Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Polydopamine-coated open cell polyurethane foams as inexpensive, flexible yet robust catalytic support: proof of concept

Elodie Pardieu,[a,b] Nguyet Trang Thanh Chau,[a,b,c] Thierry Dintzer,[a] Thierry Romero,[a] Damien Favier,[b] Thierry Roland,[b] David Edouard,*[d,e] Loïc Jierry*[b,e] and Vincent Ritleng,*[c,e,f]

[a] Institut de Chimie et Procédé pour l'Energie, l'Environnement et la Santé, UMR CNRS 7515, Ecole européenne de Chimie, Polymères et Matériaux, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France.

[b] Institut Charles Sadron, UPR CNRS 022, 23 rue du Loess, 67034 Strasbourg, France.

[c] Laboratoire de Chimie Organométallique Appliquée, UMR CNRS 7509, Ecole européenne de Chimie, Polymères et Matériaux, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France.

[d] Laboratoire d'Automatique et de Génie des Procédés, UMR CNRS 5007, Université de Lyon 1, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne, France.

[e] Institut d'Etudes Avancées de l'Université de Strasbourg (USIAS), 5 allée du Général Rouvillois, 67083 Strasbourg, France.

[f] Institut Universitaire de France, 103 boulevard Saint Michel, 75005 Paris, France.

david.edouard@univ-lyon1.fr, loic.jierry@ics-cnrs.unistra.fr, vritleng@unistra.fr

1. Materials and methods

Commercial compounds were used as received. Polyurethane open cells foams **1** (20 PPI) were purchased from FoamPartner. Dopamine hydrochloride, (99% - A11136), and acetonitrile (HPLC grade, 99.7+% - 22927) were purchased from Alfa Aesar. Titanium (IV) oxide, anatase (99.9% - AB208992) was purchased from Abcr. Tris base (99.9+% - T1503) and acid orange 7 (Dye content 85+% - 195235) were purchased from Sigma-Aldrich.

18.2 MΩ deionized water (TOC < 1 ppb), supplied by a Q20 Millipore system, was used for the preparation of aqueous solutions and washing procedures.

Scanning electron microscopy measurements were recorded on a JEOL 6700F microscope with a 2 nm point resolution. UV irradiations were performed in a UV box with a

125 W Philips HPK UV lamp (type 57203B). UV-visible measurements (250 to 580 nm; scan rate: 2 nm.s^{-1}) were performed using 96-Well UV plates with a SAFAS FLX Xenius spectrophotometer equipped with a Microplate UV reader. Compression tests were carried out on an Instron E3000 electrodynamic testing system equipped with a 100 N load cell. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo VG Multilab ESCA 3000 apparatus equipped with an Al Kα radiation source (1486.6 eV) and pass energy of 20 eV.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements were performed by the *Platefome Analytique* of the *Institut Pluridisciplinaire Hubert Curien* (UMR CNRS 7178), Strasbourg, France.

2. Open cell polyurethane foam (OCPUF) (1) coating with polydopamine (PDA)

Dopamine hydrochloride (180 mg) was dissolved in a 10 mM aqueous solution (90 mL) of Tris base buffered to pH 8.5 with aqueous HCl (1 M). A cubic sample of polyurethane open cell foam **1** (2 × 2 × 2 cm, *ca.* 200 mg) was immersed in the stirred solution for 12 h at RT. The solution slowly turned dark brown. The resulting PDA-coated foam (PDA@OCPUF, **2**) was then taken out of the solution, rinsed thoroughly with water, immersed in vigorously stirred water (70 mL) for 10 min, and air-dried. This washing procedure was repeated 5 times, and the dark brown **2** was finally dried overnight in an oven at 60 °C.

2 was characterized by SEM (Fig. 1c,d) and XPS. XPS analyses showed a significant increase of the O(1s)/C(1s) atomic ratio compared to that observed for pristine OCPUF **1** (Table S1), indicating the probable presence of oxygen atoms coming from the catechol groups of dopamine on the surface after the surface coating with PDA.

Table S1. O(1s)/C(1s) ratio measured by XPS on pristine OCPUF **1** and PDA@OCPUF **2**.

	% C(1s)	% O(1s)	O(1s)/C(1s)
OCPUF **1**	78.60	18.44	0.2346
PDA@OCPUF **2**	66.67	24.18	0.3627

3. Functionalization of PDA@OCPUF (2) with TiO_2

TiO_2 (1.6 g) was added to a 10 mM aqueous solution (80 mL) of Tris base buffered to pH 8.5 with aqueous HCl (1 M). The resulting suspension was stirred at 1500 rpm for 12 h at RT, and then sonicated for 30 min. The temperature was increased to 40 °C under rapid stirring, and a cubic sample of **2** (2 × 2 × 2 cm) was immersed in the well-dispersed TiO_2 suspension for 12 h at this temperature. The resulting TiO_2-functionalized foam (TiO_2@PDA@OCPUF, **3**) was then taken out of the solution, rinsed thoroughly with water, immersed in vigorously stirred water (70 mL) for 10 min, and air-dried. This washing procedure was repeated 8 times, and the beige **3** was finally dried overnight in an oven at 60 °C.

3 was characterized by XPS (Fig. S1), SEM (Fig. 3 and S2), and SEM-EDX (Fig. 3).

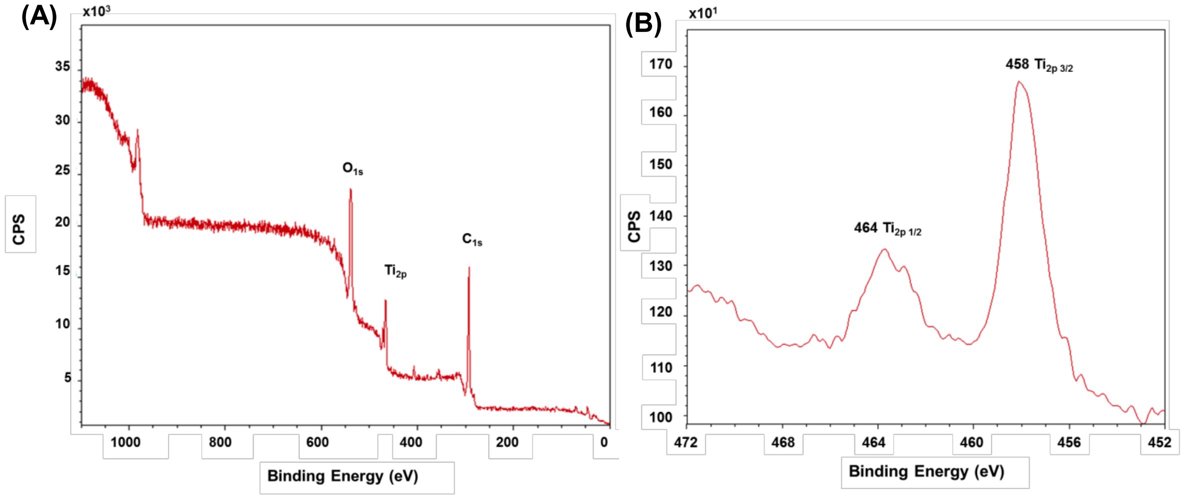

Figure S1. XPS spectrum of **3**: all spectrum (A), titanium area (B)

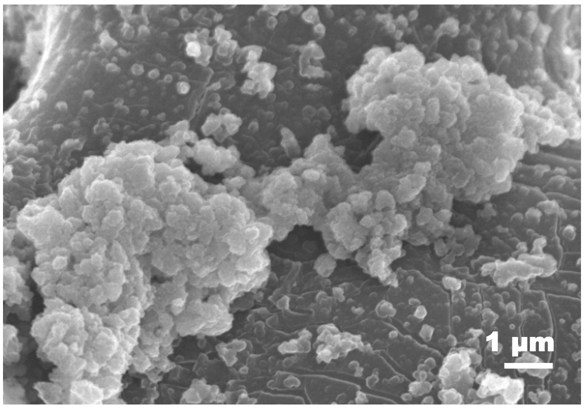

Figure S2. SEM image (COMPO) of **3**

4. TiO_2@PDA@OCPUF-catalyzed degradation of acid orange 7 (AO7) under UV irradiation

4.1. Typical procedure

AO7 (2 mg, 5.71 µmol – Fig. S3) was dissolved into deionized water (200 mL), and the resulting orange solution was allowed to equilibrate over 45 min in the absence of light. 40 mL of this solution was then transferred into a UV-transparent glass reactor into which were also added 3 pieces of **3** of 0.5 × 2 × 2 cm each, *i.e.* of 50 mg each. The reaction medium was then put under UV irradiation (125 W) for 200 min without stirring in a UV box (Fig. S4), and the conversion was followed by UV spectrophotometry. For that purpose, aliquots of 100 µL were removed at T = 0, 20, 40, 60, 80, 100, 120, 150 and 200 min, and the decomposition of AO7 was followed by measuring the decrease of the absorbance at 485 nm. During the reaction, the solution color turned from orange to colorless (Fig. S5). After 200 min, the reaction was stopped, the pieces of **3** were taken out of the solution to be re-used (see Section 4.2), and a sample of the solution was analyzed by ICP-OES to determine the titanium content.

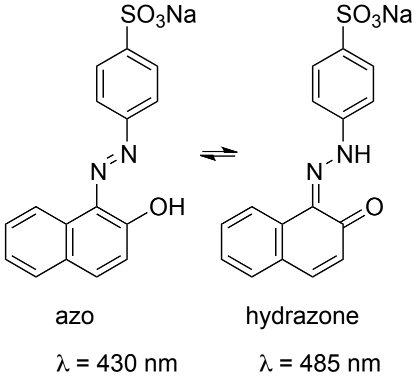

Figure S3. Structure of AO7

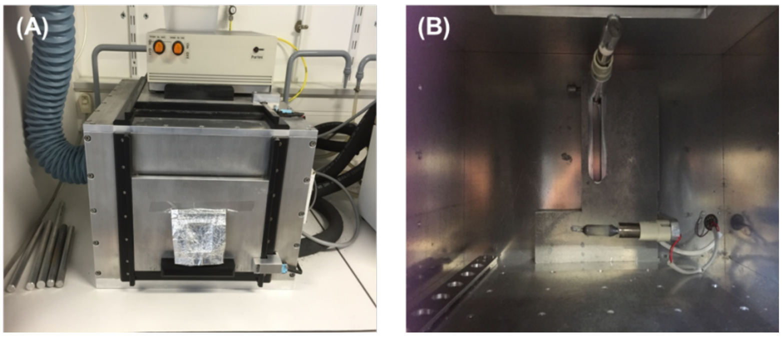

Figure S4. UV box used for the irradiation experiments: (A) outside, (B) inside

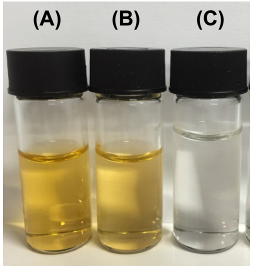

Figure S5. Color of AO7 solutions before irradiation (a), after 200 min UV irradiation in the absence of catalyst (b), after 200 min UV irradiation with **3** (c)

4.2. OCPUF@PDA@TiO$_2$ reusability procedure

After each run, the pieces of OCPUF@PDA@TiO$_2$ (**3**) were taken out of the solution, rinsed thoroughly with water, immersed in vigorously stirred water (70 mL) for 12 h, air-dried, and re-used (up to 5 times) as described in Section 4.1.

4.3. Stop-and-go experiment

AO7 (2 mg, 5.71 µmol) was dissolved into deionized water (200 mL), and the resulting orange solution was allowed to equilibrate over 45 min in the absence of light. 40 mL of this solution was then transferred into a UV-transparent glass reactor into which were also added 3 pieces of **3** of 0.5 × 2 × 2 cm each, *i.e.* of 50 mg each. The reaction medium was then put under UV irradiation using the same set-up than in typical procedures (see Section 4.1). After 60 min, **3** was removed from the reaction medium, which was let under UV irradiation for 60 minutes in the absence of catalyst before **3** was re-immersed in the solution. Aliquots of 100 µL were removed at T = 0, 60, 120, and 200 min to follow the conversion by UV spectrophotometry (Fig. S6).

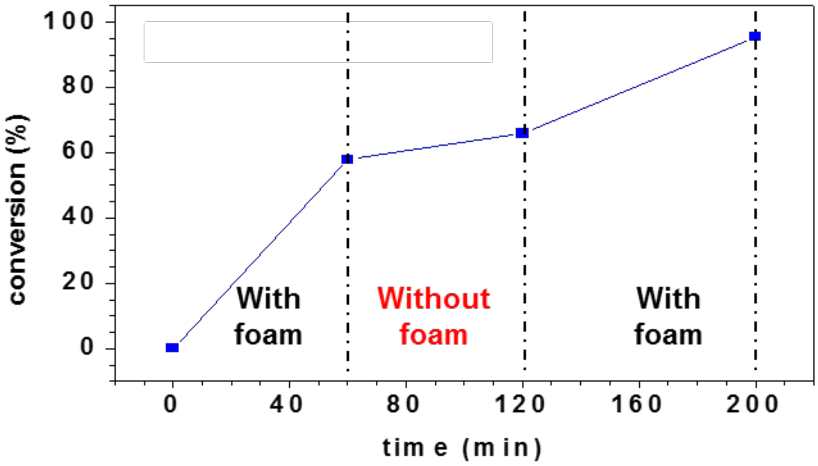

Figure S6. Degradation of AO7 *vs.* time during the stop-and-go experiment; the slight slope observed between T = 60 and T = 120 min is due to the direct influence of UV on the substrate (see Fig. 4C).

5. Compression tests

5.1. Fatigue test

A fatigue test was performed at room temperature on a cubic sample (3 × 3 × 3 cm) of **3** by compressing it at a rate of 0.1 mm.s^{-1} between two cylindrical platens to a strain of *ca.*

75% (Fig. S7b), then 5000 times to a strain of *ca*. 25% through sinusoidal cycles of 1 Hz (Fig. S7c), and finally again to a strain of 75% (Fig. S7d).

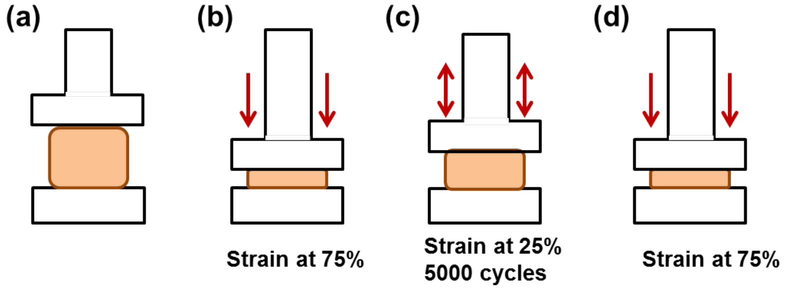

Figure S7. Schematic representation of the fatigue test

5.2. Compressive stress/strain response tests

Compression tests were performed at room temperature on cubic samples (3 × 3 × 3 cm) of **1**, **2**, and **3** (before and after a fatigue test - see Section 5.1.), by compressing it between two cylindrical platens at a rate of 0.1 mm.s^{-1} to a strain of *ca*. 75%, and recording the stress/strain response (see Fig. 4A).

5.3. Relevance of compressive stress/strain response tests to evaluate the robustness of the PDA coating compared to tensile stress/strain response tests

Compressive loading causes cell wall bending mechanism, specially at a high strain, and classical beam theory can be applied to the micromechanical scale of the unit cell, showing that each strut undergoes a gradual stress that goes from compression to tension from one side to the opposite, at least in the elastic region. Then, the stress in the struts continues to rise as they buckle or bend plastically leading to distortion and local collapses. Thus, a compression test will principally stress the struts surface where the PDA coating has to adhere, whereas tensile loading at high strain will conduct to a better distributed stress along the cell wall and the struts thicknesses, and will imply an orientation of these microstructures in the stretch direction.[1,2]

6. References

[1] L. J. Gibson, M. F. Ashby, *Cellular Solids: Structure and Properties*, Pergamon Press, Oxford, 1988.

[2] D. Mouhamadou, T. Roland, P. Kékicheff, C. Gauthier, *Physically and finite element based modeling of polymer foam microstructure for the analysis of their mechanical behavior*, 16th International Conference on Experimental Mechaniscs, Cambridge, 2014.