

Three-dimensional motion and transformation of a photoelectrochemical actuator

Kazutake Takada, Taichi Miyazaki, Nobutaka Tanaka and Tetsu Tatsuma*

Received (in Cambridge, UK) 13th January 2006, Accepted 28th March 2006

First published as an Advance Article on the web 11th April 2006

DOI: 10.1039/b600442c

A new “photoelectrochemical actuator” consisting of poly(acrylic acid)/copper gel and TiO₂ nanoparticles has been developed, which undergoes reversible expansion/contraction upon UV light irradiation/termination, likely due to dissociation/formation of carboxylic group/Cu²⁺ binding.

Recently, much attention has focused on electrochemical actuators, which stretch and shrink due to redox reactions, because of their softness and delicate motion.^{1,2} Although they have another potential advantage of complicated three-dimensional expansion and contraction, this has never been realized due to an electrode tightly attached to the redox-active material. The electrode, which is essential for the redox reactions, has restricted the shape and motion of the actuators to one-, or at most, two-dimensional. In the present work, to remove the limitation, we introduced TiO₂ nanoparticles, which convert energy of UV light into electrochemical energy,³ into a redox-active gel. The dispersed “nanoelectrodes” allow the redox reaction without limiting the three-dimensional motion. Gel-based actuators driven by light irradiation such as VIS,⁴ UV⁵ and IR⁶ have been reported. However, their changes in volume are relatively small (volume ratios are typically ~10). Although the actuator consisting of a liquid-crystalline azobenzene^{7,8} has the advantage of fast actuation rate (*ca.* 10 s) it requires polarized light for three-dimensional motion and, in principle, a large volume change can not be expected. On the other hand, the volume ratio of the present photoelectrochemical actuator was found to be up to an order of magnitude larger (up to *ca.* 100). Remote operation is an additional advantage of the photoelectrochemical actuator. It is also possible to expand only the irradiated regions of the material. If TiO₂ particles are embedded in specific portions of the gel, these parts can be actuated selectively even by irradiating the whole gel with UV light. Thus, this gel can be used as a metamorphic and shape-memory material. Potential applications of light-driven actuators include tactile graphic displays and rewritable stamps, in addition to active bending catheters and micro-valves. In these applications, it is also convenient not requiring cables. There is also the possibility to develop multi-stimuli (electrical and optical) responsive actuators.

As a redox-active material, we used a poly(acrylic acid) gel containing Cu²⁺ ion, which swells and shrinks upon reduction of Cu²⁺ to Cu⁰ and its re-oxidation, respectively.⁹ The gel dispersing TiO₂ particles (ST-01, particle size ~7 nm, Ishihara Sangyo) was prepared following basically the same procedure described

elsewhere.⁹ In brief, this is by radical polymerisation of acrylic acid (700 mM) and *N,N'*-methylenebis(acrylamide) (7 mM) with ammonium peroxydisulfate (3.5 mM) and *N,N,N',N'*-tetramethylethylenediamine (8 mM) as an initiator and an accelerator, respectively, and TiO₂ particles (0.056 g ml⁻¹) (60 °C under nitrogen). In the current work, to disperse the TiO₂ particles, the mixed solution was stirred while heated. The resulting poly(acrylic acid) gel containing dispersed TiO₂ particles was immersed in an ethanol–water mixture (20 v/v% ethanol) containing 1 × 10⁻³ M Cu(NO₃)₂, so that the gel collapsed due to formation of coordination and/or electrostatic bonds between Cu²⁺ ion and carboxylate groups of the gel (Fig. 1(a)). The gel changed from colourless to blue and its width was 4.5 mm. When the gel was irradiated with UV light (*ca.* 10 mW cm⁻², 340–380 nm) by an Hg–Xe lamp (LA-210UV, Hayashi Tokei) with a bandpass filter, the poly(acrylic acid)/Cu gel turned black and expanded three-dimensionally (Fig. 1(b) and (c)). The final volume ratio, *v/v*₀, (*v*₀ is the volume before the irradiation) was found to be ~100. The volume was calculated from photos taken by a digital camera (Canon, Powershot A80). Here, the ratios of the width to depth was confirmed to be always essentially the same during actuation. This volume ratio is much larger than that of conventional photo-responsive gels (typically ~10).^{4–6,10} In addition, such a three-dimensional volume change can not be achieved by film type photo-responsive actuators.^{7,8,11}

The black colour likely reflects deposition of small Cu⁰ particles on TiO₂ by photocatalytic reduction. Electrons in the valence band of TiO₂ were excited to the conduction band upon UV irradiation (TiO₂ + UV → TiO₂* (e⁻ + h⁺)), and the excited electrons, in turn, reduce Cu²⁺ (Cu²⁺ + 2e⁻ → Cu). The reduction of Cu²⁺ gives rise to dissociation of the coordination and/or electrostatic bonds between Cu²⁺ and carboxylate groups of the gel, resulting in the swelling. Simultaneously, holes in the valence band (h⁺) should be consumed to oxidize ethanol in the medium. Ethanol has generally been used as a hole scavenger and oxidized to acetaldehyde, acetic acid and CO₂.¹² In fact, in the absence of ethanol, blackening and expansion of the gel were not evident. On the other hand, at concentrations of ethanol higher than *ca.* 50%, although the gel turned black upon UV irradiation, essentially no expansion was observed. These results indicate that the swelling of the gel requires water and the photoelectrochemical reaction requires ethanol. Fig. 2(a) shows time courses of volume ratios of the gel in ethanol–water mixtures (20, 30 and 40 v/v%) upon UV irradiation. As can be seen in Fig. 2(a), all experiments carried out in 20, 30 and 40% ethanol solutions showed a swelling ratio higher than 50. Thus, 20 v/v% ethanol solution was used for all the following

Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan. E-mail: tatsuma@iis.u-tokyo.ac.jp; Fax: +81 3 5452 6338; Tel: +81 3 5452 6337

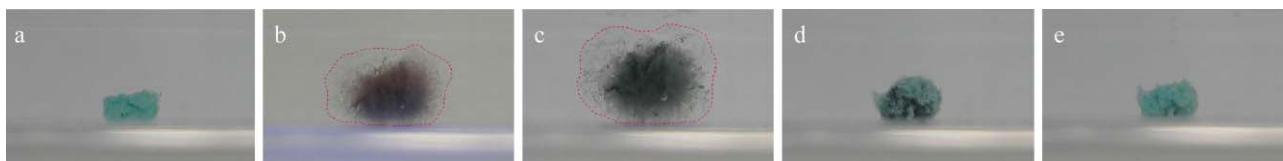


Fig. 1 Photo-induced three-dimensional actuation of the poly(acrylic acid)/Cu gel containing TiO₂. (a) Before UV light irradiation in a 20 v/v% ethanol solution (the width of the gel is 4.5 mm); (b) after 1.5 h UV irradiation (*ca.* 10 mW cm⁻², 340–380 nm); (c) after 3 h irradiation (steady state); (d) 2.5 h after termination of the irradiation; (e) 5 h after the termination (steady state). The broken lines indicate the boundary between the gel and solution.

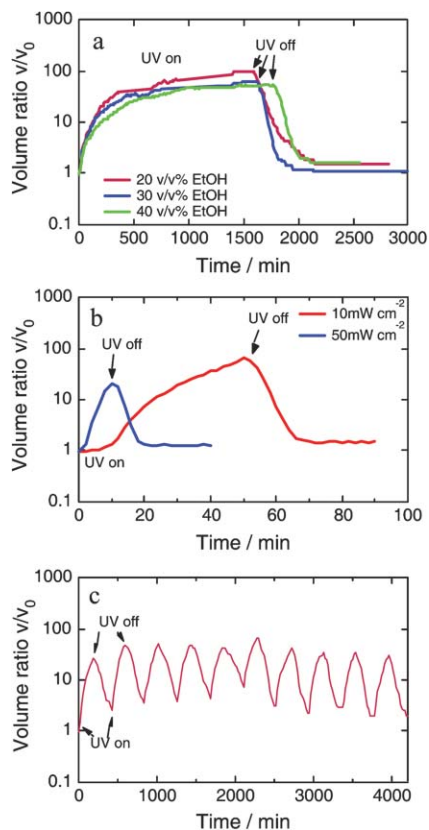


Fig. 2 Volume changes of the photoelectrochemical actuator. (a) Effect of ethanol concentration on the gel (4.5 mm width at shrunken state). (b) Effect of UV light intensity on the gel (*ca.* 0.5 mm diameter at shrunken state). (c) Repeated photoelectrochemical actuation (3 h irradiation and 4 h non-irradiation) in a 20 v/v% ethanol solution for the gel (4.5 mm width at shrunken state).

experiments since lower concentrations of ethanol are more suitable for practical applications.

As can be seen in Fig. 2(a), when the UV irradiation was stopped, the gel gradually re-collapsed and the volume essentially returned to the original value, even under fluorescent lamps. Fig. 1(d) and (e) show images of the gel 2.5 and 5 h (steady state), respectively, after the termination of the UV irradiation. These results clearly suggest that the poly(acrylic acid)/Cu gel containing TiO₂ operates as a photoelectrochemical actuator.

In order to improve the actuation time, smaller gel particles (diameter is *ca.* 0.5 mm at shrunken state, which is one ninth the size of the larger sample) were employed, as the shrinking/swelling time is known to be proportional to the squared diameter of the gels. The smaller gels were prepared by crushing the bulk. The red

line in Fig. 2(b) shows a typical time course of the volume ratio of the smaller gel with other experimental conditions being the same as for the larger gel. As can clearly be seen in Fig. 2(a) and (b), swelling and shrinking of the smaller gel was found to be *ca.* four and ten times, respectively, faster than those of the larger one. When the intensity of UV light irradiated for the smaller gel was increased from 10 to 50 mW cm⁻² (340–380 nm), the swelling rate appeared to be *ca.* three times faster, whereas the shrinking rate virtually remained unchanged (Fig. 2(b)). In addition, further enhancement could be expected by reducing the gel size, which gives rise to improvement of water exclusion for the shrinking process, and increasing photon supply and optimising concentration and particle size of TiO₂ for the swelling process. In the case of the larger gel, both the rates were found to be independent of the light intensity at 10 and 50 mW cm⁻². These results indicate that the rate limiting step of the actuation is likely water incorporation/exclusion. Therefore, in order to improve the actuation, use of porous gels, which give rise to an increase in mobility of water, is expected to be effective.

In order to study the contracting mechanism of the gel, changes in volume of the gel were measured under deaerated and ambient conditions. The gel with *ca.* 0.5 mm diameter in a solution deaerated with N₂ gas showed normal swelling upon UV irradiation (swelling ratio was *ca.* 20 in 10 min) and virtually no re-shrinking for at least 20 min upon termination of the irradiation. On the basis of this, contraction of the gel can be attributed, at least in part, to oxidation of Cu⁰ to Cu²⁺ by dissolved oxygen in the solution ($2\text{Cu} + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 2\text{H}_2\text{O}$), which gives rise to reformation of the coordination and/or electrostatic bonds between Cu²⁺ ion and carboxylate groups of the gel.

Repeatability of the actuation was also examined using the larger gel (Fig. 2(c)). Although ethanol oxidation is irreversible and thus it was consumed, for the time period used in this work, the changes in ethanol concentration did not essentially affect the performance as shown in Fig. 2(c). Leaking of Cu²⁺ ions was anticipated to affect the repeatability of the actuation. However, in a 1×10^{-4} M Cu²⁺ solution, a similar behaviour observed at 1×10^{-3} M was observed. This is reasonable because the gel totally shrinks at concentration higher than 10^{-4} M. In other words, the gel loaded with Cu²⁺ ions at $>10^{-4}$ M actuates even if some Cu²⁺ ions leak. In fact, repeated irradiation–non-irradiation cycles (3 and 4 h, respectively) gave at least 10 cycles of expansion and contraction of the gel (loaded at 10^{-3} M Cu²⁺). The relatively low reproducibility upon the repeated actuation would be attributed, at least in part, to the fact that the shrinking/swelling rate generally slows down as the system approaches equilibrium. Changes in gel morphology are likely another possibility. To eliminate this problem, mechanical strength

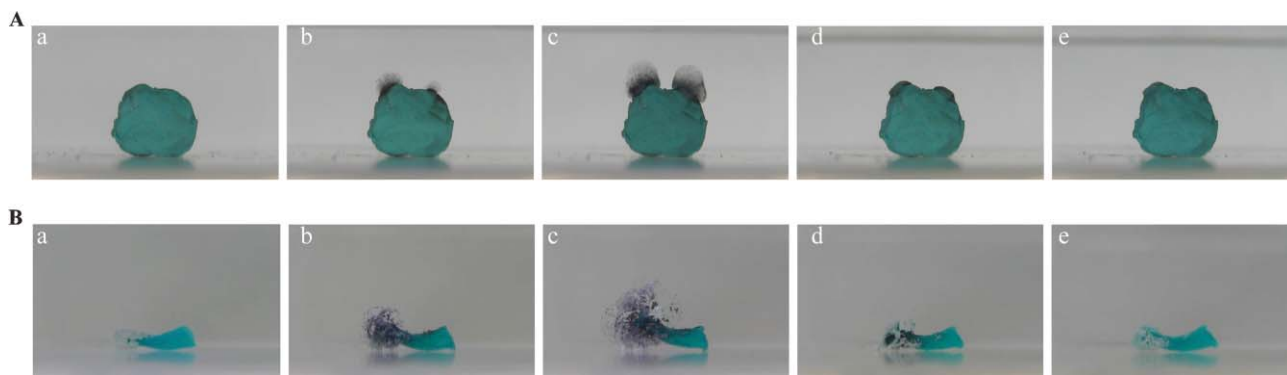


Fig. 3 (A) Reversible “jelly bear” transformation of the photoelectrochemical actuator. (a) Before UV light irradiation in a 20 v/v% ethanol solution (the width of the gel is 7.5 mm); (b) after 3 h UV irradiation (ca. 20 mW cm⁻², 340–380 nm) through a photomask with two 1 mm diameter holes (3 mm apart); (c) after 6 h irradiation; (d) 2.5 h after termination of the irradiation; (e) 5 h after the termination (steady state). (B) Partial transformation of the gel embedding TiO₂ particles in the left half. (a) Before UV light irradiation in a 20 v/v% ethanol solution (the width of the gel is 7 mm); (b) after 2.5 h UV irradiation (ca. 20 mW cm⁻², 340–380 nm) on the whole gel; (c) after 5 h irradiation; (d) 3 h after termination of the irradiation; (e) 6 h after the termination (steady state).

and elasticity of the gel need to be optimised by, for instance, selecting a more appropriate crosslinking agent and/or increasing its concentration.

Although the output force was difficult to measure, it was anticipated to be of the order of 10 mgf (~1 Pa per unit area), which has been measured for an electrochemical actuator consisting of the same materials without TiO₂ particles.⁹

As mentioned above, partial actuation or transformation is one of the potential features of photo-controlled actuators. In order to demonstrate this, we shaped the gel into a roughly round shape of 6–7 mm diameter (Fig. 3A(a)), and irradiated it with UV light (ca. 20 mW cm⁻²) through a photomask with two 1 mm diameter holes (3 mm apart). As a result, “bear ears” gradually appeared (Fig. 3A(b)) and were clearly formed in 6 h (Fig. 3A(c)). When the irradiation was stopped, the “ears” gradually shrunk (Fig. 3A(d)) and disappeared in 5 h (Fig. 3A(e)). This reversible “jelly bear” metamorphosis clearly indicates that the present photoelectrochemical actuator can be partially actuated or transformed by controlled irradiation. The slight difference in the shapes before and after the irradiation would arise from the same reasons mentioned for the repeatability.

A gel partially embedding TiO₂ particles also showed partial swelling upon UV light irradiation on the whole gel as shown in Fig. 3B(a)–(c). Upon termination of the irradiation, the gel gradually shrunk (Fig. 3B(d) and (e)). Here, TiO₂ particles were

embedded in the left half of the swollen gel by injection of their suspension (56 g l⁻¹) using a syringe. The gel was then immersed in a 20 v/v% ethanol solution containing 1 × 10⁻³ M Cu(NO₃)₂.

In order to improve the performance such as actuation speed and swelling ratio of the actuator, the composition and the degree of cross-linking of the gel need to be optimised. In addition, use of porous gels, which give rise to an increase in mobility of water as well as Cu²⁺ ion in the gel, is expected to improve the actuation speed.

Notes and references

- 1 S. Ashley, *Sci. Am.*, 2003, **289**, 52.
- 2 E. Smela, *Adv. Mater.*, 2003, **15**, 481.
- 3 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
- 4 A. Suzuki and T. Tanaka, *Nature*, 1990, **346**, 345.
- 5 A. Mamada, T. Tanaka, D. Kungwachakun and M. Irie, *Macromolecules*, 1990, **23**, 1517.
- 6 X. Zhang, Y. Li, Z. Hu and C. L. Littler, *J. Phys. Chem.*, 1995, **102**, 551.
- 7 Y. Yu, M. Nakano and T. Ikeda, *Nature*, 2003, **425**, 145.
- 8 T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi and A. Kanazawa, *Adv. Mater.*, 2003, **15**, 201.
- 9 K. Takada, N. Tanaka and T. Tatsuma, *J. Electroanal. Chem.*, 2005, **585**, 120.
- 10 S. Juodkazis, N. Mukai, R. Wakaki, A. Yamaguchi, S. Matsuo and H. Misawa, *Nature*, 2000, **408**, 178.
- 11 S. V. Ahir and E. M. Terentjev, *Nat. Mater.*, 2005, **4**, 491.
- 12 D. S. Muggli, J. T. McCue and J. L. Falconer, *J. Catal.*, 1998, **173**, 470.