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Graphene oxide catalyzed cis-trans isomerization of azobenzene

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We report the fast cis-trans isomerization of an amine-substituted azobenzene catalyzed by graphene oxide (GO), where the amine functionality facilitates the charge transfer from azobenzene to graphene oxide in contrast to non-substituted azobenzene. This catalytic effect was not observed in stilbene analogues, which strongly supports the existence of different isomerization pathways between azobenzene and stilbene. The graphene oxide catalyzed isomerization is expected to be useful as a new photoisomerization based sensing platform complementary to GO-based fluorescence quenching methods. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4886215>]

Photoisomerization is one of the well-known photo-induced unimolecular chemical reactions that occur in photochromic molecules such as azobenzene (AB) and stilbene (SB).^{1,2} In this reaction, reversible switching actions between two isomeric can be controlled by distinctive wavelengths of light or heat, which makes photochromic molecules to attract tremendous attentions for various photochemical applications ranging from industrial dyes,³ actuators,⁴ optical memory and devices,⁵ molecular switches/motors,⁶ etc. Recently, as great interest has been focused on the new carbon-based materials including carbon nanotubes and graphene, the photochromic functionality has been grafted on these materials to be applied to various photoresponsive devices.^{7,8}

Recently, several studies on graphene-based photoresponsive devices have been reported. Gopalan *et al.* used azobenzene moiety to modulate the doping level of graphene.⁹ They non-covalently latched a strongly dipolar azobenzene-derived molecule on graphene via pyrene moieties and observed apparent photo-induced Dirac voltage shift. Shin *et al.* used another well-known photochromic molecule, spiropyran (SP), that can be reversely switched between two conformations, a neutral form (colorless) and a charge-separated form (purple colored merocyanine) upon UV irradiation and visible light, respectively.¹⁰ They also demonstrated the light-driven reversible doping in SP-incorporated graphene field effect transistors (FET).

As mentioned above, much effort was paid on the effect of photoisomerization on the electrical properties of graphene, but how graphene or graphene oxide (GO) affect the photoisomerization reaction of a molecule has not been studied so far. Here, we report the GO induced fast cis-trans isomerization reaction of amine-substituted azobenzene molecules for the first time. Having in mind great versatility of photoisomerization reactions, our finding is expected to provide a new pathway to control photoisomerization reactions to be utilized for molecular switches or photochemical sensors.

Aqueous GO solution was purchased from Graphene Square Inc. The concentration of GO was 5.77 g/l, the total atomic C/O ratio was ~4, and the average flake size was 0.5–0.7 μm. Azobenzene (99%) and 4,4'-diaminoazobenzene (95%) were purchased from Sigma Aldrich and Acros Organics,

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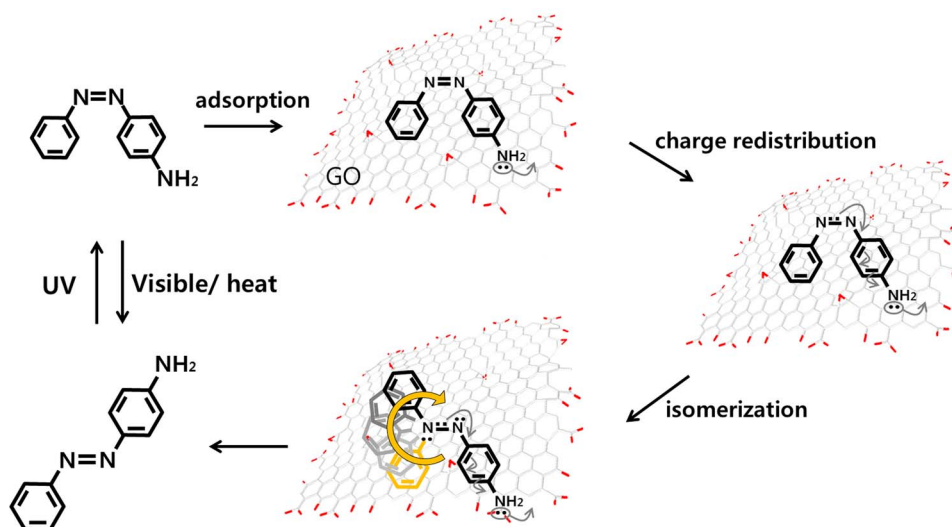


FIG. 1. Schematic diagram of GO catalyzed cis-trans isomerization of 4-aminoazobenzene.

respectively. The 4-amino-azobenzene (98%), 4-amino-4'-(N,N-dimethylamino)azobenzene (95%), and 4-amino-4'-(N,N-dimethylamino)stilbene (98%) were purchased from TCI. All reagents were used without further purification.

For each absorption measurements, 3 ml of acetonitrile was used as blank solvent. Then, 30 μl of 2 mM of azobenzene (or stilbene) derivatives was dispersed in acetonitrile and loaded into a quartz cell with 1 cm path length. To convert the molecular conformation from trans to cis state, 4 W UV lamp ($\lambda_{\text{max}} = 356 \text{ nm}$) was irradiated for 30 s. All measurements were conducted at room temperature.

Figure 1 summarizes the concept of our experiment. Generally, the azobenzene derivative exists as a trans form that is more thermodynamically stable in dark environment. UV irradiation produces a large fraction of cis isomers, which can be recovered to a trans form by applying heat or visible light.

Figure 2(a) shows the UV-Vis absorption spectra of 4-aminoazobenzene in solution state. It was started from the thermally stable trans isomer. After irradiating UV light (365 nm), the peak at $\lambda = 384 \text{ nm}$ corresponding to $\pi-\pi^*$ transition was clearly decreased, while the shoulder near 475 nm corresponding to $n-\pi^*$ transition was increased. This indicates that the trans to cis isomerization reaction of molecule is taken place upon the irradiation of UV light. The isosbestic points at 340 nm and 454 nm in the absorption spectra implies the existence of two species during the isomerization process. The reverse reaction from cis to trans was also observed via irradiation of visible light or heat treatment (not shown here) that provides activation energy to overcome the barrier to a thermodynamically more stable trans form. It is also well known that the cis-trans isomerization rate can be affected by solvent polarity or temperature.¹¹ To exclude this effect, we used acetonitrile solvent that suppresses cis-trans isomerization at room temperature.

Interestingly, it was observed that the addition of small amount GO immediately converts cis conformation to trans one. Figure 2(b) shows the absorbance change of 4-aminoazobenzene measured after the addition of 30 μl GO solution (0.72 g/l). The absorbance spectra indicate that the trans state was fully recovered 500 s after adding GO. We also observed that the rate of cis-trans isomerization depends on the amount of added GO (Fig. 2(c)). The rate constant exponentially increasing with GO concentration reveals that the addition of GO (2.89 g/l) accelerates the cis-trans isomerization rate more than 1000 times compared to the case without GO, which clearly demonstrates the catalytic function of GO on the cis-trans isomerization reaction in our experiment.

To rationalize the GO induced fast cis-trans isomerization, we carried out the same experiments using different types of AB molecules. Figure 3(a) shows the absorbance change of non-substituted AB after GO was added. No clear absorbance change indicating cis-trans isomerization was observed

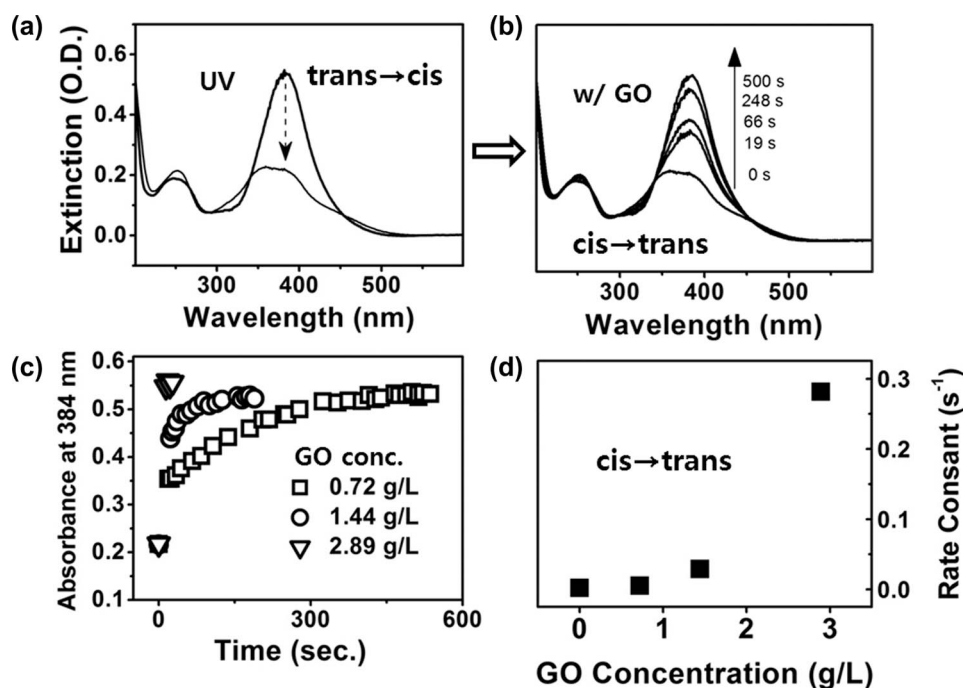


FIG. 2. (a) and (b) Absorbance change of 4-amino-azobenzene in acetonitrile by UV irradiation (365 nm) and GO (0.72 g/l), respectively. (c) Absorbance at 384 nm as a function of time with varying GO concentration. (d) Cis-to-trans isomerization rate constant with respect to GO concentration, calculated from (c). Pure water was used as control solvent.

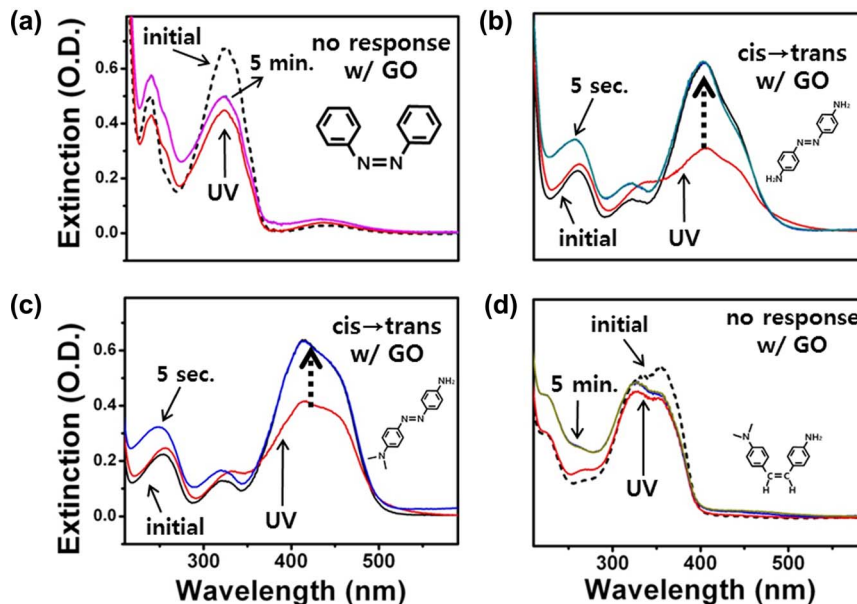


FIG. 3. GO induced absorbance changes of (a) AB, (b) 4,4'-diaminoAB, (c) 4-amino-4'-(N,N-dimethylamino) AB, and (d) 4-amino-4'-(N,N-dimethylamino) SB.

even after 5 min, which implies that the amine substituent of 4-amino-AB plays an important role in the GO catalyzed fast cis-trans isomerization. The importance of the amine functionality was further confirmed with other amine-substituted AB derivatives such as 4,4'-diaminoAB and 4-amino-4'-(N,N-dimethylamino)AB that show the same GO catalyzed cis-trans isomerization effect with fast recovery time (<5 s). To exclude the possibility of pH-related isomerization, we performed a control

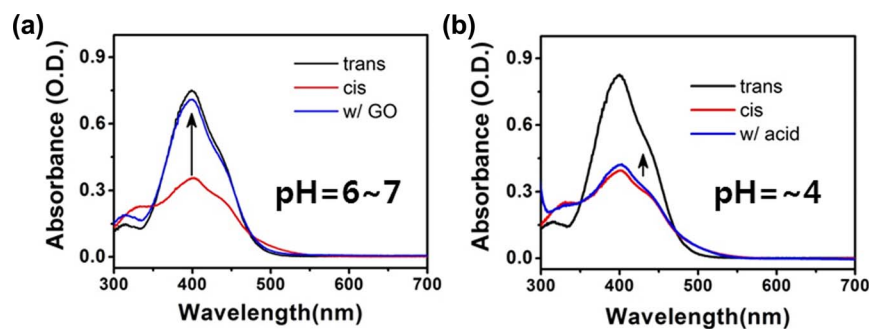


FIG. 4. Control experiment showing no effect of acidic environment on the cis-trans isomerization of 4-amino-AB. The GO-added solution is slightly acidic (pH = 6–7) because of intrinsic acidity of GO (a), but even more acidic condition does not promote the isomerization reaction (b), which excludes the possibility of acid-catalyzed isomerization reaction.

experiment in an acidic buffer solution, and confirmed that the acidic condition without GO does not catalyze the cis-trans isomerization reaction (Figure 4).

On the other hand, SB, of which its structure is only different with AB in that the nitrogen atoms are replaced with carbon and hydrogen atoms, is also one of the attractive photoisomerizable molecules. Various theoretical and experimental studies revealed that the isomerization mechanism of AB and SB are distinctly different each other. For AB, four different mechanisms including rotation, inversion, inversion-assisted rotation, and concerted inversion were proposed. However, it is believed that the rotation is the only pathway to isomerize for SB.¹² Thus, we applied our GO effect on the isomerization to SB derivatives. As is shown in Figure 3(d), no catalytic effect of GO was observed in cis-trans isomerization of 4-amino-4'-(N,N-dimethylamino) SB, whereas the AB with identical substituents clearly shows the GO catalyzed cis-trans isomerization (Fig. 2(c)). This indicates the clear difference in isomerization mechanism between AB and SB derivatives, and we suppose that the inversion is the main pathway of cis-trans isomerization for AB,¹³ when GO is involved.

We attribute this catalytic effect of GO to the strong electron-donating property of the amine group attached to AB. The charge transfer from the lone-pair electrons of the amine group to GO induces the charge redistribution of AB softening the N = N bond. Accordingly, this reduces the inversion energy barrier for cis-trans isomerization, which considerably accelerates the reaction rate. On the other hand, SBs do not show such GO-catalyzed isomerization effect possibly due to the different isomerization mechanism including rotational pathway that is hindered by $\pi-\pi$ interaction with GO.

In summary, we observed for the first time that graphene catalyzed the cis-trans isomerization reaction of amine-substituted AB in solution. Considering the importance of the photoisomerization in various biological systems and molecular switching applications, it is crucial to find a new way of controlling isomerization effectively, which has been successfully demonstrated by utilizing GO as catalyst. Combined with various functional molecules and polymers, we also expect that the GO-catalyzed isomerization will provide an important platform for biological or chemical sensing/diagnosis. For example, if amino-azobenzene is tethered by DNA strands, the GO-induced fast isomerization can be utilized to detect the hybridization with complementary DNA strands simply by monitoring UV-Vis spectra (as single strand DNAs interact more strongly with GO than double strand DNAs), which would be as useful as GO-quenched fluorescence methods for biosensing.¹⁴ Further study on various photochromic molecules would also contribute to the better understanding of molecular photoisomerization mechanisms, which can be also occurred at the interface with CVD-grown graphene.

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- ¹D. H. Waldeck, *Chem. Rev.* **91**, 415–436 (1991).
- ²H. Rau, in *Photochemistry and Photophysics*, edited by J. F. Rabek (CRC Press, Boca Taton, FL, 1990), Vol. 2, pp. 119–141.
- ³K. Venkataraman, *The Chemistry of Synthetic Dyes* (Academic Press, New York, 1956).
- ⁴D. Bléger, Z. Yu, and S. Hecht, *Chem. Commun.* **47**, 12260–12266 (2011).
- ⁵J. A. Delaire and K. Nakatani, *Chem. Rev.* **100**, 1817–1846 (2000).
- ⁶E. R. Kay, D. A. Leigh, and F. Zerbetto, *Angew. Chem., Int. Ed.* **46**, 72–191 (2007); V. Balzani, A. Credi, and M. Venturi, *Molecular Devices and Machines* (Wiley-VCH, Weinheim, 2008).
- ⁷Z. Li, P. Dharap, S. Nagarajaiah, E. Barrera, and J. Kim, *Adv. Mater.* **16**, 640–643 (2004).
- ⁸X. Guo, L. Huang, S. O'Brien, P. Kim, and C. Nuckolls, *J. Am. Chem. Soc.* **127**, 15045–15047 (2005).
- ⁹M. Kim, N. S. Safron, C. Huang, M. S. Arnold, and P. Gopalan, *Nano Lett.* **12**, 182–187 (2012).
- ¹⁰A. R. Jang, E. K. Jeon, D. Kang, G. Kim, B. Kim, D. J. Kang, and H. S. Shin, *ACS Nano* **6**, 9207–9213 (2012).
- ¹¹D. G. Whitten, P. D. Wildes, J. G. Pacifici, and G. Irick, Jr., *J. Am. Chem. Soc.* **93**, 2004–2008 (1971).
- ¹²H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.* **41**, 1809–1825 (2012).
- ¹³L. Wang and X. Wang, *J. Mol. Struct: THEOCHEM.* **806**, 179–186 (2007).
- ¹⁴H. Jang, Y.-K. Kim, H.-M. Kwon, W.-S. Yeo, D.-E. Kim, and D.-H. Min, *Angew. Chem., Int. Ed.* **122**, 5839–5843 (2010).