ARTICLE

Self-defending anti-vandalism surfaces based on mechanically triggered mixing of reactants in polymer foils

Jonas G. Halter, Nicholas H. Cohrs, Nora Hild, Daniela Paunescu, Robert N. Grass and Wendelin J. Stark*

The bombardier beetle uses attack-triggered mixing of reactants (hydrochinone, hydrogen peroxide H_2O_2 and enzymes as catalysts) to defend itself against predators. Using multi-layer polymer sheets with (H_2O_2) and catalyst (MnO_2) filled compartments we developed a 2D analogous bio-inspired chemical defence mechanism for anti-vandalism applications. The reactants were separated by a brittle layer that ruptures upon mechanical attack, and converts the mechanical energy trigger (usually a few Joules) into a chemical self-defence reaction involving release of steam, and optionally persistent dyes and a DNA-based marker for forensics. These surfaces effectively translate a weak mechanical trigger into an energetic chemical reaction with energy amplification of several orders of magnitude. Since the responsive materials presented here do not depend on electricity, they may provide a cost effective alternative to currently used safety systems in the public domain, automatic teller machines and protection of money transport systems. Anti-feeding protection in forestry or agriculture may similarly profit from such mechanically triggered chemical self-defending polymer surfaces.

1. Introduction

Self-defence is a key function of all organisms and particularly arthropods have developed sophisticated systems against predators, often involving efficient use of chemically aggressive compounds.[1, 2] Compartmented systems with defence or protection functions are indeed commonly found in many organisms: For example, bitter almonds and other *Rosaceae* species produce hydrogen cyanide (HCN) when attacked through mixing of cyanogenic precursors and corresponding enzymes[3] stored in specialized compartments or on subcellular basis[4] and effectively keep off herbivores. We most recently transferred such protection mechanisms onto wheat seed crops allowing them to defend themselves using triggered cyanogenesis.[5] Biomimetic materials are attractive for their often elegant and efficient mechanisms.[6] At present, protective surfaces provide antimicrobial and antifouling activity.[7] Other enzyme functionalised surfaces provide protection from contamination and easy cleaning ability.[8] Bacterial feeding induced antibacterial activity was introduced by Loher et al when providing 1-2 nm silver loaded phosphate containing nanoparticles as a bait to growing bacteria.[9] A coating with antibacterial and antifungal functionality was developed recently as a self-defensive biomaterial against biofilm formation.[10] Living surfaces, which contain a fungus, provide antibiotics upon infection.[11]

In nature, the most aggressive chemical defence system may be found in the bombardier beetle. When in danger, the beetle emits a hot and corrosive spray. Its specialized organs are sectioned in an inner part (reservoir) containing hydrogen peroxide and hydroquinones and an outer part (reaction chamber) holding an enzyme mixture (catalases and peroxidases, see Scheme 1b). In order to eject its defensive spray, the beetle first squeezes the liquid of the reservoir into the reaction chamber. High concentrations of catalase induce a violent decomposition of hydrogen peroxide to oxygen and water while peroxidases convert hydroquinones into toxic quinone. The hot mixture is a highly effective repellent for predators[12, 13] and usually emitted in a pulsatile manner.[14, 15]
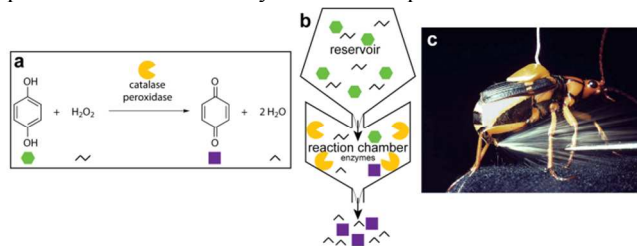
Scheme 1 Catalytic defensive decomposition of hydrogen peroxide (H_2O_2) and reaction with hydroquinone (a). Enzymes and reagents are stored in compartment chambers (b). Upon contraction of the reservoir and discharge of reagents into the enzyme loaded reaction chamber, a rapid and strongly exothermic reaction (overall heat release is -202.8 kJ mol^{-1})[15] produces a defensive spray (c)[16]. Copyright (1999) National Academy of Sciences, U.S.A.

Since 1972, automatic teller machines (ATMs) are common devices for local money withdraws. The banknotes are stored in cassettes and exchanged in regular intervals. The high cash reward as banknotes has made ATMs and money transport cassettes a favoured object for robbery and physical ATM fraudster.[17] In Europe, the first half (H1) of the year 2012 had a total of 968 reported incidents with a correlated loss of 8 million €. For the H1 of 2013, an increase to 1007 incidents (+4%) and 10 million € damage (+25%) has been observed.[18] Complex, electronics-based defensive spray mechanism are currently used to devalue banknotes and spray bandits in case of improper or forced opening,[19] which lowers expected criminal reward while increasing the risk for robbers. This process implements either glue or, more often, an indelible colour agent[20] and/or a forensic marker, *e.g.* DNA, assisted by mechanical triggers, *e.g.* springs.[21] An insight of the state of art and its complexity is given in (ESI† S1).

The present work relates to defence or devaluation systems inspired by the bombardier beetle, to apply forensic colouring or marks onto ATMs, money transport cassettes, and may later be extended for other applications. A compartmented surface system was developed to store dissolved, dispersed or liquid reactants. A thin and brittle barrier layer is used to selectively mix reactants upon mechanical attack *e.g.* forced opening. For a first proof of principle study, a chemical reaction similar to the bombardier beetle's defence spray was chosen and is based on the highly exothermic, catalytic decomposition of hydrogen peroxide (H_2O_2) using manganese dioxide (MnO_2) instead of an enzyme (cost advantage). Additionally, a less violent reaction due to relatively low H_2O_2 content (30%) was chosen as it showed efficient enough for an anti-vandalism purpose. In order to encapsulate a sufficiently high volume of reagents, the compartments were designed as a matrix of hexagonal cells between sandwiched layers (see Scheme 2).
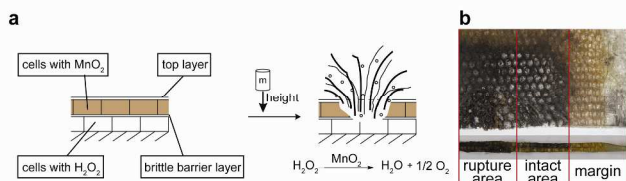
Scheme 2 Working principle of a reactive surface with mechanical sensitivity. The reagents are stored within the surface's cells and separated by a brittle layer. Upon mechanical impact, the brittle layer breaks which results in mixing and start of the reaction. In this example, hydrogen peroxide (H_2O_2) is catalytically decomposed by manganese dioxide (MnO_2). The reaction produces steam (water, H_2O), oxygen (O_2) and heat (-98 kJ mol-1)[22].

Frames of a film sequence and corresponding infrared pictures of the rupture of such a compartmented surface system are depicted in Fig. 1. Compared to the bombardier beetle, it was rather a foam than a spray which resulted from the reaction.

The optional addition of an oxidation-stable colour agent permits devaluation and renders bills useless. Implementation of silica-protected DNA particles allows forensic tracing of robbed bank bills as they contain a unique code[23].

2. Experimental

2.1. Preparation of compartmented, reactive foils

The multi-step preparation procedure is illustrated in (ESI† S3). A thin polyvinylidene chloride (PVdC, 14-20 μm) foil was wrapped around an aluminium plate (16.6 cm x 16.6 cm x 0.3 mm) and attached at the bottom with adhesive tape. A thin layer of a poly-acrylate glue (UHU Sprühkleber, Art.-Nr: 44430) was sprayed on the top side to fix an aramid comb (12 cm x 10 cm x 1.5 mm, Aramid-Wabenplatte C2-3,2-29 Luftfahrt, swiss-composite). Silicon seal glue (UHU Art.-Nr: 47855) was used to fill the edge margin of the comb cavities. The samples were left to dry for at least 12 h, and then the remaining comb cavities were filled with one of the two reactants: Hydrogen peroxide (H_2O_2, Merck, 30%) and dispersions of the catalyst manganese (IV) dioxide (5 wt%, MnO_2, VWR International, 99%) in distilled water were used. The two kinds of plates were treated 5-6 times with an acrylate-based spray-on clear coat (Dupli-Color Klarlack) in order to get a thin and brittle layer as cover. After carefully separating the foil containing MnO_2 from the aluminium plate with a scalpel knife, it was flipped and glued on the second part of the sandwich holding the H_2O_2. Glue was applied as a spray on the surface and as a luting agent on the edges to prevent leakage at the borders. The so obtained surface was dried for 2 h and used to perform the impact tests.

2.2. General impact test procedure

A steel cylinder (diameter = 1.9 cm, height = 5.9 cm, mass = 137 g) was dropped from a defined height through a tube (inner diameter = 2.5 cm) on the previously weighted reactive surfaces (see preparation above). The guiding tube allowed better targeting to direct the iron weight onto the test surfaces and prevented lateral rotation of the cylinder. The experiments were filmed and IR images were recorded with an infrared camera (FLIR i7 from FLIR systems) to follow the temporal evolution of the temperature. First, IR images were taken every 5 s during 1 min, then every 10 s during 1 min and finally every 30 s
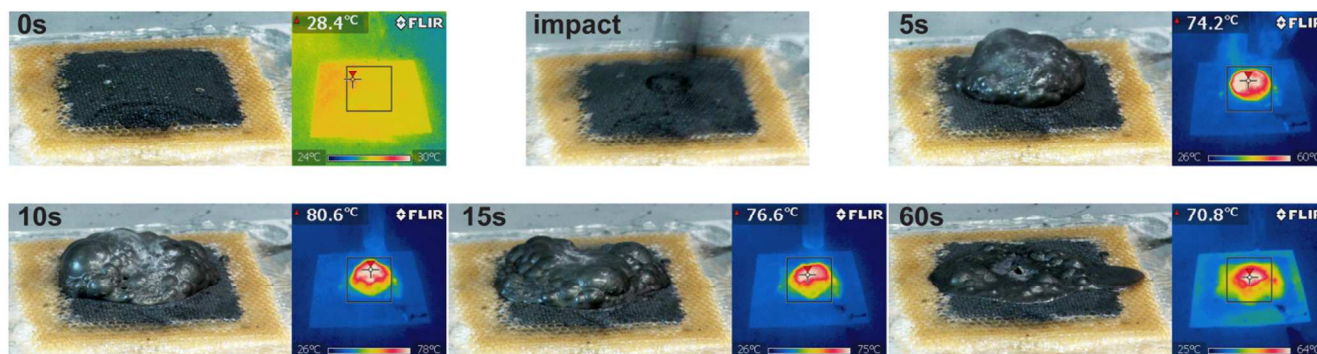

Fig. 1 Visual effect and corresponding temperature evolution upon mechanical rupture. The compartmented foil burst by impacting a steel cylinder. Only 5 seconds after the impact a region bigger than the rupture area was covered with hot foam and a temperature of 74.4°C was measured. The maximum temperature was reached 10 seconds after the impact and subsequently the foam spread further while the temperature slowly decreased. More frames of this experiment are depicted in Fig. S2 (ESI†).

during 3 min. After 10 min, the foil-plate was cleaned with household paper and weighted to measure the mass loss of all of materials that leached out or left the test plate. These materials are, when the orientation of the reactive surface was chosen properly, able to act as an anti-vandalism or anti-theft component, *e.g.* as a colouration agent.

2.3. Influence of the H_2O_2 concentration

The influence on the H_2O_2 concentration was evaluated by dropping the steel cylinder on the surfaces from a constant height (180 cm). In these experiments, the MnO_2 concentration was maintained constant while the H_2O_2 concentration varied (0%, 10%, 20% and 30%). The surfaces were tested as described above to observe the H_2O_2 concentration effect on the temperature profile.

2.4. Influence of the dropping height

Changing the steel cylinder dropping height corresponds to a variation in the mechanical impact energy. To investigate its influence, surfaces with constant H_2O_2 concentration (30%) were used throughout this test series. The cylinder was dropped from 3 different heights (120 cm, 180 cm and 240 cm).

2.5. Comparison of reaction released chemical energy and potential energy

To compare the energy that originates from the impact (mechanical energy) to the energy of the reaction (chemical energy), both were first estimated. The mechanical energy (E(mech)) was derived from equation (1) using the mass of the cylinder ($m_{cyl.}$), the gravitation acceleration (g) and the impact height (h), neglecting friction or air resistance.

$$E(mech) = m_{cyl.} * g * h \qquad (1)$$

The maximum chemical energy release (E(chem)) was evaluated according to equation (2) where the reaction enthalpy of the H_2O_2 decomposition (ΔH_r = -98 kJmol^{-1}, obtained from the enthalpies of formation of the educts and products[22]) , the total amount of H_2O_2 in the surface-plate (H_2O_2 mass ($m_{H_2O_2}$) divided by H_2O_2 molecular mass ($M_{H_2O_2}$)), the impact area (A_{impact}) and the total area containing H_2O_2 (A_{total}) are considered. This estimate assumes complete decomposition, a valid assumption since the MnO_2 catalyst is abundantly available. The two areas (A_{impact}) and (A_{total}) were measured in each case separately.

$$E(chem) = \Delta H_r * \frac{m_{H_2O_2}}{M_{H_2O_2}} * \frac{A_{impact}}{A_{total}} \qquad (2)$$

2.6. Examination of colour agents as devaluing agent

For tracking and devaluation, a dye must be resistant enough against oxidation. In order to identify a well-suited dye, different compounds were tested at various concentrations on a sheet of paper. The coloured area was covered with H_2O_2 and let to dry for an hour. Nile Blue A (Fluka) and Amaranth (Serva Feinbiochemica) appeared suitable for staining. Because of its darker appearance, Nile Blue A was chosen for further experiments and implemented in the MnO_2 part of the foil (5 g MnO_2, 1 g Nile Blue in 100 mL H_2O).

2.7. Implementation of silica encapsulated DNA particles as forensic tracer

In addition to the colour agent for devaluation of the bills, DNA containing silica nanoparticles (Genuine-ID) were implemented in the MnO_2 part of the system (50 µL dispersion of 20 mg/ml in 100 mL MnO_2 dispersion with dissolved Nile Blue as specified above). Such identity tag particles were most recently developed for industrial goods tracing[23]. Resulting foils were tested as described above with a constant H_2O_2 concentration (30%) and dropping height (180 cm). Here, the angle of the foil was slightly tilted (6.4°) so that escaping foam and liquid swamped to the downside, where two 5 € bills were placed. This experiment simulates Euro bills devaluated (*i.e.* coloured) and forensically marked.

Part of the thus obtained coloured bills (3 cm x 3 cm) were washed with water, cut into small pieces (~ 0.5 mm x 0.5 mm) and put in Eppendorf tubes. After addition of water (1 mL), the pieces were shaken for 1 day. The liquid phase was separated from the bill pieces and centrifuged 3 times where samples were carefully decanted and filled with water to wash the particles. Pellet was directly dissolved by adding an etch solution (NH_4FHF/NH_4F) and purified by QIAquick PCR purification kit according to Paunescu *et al.*[24] Detection of the DNA code was accomplished by real-time Polymerase Chain Reaction (PCR, Light cycler 96 from Roche) analysis.

2.8. Statistical Analysis

The results are expressed as mean average ± standard deviation. Impact experiments were carried out in triplicate (n = 3). Statistical significance was determined using one-way analysis of variance (ANOVA) and t-tests with post-hoc Bonferroni correction. The assumption of ANOVA was checked.

3. Results and discussion

Fig. 2 exemplifies the results obtained from typical impact tests using 180 cm dropping height and 30% H_2O_2 concentration. Each of the 3 runs for these conditions presented different maximum temperatures and variable cooling-down profiles. However, all samples consistently reached their maximum temperature within 25 seconds. An image series of one of these runs is depicted in (ESI† S2).
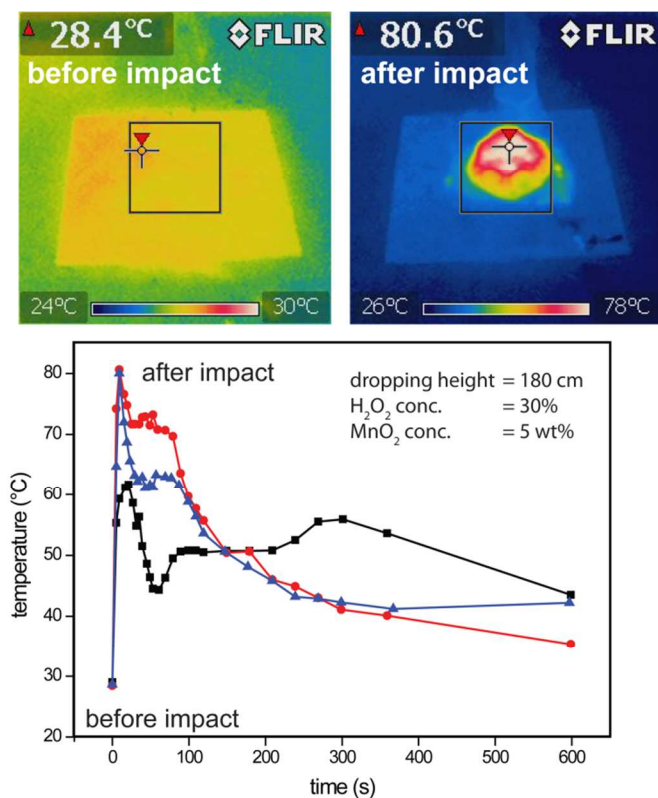
Fig. 2 *Top*: Infrared images of a surface before (left) and after (right) the impact. A temperature raise of more than 50°C was observed. *Bottom*: Typical temperature profiles of surfaces after impact. Shown curves all correlate to a dropping height of 180 cm, hydrogen peroxide (H_2O_2) concentration of 30% and manganese dioxide (MnO_2) concentration of 5 wt%. Mechanical rupture and mixing are very different from run to run, resulting in various temperature profiles.

3.1. Influence of the H_2O_2 concentration

Different H_2O_2 concentrations were incorporated in the surfaces while keeping the MnO_2 concentration constant. The temperature maximum after impact and the mass loss due to steam, gas and liquid loss are depicted in Fig. 3. As expected, the temperature and the mass loss show a dependency on the H_2O_2 concentration. Without H_2O_2 (pure water; a control experiment), no chemical energy was released because no reaction could take place. In that case only the mechanical impact of the cylinder could induce a slight increase in temperature. This minor energy was insufficient to result in distinguishable changes of temperature after 10 minutes. Interestingly, H_2O_2 concentrations of 10% or 20% were
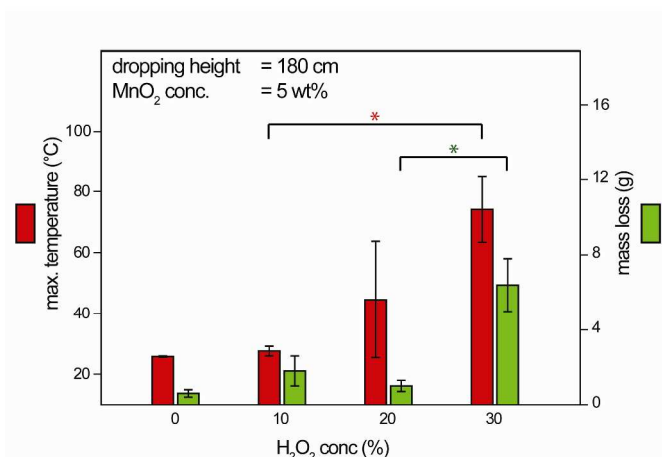

Fig. 3 Influence of the hydrogen peroxide (H_2O_2) concentration on the maximal temperature (red) and mass loss (green) of self-defending surfaces.

insufficient to lead to significant temperature increases, and experiments varied widely. In some cases the smaller H_2O_2 concentrations did not initiate a violent reaction. For the 20% sample, the variation of temperature values ranged from 30.0°C to 66.3°C. At this concentration, the extent of reactions seemed to strongly depend on the impact geometry. However, the values using a H_2O_2 concentration of 30% were significantly higher in terms of maximum temperature and mass loss. Hence, all further tests were carried out using surfaces with a H_2O_2 concentration of 30%.

3.2. Influence of the dropping height (mechanical impact energy)

Three different steel weight dropping heights (120 cm, 180 cm and 240 cm) were tested at a constant H_2O_2 concentration of 30%. The achieved maximum temperature and the mass loss are shown in Fig. 4a. A significant increase of the maximum temperature was observed when the values obtained for dropping heights of 120 cm and 240 cm were compared. The stronger impact for the higher dropping height probably led to better mixing of the two compartmented reactants which resulted in a faster reaction. Additionally, a bigger area on the plate was raptured when the cylinder was dropped from 240 cm. The 120 cm dropping height resulted in a poor mixing and, therefore, a slower reaction that released its energy in smaller doses. These results were in agreement with the observed mass loss dependency. A faster reaction yielded a more efficient effervescence and thus a higher mass loss.
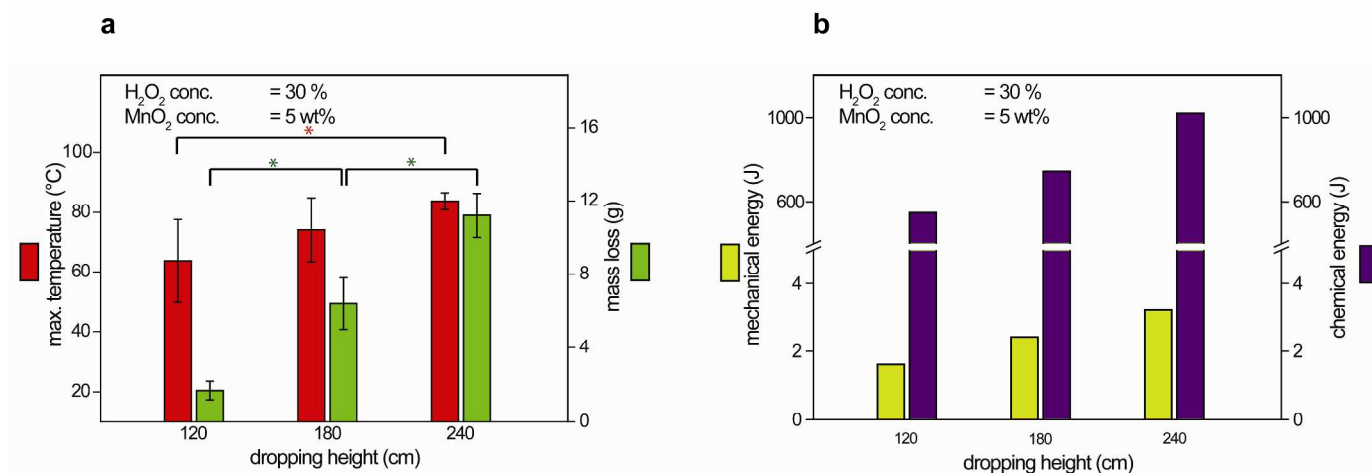
Fig. 4 Influence of the steel weight dropping height on the maximal temperature (red) and mass loss (green) of the self-defending surfaces. Both values rise for higher impacts (a). Calculated mechanical energy (yellow) of an impacting cylinder and estimated, released chemical energy (purple). The chemical energy exceeds the *mechanical* energy by two orders of magnitude (b).
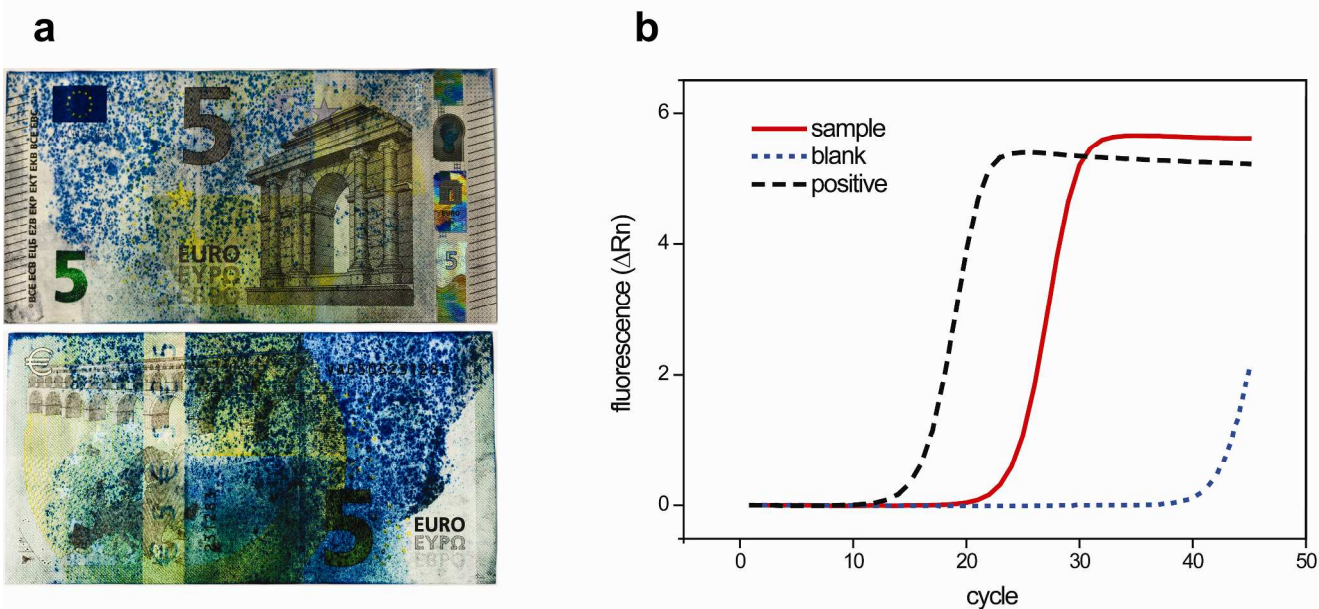

Fig. 5 Front and back side of a stained 5 € banknote (a). The bills were placed next to the surface plate which contained Nile Blue and forensic tracers (DNA/SiO$_2$ particles) in the MnO$_2$ compartment. The freshly coloured notes were washed with water and photographs were taken before performing PCR. The results prove that DNA/SiO$_2$ particles were present in the 5€ bill (b).

Compared to the chemical energy, which can be released from the raptured area, the mechanical energy is 300-400 times smaller as shown in Fig. 4b. This is consistent with the observations made for H$_2$O$_2$-free plates (control experiments) described above in section 3.1. Therefore, our experiments prove the possibility to use a small amount of mechanical energy to release a much larger quantity of chemical energy, similar to an ignition capsule or an electrically triggered combustion cycle in an engine.

3.3. Applying colour agents and DNA/SiO$_2$ particles

Bank notes (bills of 5€) were dyed with a colouring agent and DNA tracers released after impact. Fig. 5 shows a representative stained bill (front and backside). Forensic analysis of the protected DNA (see Experimental) using real-

time PCR yielded detection after a cycle number (C(T)) of 22.3. A positive control was performed for normalization and to ensure the amplification of the free DNA and had a C(T) of 14.6 and the negative control (no DNA label) yielded a C(T) of >40 as depicted in Fig. 5. The sample showed a clear and unambiguous amplification of the encoded DNA and thus proves the presence of DNA/SiO$_2$ particles in the stained banknotes.

3.4. Durability

A durability analysis by means of the self-decomposition of H$_2$O$_2$ and the dehydration rate of the reactive surface was carried out. It is well known that impurities, *e.g.* heavy metals drastically accelerate the decomposition reaction.[25] The H$_2$O$_2$ used in the experiments has a minimum shelf life of 3 years at

storage temperatures from 5°C to 30°C as labelled on the bottle. It is believed, that the shelf life could be preserved upon an industrial production. The other factor which could limit the life time of a reactive surface is the dehydration of it due to diffusion of water vapour. While the used cover foil composed of PVdC with a thickness of 14-20 µm results within 18-25 days in a mass loss of 5%, a aluminium foil with a thickness of 100 µm would enhance the timespan until 5% of the mass is lost up to 3 years.[26] To conclude, a theoretical defensibility of 3-4 years can be achieved. For more details please consider (ESI† S4).

3.5. Comparison of existing ATM security systems with the novel reactive surface

Complexity, durability, colouring efficiency and cost were compared (ESI† S5) and resulted in comparable performance in durability and colouring efficiency. Aforesaid properties are assumptions made for an improved and marketable defence system. Nevertheless, the comparison in complexity is clearly in favour of the novel reactive surface system. A conservative cost analysis induced a maximal material price for the reactive surface of 41 $m^{-2}.

4. Conclusions

A two component reactive surface layer with broad application options was developed. The system in principle can contain any two-component reaction that runs spontaneously and does not attack the supporting matrix. In this work, H_2O_2 and MnO_2 were incorporated which enchains the catalytic decomposition of H_2O_2 to H_2O and O_2. Both the partition of the system and the decomposition reaction are inspired by the bombardier beetle. This exothermic reaction is accompanied by a volume gain as a result of the gas formation. The system could be applied as an anti-vandalism device or as a protection layer of vulnerable goods from animals, *e.g.* birds. The optimal conditions concerning reagent concentration and impact strength were evaluated by recording the temperature profiles. Another success factor in addition to the maximal temperature was the mass loss due to evaporation and leakage. As illustration of a possible application area, a colour agent and DNA/SiO_2 particles were incorporated in the system additionally to the reagents. Proof of principle was delivered with banknotes that were first spoiled by the coloured leakage and afterwards determined with the respective DNA tracer code. This would be a useful tool when implemented in anti-vandalism or anti-theft devices for instance in ATMs or money transport cassettes. The durability for a hypothetic improved system was evaluated and is more than a year and a cost analysis predicts a reasonable material price of 41 $m^{-2}. Next steps towards this practice should include aging test of the improved surface and the development of a mechanical trigger system.
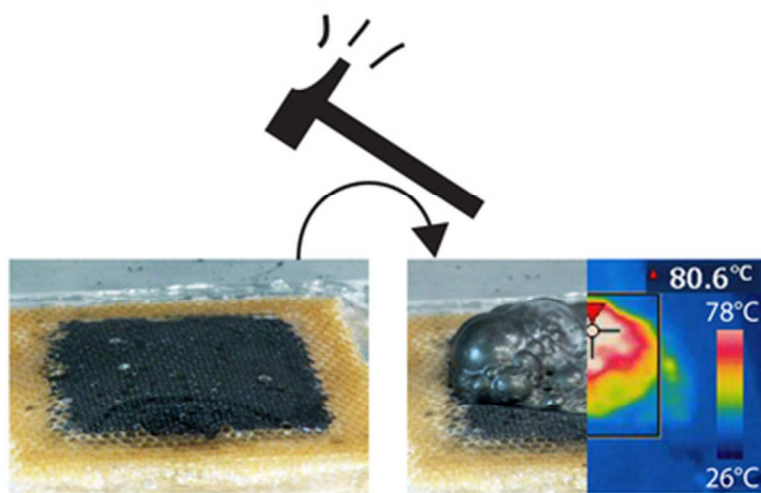
Notes and references

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Bioscience, ETH Zurich, 8093 Zurich, Switzerland. E-mail: wendelin.stark@chem.ethz.ch; Fax: +41 44 633 1083; Tel: +41 44 632 0980

1. S. B. Blum, *Chemical defenses of arthropods*, Academic Press, New York, 1981.
2. P. Laurent, J. C. Braekman and S. Daloze, in *Chemistry of Pheromones and Other Semiochemicals Ii*, ed. S. Schulz, 2005, pp. 167-229.
3. E. E. Conn, ed., *Cyanogenic glycosides*, Academic Press, Inc., 1981.
4. J. E. Poulton, *Plant Physiol.*, 1990, **94**, 401-405.
5. J. G. Halter, W. D. Chen, N. Hild, C. A. Mora, P. R. Stoessel, F. M. Koehler, R. N. Grass and W. J. Stark, *J. Mat. Chem. A*, 2014, **2**, 853-858.
6. N. F. Lepora, P. Verschure and T. J. Prescott, *Bioinspir. Biomim.*, 2013, **8**.
7. P. Zou, W. Hartleb and K. Lienkamp, *J. Mater. Chem.*, 2012, **22**, 19579-19589.
8. S. T. Wu, A. Buthe, H. F. Jia, M. J. Zhang, M. Ishii and P. Wang, *Biotechnol. Bioeng.*, 2013, **110**, 1805-1810.
9. S. Loher, O. D. Schneider, T. Maienfisch, S. Bokorny and W. J. Stark, *Small*, 2008, **4**, 824-832.
10. G. Cado, R. Aslam, L. Séon, T. Garnier, R. Fabre, A. Parat, A. Chassepot, J. C. Voegel, B. Senger, F. Schneider, Y. Frère, L. Jierry, P. Schaaf, H. Kerdjoudj, M. H. Metz-Boutigue and F. Boulmedais, *Adv. Funct. Mater.*, 2013, **23**, 4801-4809.
11. L. C. Gerber, F. M. Koehler, R. N. Grass and W. J. Stark, *Angew. Chem. Int. Edit.*, 2012, **51**, 11293-11296.
12. Aneshans.Dj, T. Eisner, J. M. Widom and B. Widom, *Science*, 1969, **165**, 61-&.
13. T. Eisner, *J. Insect Physiol.*, 1958, **2**, 215-220.
14. J. Dean, D. J. Aneshansley, H. E. Edgerton and T. Eisner, *Science*, 1990, **248**, 1219-1221.
15. N. Beheshti and A. C. McIntosh, *Bioinspir. Biomim.*, 2007, **2**, 57-64.
16. T. Eisner and D. J. Aneshansley, *P. Natl. Acad. Sci. USA*, 1999, **96**, 9705-9709.
17. E. A. S. T. (EAST), European ATM fraudsters shift to lower tech attacks, https://www.european-atm-security.eu/Press%20and%20Media/.
18. E. A. S. T. (EAST), ATM explosive attacks and low tech fraud incidents increase in Europe, https://www.european-atm-security.eu/Press%20and%20Media/.
19. A. R. Searle and G. K. Hill, Security system, US 7428873, 2008.
20. M. Lopez, ATM anti-theft device, US 5598793, 1997.
21. T. K. Abe, H. K. Minamishin and M. K. Koike, Theft-prevention ink pack device, and treasure safe having the same, US 7100520, 2006.
22. *CRC Handbook of Chemistry and Physics, 94th ed*, 2013-2014.
23. D. Paunescu, R. Fuhrer and R. N. Grass, *Angew. Chem. Int. Edit.*, 2013, **52**, 4269-4272.
24. D. Paunescu, M. Puddu, J. O. B. Soellner, P. R. Stoessel and R. N. Grass, *Nat. Protoc.*, 2013, **8**, 2440-2448.
25. P. Chirita, *Chem. Biochem. Eng. Q.*, 2007, **21**, 257-264.
26. M. D. Steven and J. H. Hotchkiss, *Packag. Technol. Sci.*, 2002, **15**, 17-27.

Journal of Materials Chemistry A Accepted Manuscript

36x22mm (300 x 300 DPI)