12). This difference was more pronounced when sodium hydroxide was used; GO yielded 75% and CE yielded 41% (entries 16 and 17). The yield from GO-catalyzed reactions was nearly independent of the metal cation used: 83% for KOH, 75% for NaOH, and 80% for CsOH, respectively. This suggests that the cations were indeed intercalated between GO layers as in Scheme 1. As expected, the CE catalyst performed best with the correctly sized K^+ cation (76% yield for KOH) and more poorly with the other two alkali bases (41% for NaOH and 55% for CsOH, respectively). However, even in the best case, CE did not perform well. The GO catalyst provided faster reactions and higher yields in all experiments. We suggest that the observed reactivity of GO was due to its hold on the cation, making the hydroxide base stronger in the organic phase. Furthermore, because yield was high and the reaction was faster compared with that of CE, we could conclude that individual GO sheets could carry more cations than that of CE. We also used 2-methyl tetrahydrafuran (2MTHF) as organic solvent instead of MC for the greenery reaction and it was acted similarly as MC (entry 2 and 11) which could be replaced with MC in respect to greenery. The used GO could be easily recovered and reused by a simple process of filtering and washing with MC (see ESI† Table S1). The recovered GO could be reused at least nine times almost without reduction of reaction yields. It was assumed that the recovered GO retained its catalytic activity due to the presence of undamaged many oxygen functional groups on the GO surface.

To further explore our methodology, we carried out related reactions using a series of trans-β-nitroolefin Michael acceptors, with a variety of substituents on the benzene ring including electron-donating groups such as methoxy and methyl, and electron-withdrawing halogen groups (F, Cl, and Br). As summarized in Table 2, the GO system showed fairly good yields and short reaction times. Next, we evaluated the scope of the reaction with a variety of 1,3-dicarbonyl compounds as Michael donors, with substituents including methyl, methoxyl, tert-butyl, and cycloolefins (Table 3). Like the derivative Michael acceptors, most of the Michael donors showed fairly good yields and reasonable reaction times. According to our experimental data, we can suggest that oxygen functional groups in GO, including carbonyl, carboxylic, lactone, and quinone, and especially epoxy and hydroxyl groups, are responsible for interaction with the base cations, increasing the catalyst's ability to react strongly and quickly with reactants. We also measured enantiomeric selective property of **3a** product with the GO PTC and it showed ~7% enantiomeric excess. The CE PTC product and only base treated product were racemic in comparison to GO PTC product (see ESI†). The 2D template structure of GO helps to get an enantiomerically selective product even though the ee value is not high.

In summary, we successfully demonstrated that GO sheets can be functioned as PTC for the Michael addition reaction. For reactants, trans-β-nitrostyrene and 2,4-pentanedione and their derivatives were used, as well as differently sized alkali metal bases. GO was compared with 18-crown-6 ether, the well-known conventional PTC. The GO promoted the formation of C-C bonds in the Michael adducts, giving short reaction time and high yield compared with CE. The used GO PTC could be recovered by simple filtering and washing and could be reused many times, while PTC such as CE are difficult to recover. Furthermore, the GO PTC was effective with differently sized metal cation bases, while the CE catalyst worked effectively only with a specifically sized metal cation. And also, GO have the potential to provide an environmentally friendly, inexpensive and easy way to produce commercial products on a large scale. Thus, the GO PTC provides a novel method for the synthesis of new C-C bonds, and can be used in an open system. This is the first observation of GO's ability to provide greatly enhanced phase transfer catalysis. Now our current work is focused on improving the yield and enantiomeric selectivity of GO PTC product.

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Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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1 D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim and K. S. Novoselov, *Science* 2009, **323,** 610.

2 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282.

3 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mulhaupt, *J. Am. Chem. Soc*. 2009, **131**, 8262.

4 (a) D. R. Dreyer, H. P. Jia and C. W. Bielawski, *Angew. Chem. Int. Ed*. 2010, **49**, 6813; (b) S. Verma, H. P. Mungse, N. Kumar, S. Choudhary, S. L. Jain, B. Sain and O. P. Khatri, *Chem. Commun*. 2011, **47**, 12673 12675; (c) C. Su and K. P. Loh, Acc. Chem. Res. DOI: 10.1021/ar300118v.

5 A. K. Geim and K. S. Novoselov, *Nat. Mater*. 2007, **6**, 183.

6 C. G. Lee, X. D. Wei, J. W. Kysar and J. Hone, *Science* 2008, **321**, 385.

7 C. N. R. Rao, A. K. Sood, K. S. Subrahamanyam and A. Govindaraj, *Angew. Chem*. 2009, **121**, 7890; *Angew. Chem. Int. Ed*. 2009, **48**, 7752.

8 A. K. Geim, *Science* 2009, **324**, 1530.

9 M. Raj and V. K. Singh, *Chem. Commun*. 2009, 6687.

10 I. T. Horváth and P. T. Anastas, *Chem. Rev*. 2007, **107**, 2169.

11 (a) K. Ding and Y. Uozomi, Handbook of Asymmetric Heterogeneous Catalysis, Wiley-VCH, Verlag, Weinheim, 2008; (b) M. Benaglia, Recoverable and Recyclable Catalysts, Wiley-VCH, Weinheim, 2009.

12 (a) F. Wu, H. Li, R. Hong and L. Deng, *Angew. Chem. Int. Ed.* 2006, **45**, 947; (b) H. Y. Bae, S. Some, J. S. Oh, Y. S. Lee and C. E. Song, *Chem. Commun.* 2011**,** **47**, 9621; (c) S. Banerjee and S. Santra, *Tetrahedron Lett.* 2009, **50**, 2037.

13 (a) D. Landini, A. Maia, F. Montanari and F. M. Pirisi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 46; (b) S. Bai, X. Shen, G. Zhu, Z. Xu and Y. Liu, *Carbon* 2011, **49**, 4563.

14 I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun*. 2010, ***1***, 73.

15 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon* 2007, **45**, 1558.