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Photon-driven nanomechanical cyclic motion

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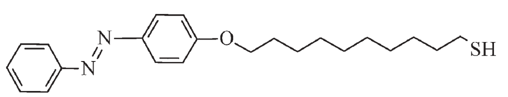
Microcantilevers modified by a monolayer of azobenzene molecules bend up and down periodically, switched by a 365 nm UV light, as a result of the conversion of the two configurations of azobenzene molecules in the monolayer.

Microcantilevers undergo bending due to surface stress changes upon molecular adsorption, which is one of the most overlooked, yet fascinating aspects of adsorption.[1–3] A promising application of this concept is to develop chemically specific microsensors by coupling molecular recognition agents to the microcantilevers for identification of chemicals in air and in water. Recently, many microcantilever-based chemical and biological sensors have been demonstrated.[4–6] Since cantilevers are extremely sensitive, they have the capability to detect chemicals from the parts-per-billion to the parts-per-trillion range.

However, so far, few attempts have been made to exploit another concept: light-induced surface stress change based on photo-induced conformational change of light-sensitive materials. This concept will have applications in developing novel micro/nanomechanical devices. It is well known that some molecules, such as azobenzene compounds, can be reversibly switched between their *trans*- and *cis*-configurations with two different wavelengths (Scheme 1).[7] The *cis–trans* conversion can take place on the ground state in the dark at room temperature as well.[8] It is anticipated that if a monolayer of azobenzene compounds is immobilized on the surface of a microcantilever, *trans–cis* and *cis–trans* isomerism of the compounds induced by light could markedly change the surface characteristics of the microcantilever, and results in the bending motion of the microcantilever. In this paper, we report that a microcantilever modified by azobenzene components can bend up and down periodically because of the *cis–trans* conversion of the azobenzene groups.

A thiol group-terminated azobenzene derivative **trans-1** was synthesized using a procedure described in the literature.[9] A self-assembled monolayer of **trans-1** has previously been characterized.[10]



We used commercially available silicon microcantilevers (Veeco Instrument, CA) in all of our experiments. The dimensions of the V-shaped silicon microcantilevers were 180 μm in length, 40 μm in leg width, and 2 μm in thickness. One side of the cantilever was covered with a thin film of chromium (3 nm) followed by a 20 nm layer of gold, both deposited by e-beam evaporation. The other side of the microcantilever was silicon. In these experiments, a **trans-1** monolayer on a gold-coated microcantilever was formed by immersing the cantilever into a 10^{-3} M solution of **trans-1** in CH_2Cl_2 for 24 h and it is assumed that a complete self-assembled monolayer was formed. The microcantilever was then rinsed with EtOH. The bending of the cantilever was measured by monitoring the position of a laser beam reflected from the cantilever onto a four-quadrant photodiode. A schematic diagram of the apparatus used in this study has been previously reported.[5] A high pressure mercury lamp with a 365 nm bandpass filter was used to obtain light centered at 365 nm at a photointensity of 6.5 mW cm^{-2} at approximately 4 cm distance. All of these experiments were conducted in a dark room.

A microcantilever coated by a monolayer of **trans-1** was initially placed in the dark under a nitrogen atmosphere until a stable baseline was obtained (*i.e.*, thermal equilibrium was obtained due to the absorption of laser energy by the gold surface of the microcantilever). When UV light at 365 nm was applied to irradiate the azobenzene monolayer, the microcantilever bent down toward the silicon side as shown in Fig. 1. Control experiments were performed with a bare gold coated reference microcantilever and a 1-dodecanethiol monolayer modified microcantilever. No deflection of these microcantilevers was observed upon exposure to the 365 nm UV light (Fig. 1). The thiolate oxidation or desorption does not occur under these conditions.[11] These observations suggest that *trans–cis* azobenzene conversion is effected within the self assembled monolayer of **trans-1** on gold surface of the microcantilever. Since the head group of a **cis-1** isomer was larger than that of a **trans-1** isomer, this conformation change resulted in the repulsion of molecules in the monolayer, and consequently the downward deflection of the microcantilever.

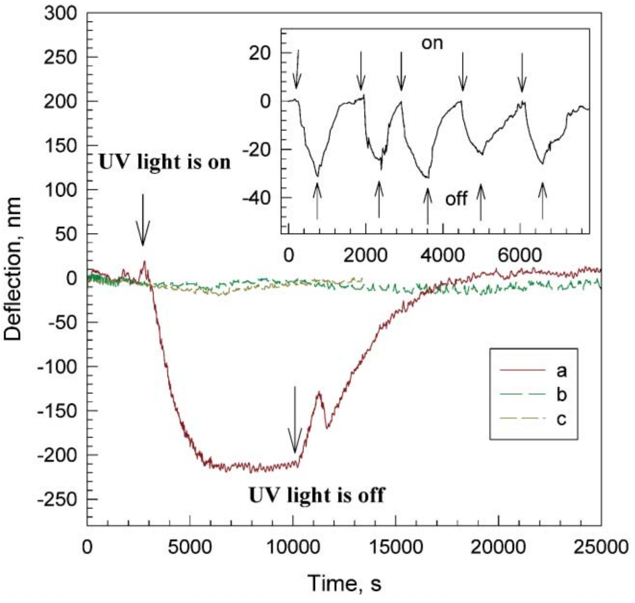
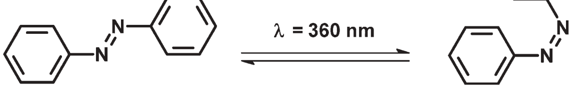


Fig. 1 Bending responses as a function of time, *t*, for silicon microcantilevers coated with (a) a monolayer of azobenzene compound **trans-1** on the gold surface, (b) a gold surface, (c) a monolayer of 1-dodecanethiol on the gold surface after exposure to a 365 nm UV light at a light intensity of 6.5 mW cm^{-2} and 90° angle of incidence. The microcantilevers were pre-equilibrated in the dark under N_2 environment before exposure to the UV light.



Scheme 1 *trans* and *cis* configurations of an azobenzene molecule switched by a UV light.

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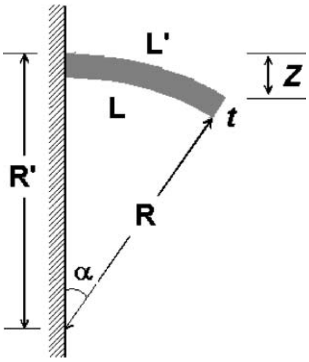

Fig. 2 Schematic presentation of side view of a microcantilever.

The microcantilever deflection reached its maximum bending amplitude at approximately 210 nm before the UV light was switched off as shown in Fig. 1. Eight cantilevers modified under the same conditions were tested for cantilever-to-cantilever reproducibility. The bending *vs.* time profiles of these cantilevers were quite similar and the maximum bending amplitudes were approximately 180 ± 40 nm. The relatively wide range of bending amplitudes might be caused by both the variability of the cantilevers (175 ± 5 μm in length, 2.0 ± 0.2 μm in thickness, 30 ± 6 μm in width) and the quality of the self-assembled monolayers (SAM).

Since the deflection of a microcantilever was generated from surface stress change or extension of the top microcantilever surface (L' in Fig. 2), the length (L) of the bottom surface (silicon surface) was constant (180 μm). Thus

$$L = \frac{\alpha}{360^\circ} 2\pi R \quad (1)$$

$$\cos\alpha = \frac{R - z}{R} \quad (2)$$

where R' and R are the radius of curvature of the bending of the cantilever's top and bottom surfaces, respectively. By using a least-squares fit to solve these equations, it was obtained that $\alpha = 0.12^\circ$, $R = 0.09$ m. Since $R' = R + t$, L' was then 2 nm greater than L. This result showed that the top surface of the microcantilever stretched by 0.001% because of the *trans–cis* conversion of the **trans-1** monolayer.

On the basis of the crystallographic data for *cis*- and *trans*-azobenzene, Mirkin *et al.* estimated that **cis-1** occupies approximately 1.5–2 times the cross-sectional area occupied by **trans-1**.[10] Assuming the cross-sectional area of a **cis-1** molecule in a self-assembled monolayer on the gold surface is 1.5 times that of a **trans-1** molecule, the length of the top surface of the microcantilever will extend by approximately 40 μm if all the **trans-1** molecules were converted to their *cis* configuration. According to these analyses, it was concluded that only 0.005% of **trans-1** were converted to their *cis* configuration in the monolayer on the microcantilever at 210 nm deflection amplitude. The *trans–cis* conversion was slow and inefficient because of the low quantum yields with respect to *trans–cis* conversion for monosubstituted azobenzenes[12] and the inhibitory steric effects within the monolayer film. Furthermore, the reverse *cis–trans* conversion can occur in the dark.[8] In contrast to the low yield *trans–cis* conversion, the *cis–trans* conversion of azobenzenes in the monolayer is very efficient. Thus, the conversion of the two configurations may reach equilibrium at the maximum microcantilever deflection amplitude. This hypothesis was further supported by the observation that when the UV light was removed, the cantilever deflection gradually returned to its original position as shown in Fig. 1. The insert in Fig. 1 shows several reversible cantilever cyclic motions when the UV is turned on and off. In these experiments, the UV was turned off before the cantilever bending reached equilibrium.

In these experiments, the UV light was brought to the cantilever surface at approximately 90° angle of incidence. Due to the limitations of the instrumental setup, the light incident angles were restricted to either 90° or between 35° and 55°. No significant differences on the cantilever deflection profiles and amplitudes were observed when different incidence angles between 35 and 55° were used. However, at 90° incidence angle, the cantilever deflection rate was approximately twice as fast as that at 45°. The cantilever deflection rates were proportional to the light intensities applied to the cantilever surface (Fig. 3).

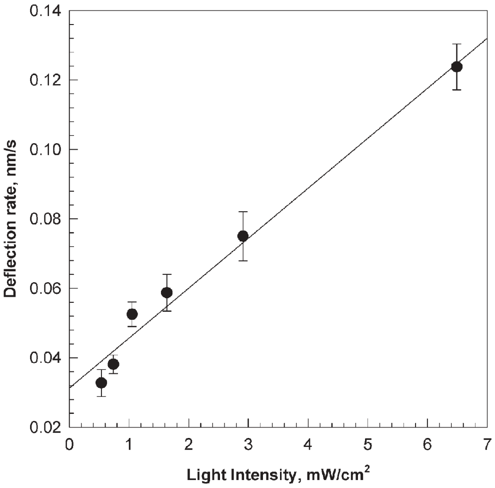

Fig. 3 The bending rates of an azobenzene monolayer modified cantilever in the first 400 s after exposure to the UV light (*i.e.* the slopes during the onset of the nanomechanical motion) as a function of light intensities.

The paper demonstrated that one can regulate microcantilever bending up and down involving two-component SAMs that are switched by a UV light. The molecular energy can be converted into nanomechanical energy driven by photons which may be used for the development of micro/nanoscale devices. We are to redesign the molecules to improve the bending amplitude. The advantage of light controlled approach of micro/nanodevices is that it is readily controlled by the specific light and no wire is needed.

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Notes and references

1 J. K. Gimzewski, C. Gerber, E. Meyer and R. R. Schlittler, *Chem. Phys. Lett.*, 1994, **217**, 589–594.
2 G. Y. Chen, R. J. Warmack, T. Thundat, D. P. Allison and A. Huang, *Rev. Sci. Instrum.*, 1994, **65**, 2532–2537.
3 T. Thundat, R. J. Warmack, G. Y. Chen and D. P. Allison, *Appl. Phys. Lett.*, 1994, **64**(21), 2894–2896.
4 H. F. Ji, T. Thundat, R. Dabestani, G. M. Brown, P. F. Britt and P. Bonnesson, *Anal. Chem.*, 2001, **72**, 1572–1576.
5 H. P. Lang, M. K. Baller, R. Berger, Ch. Gerber, J. K. Gimzewski, F. M. Battiston, P. Fornaro, J. P. Ramseyer, E. Meyer and H. J. Guntherodt, *Anal. Chim. Acta*, 1999, **393**, 59–65.
6 J. Fritz, M. K. Baller, H. P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, H.-J. Guntherodt, Ch. Gerber and J. K. Gimzewski, *Science*, 2000, **288**, 316.
7 A. Janshoff, M. Neitzert, Y. Oberdorfer and H. Fuchs, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 3212.
8 J. A. Andersson, R. Petterson and L. Tegner, *J. Photochem.*, 1982, **20**, 17.
9 W. B. Caldwell, D. J. Cambell, K. Chen, B. R. Herr, C. A. Mirkin, A. Malik, M. K. Durbin, P. Dutta and K. G. Huang, *J. Am. Chem. Soc.*, 1995, **117**, 6071.
10 D. G. Walter, D. J. Campbell and C. Mirkin, *J. Phys. Chem. B*, 1999, **103**, 402–405.
11 J. E. Chadwick, D. C. Myles and R. L. Garrell, *J. Am. Chem. Soc.*, 1993, **115**, 10364.
12 H. Rau, *J. Photochem.*, 1984, **26**, 221.