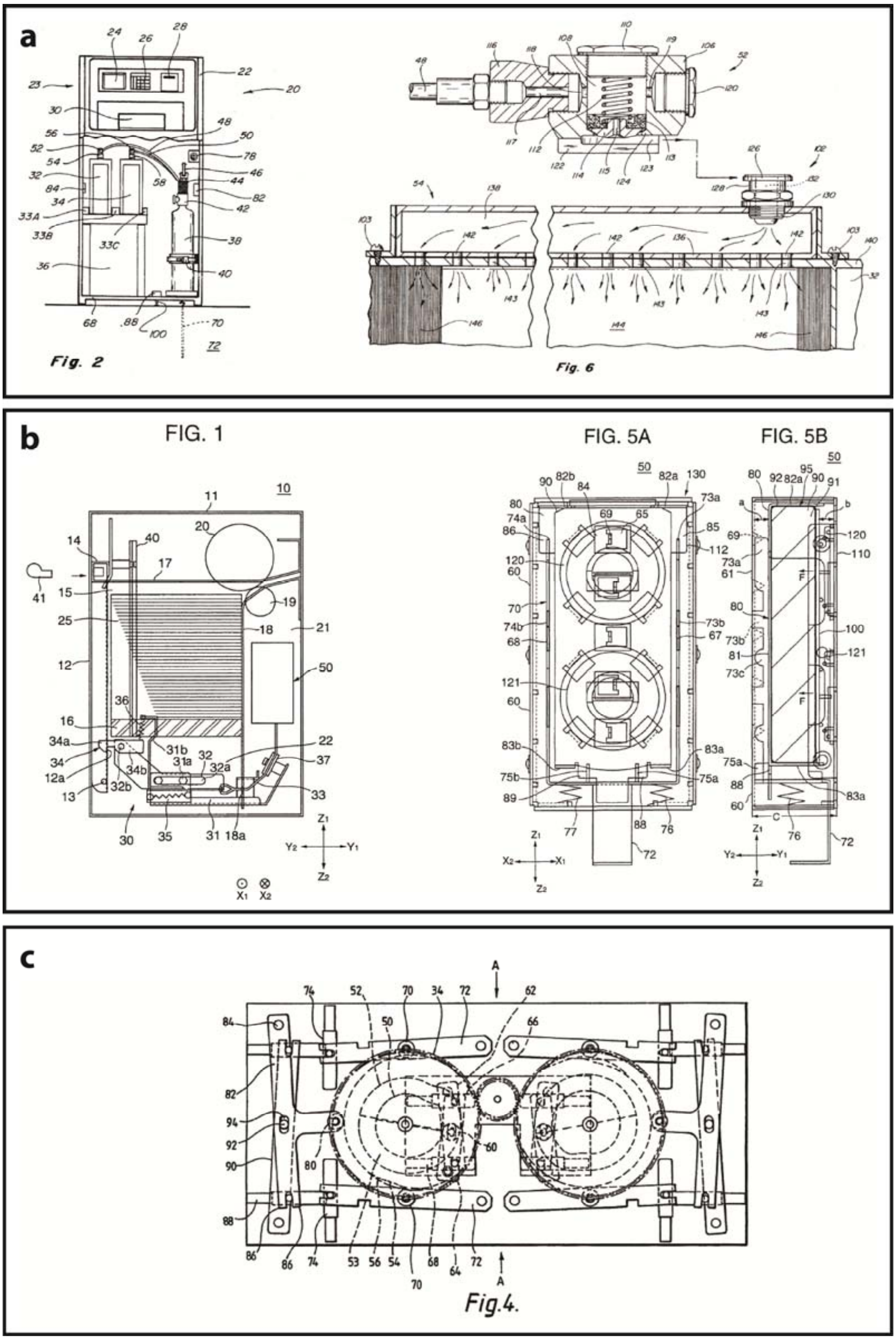
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

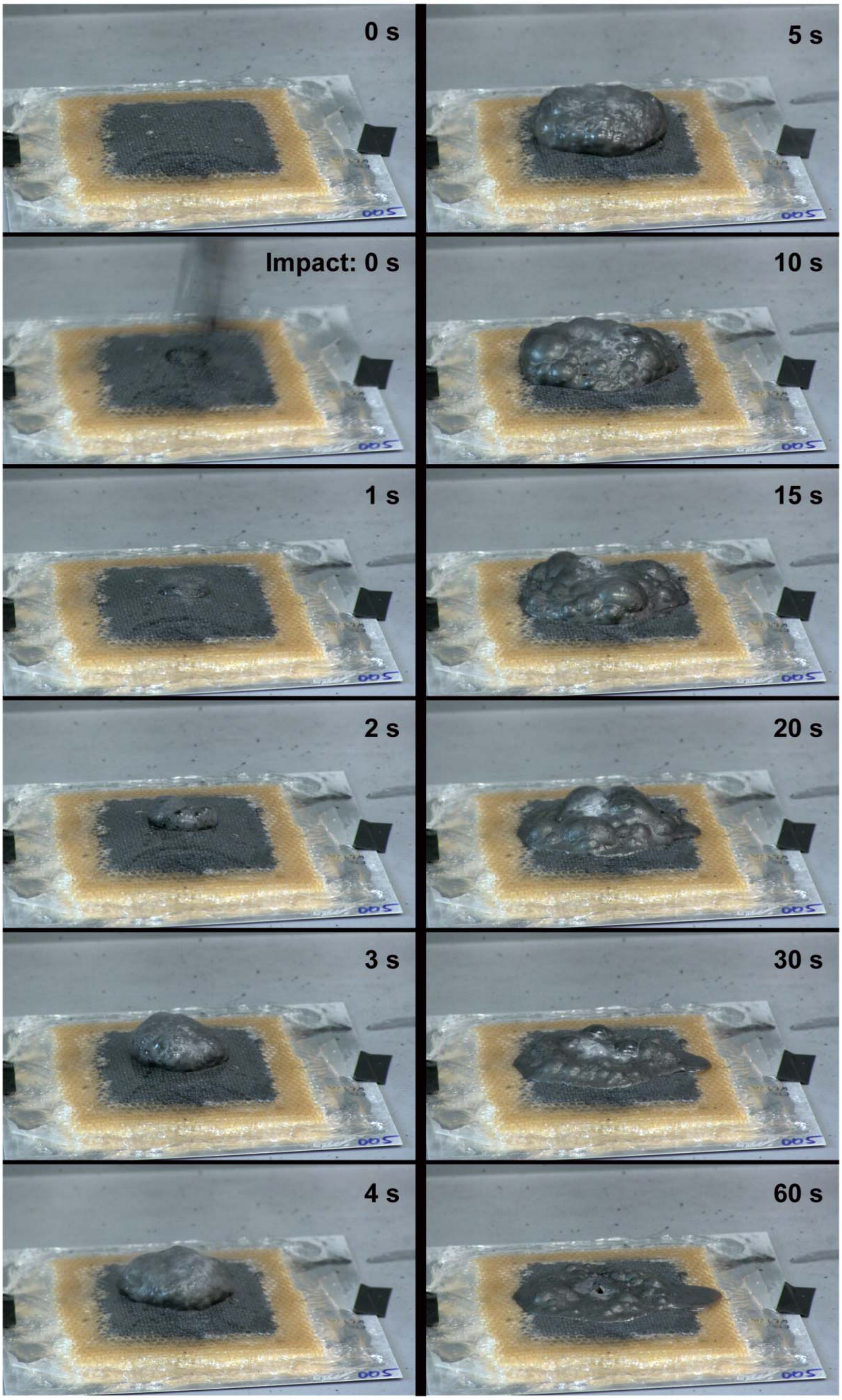
Supporting information

S1 State of the art of ATM security systems



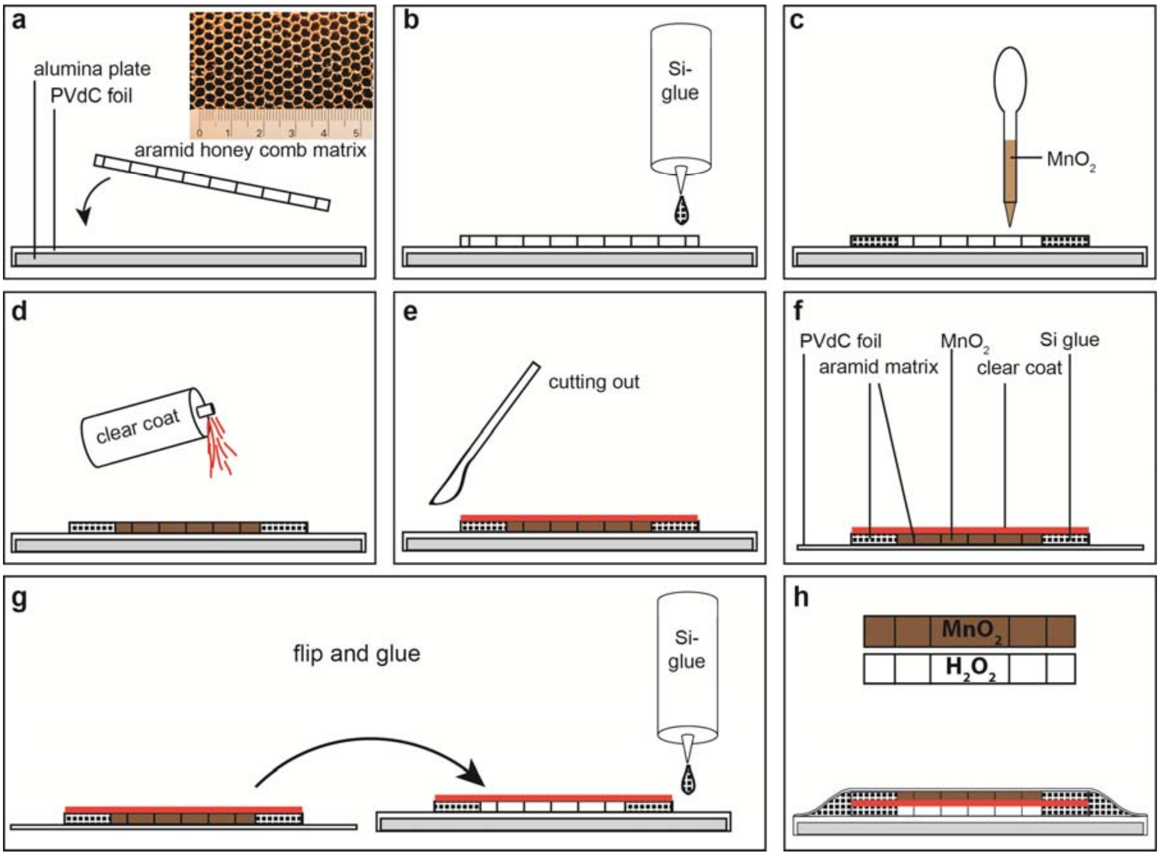
Scheme S1 Patented systems for ATM security. The complexity of these systems (*i.e.* electronics, ink cartridge, gas cartridge and mechanical parts) is visible at first sight. In a patent from 1997, a system which uses a pressured tank, an electrical device to trigger and die channels is presented (a).[1] Another patent from 2006 describes a device which consists of an ink bag which is broken by knife edges upon a trigger and springs to press the ink bag to subsequently spurt valuables with ink (b).[2] A more recent patent from 2008 comprises cash transit container with a controlling module to communicate with the ATM when the money cassette is changed (c).[3]

S2 Frames of impact on a reactive foil



Scheme S2 Image series of a typical impact test run. Shown is an experiment with following conditions: H_2O_2 conc. = 30%; MnO_2 conc. = 5 wt%; dropping height = 180 cm.

S3 Preparation of the reactive foils



Scheme S3 Schematic illustration of the production of the surface-plates. After wrapping an aluminium plate with PVdC foil, an aramid plate is glued on it (a). The edges are filled with silica glue (b) and the cavities filled with a manganese (IV) oxide dispersion (c). The application of clear coat results in a brittle layer (d). The part is cut from his supporting aluminium plate (e) and subsequently glued on the counterpart holding hydrogen peroxide – simultaneously the rims are filled with the silica glue to prevent leakage (g). In (h), the ready-for-impact-test surface-plate is schematically shown.

S4 System durability

The bleaching of the dye is assumed to be negligible. Therefore, the theoretical durability of the system is either the lifetime of the hydrogen peroxide or the time until the foil is dried out. To find out, which process gives the smaller value, a comparative study was carried out.

S4.1 Decomposition of hydrogen peroxide

It is well known that impurities, *e.g.* heavy metals, accelerate the decomposition reaction drastically[4]. In the storage container, manufacturers guarantee a shelf life of more than a year. The hydrogen peroxide used in the experiments (30%, Merck) has a minimum shelf life of 3 years at storage temperatures from 5°C to 30°C as labelled on the bottle. This leads to the assumption, that the durability of the anti-vandalism device could also be as high when impurities are avoided.

S4.2 Dehydration rate of the reactive surface

Polyvinylidene chloride (PVdC) has a water vapour permeability of 39 g µm / (m^2 day).[5] The top foil used for the experiments was PVdC with a thickness of 14 to 20 µm. This results in a water vapour transmission rate (WVTR) as shown in table S4.2. When thickening the foil or replacing with a sealable aluminium foil (water vapour permeability of 4.4 g µm / (m^2 day)),[5] the WVTR is even lower. To close the edges the sealing technique used in medical packaging can be applied. These factors support a durability of several years against dehydration.

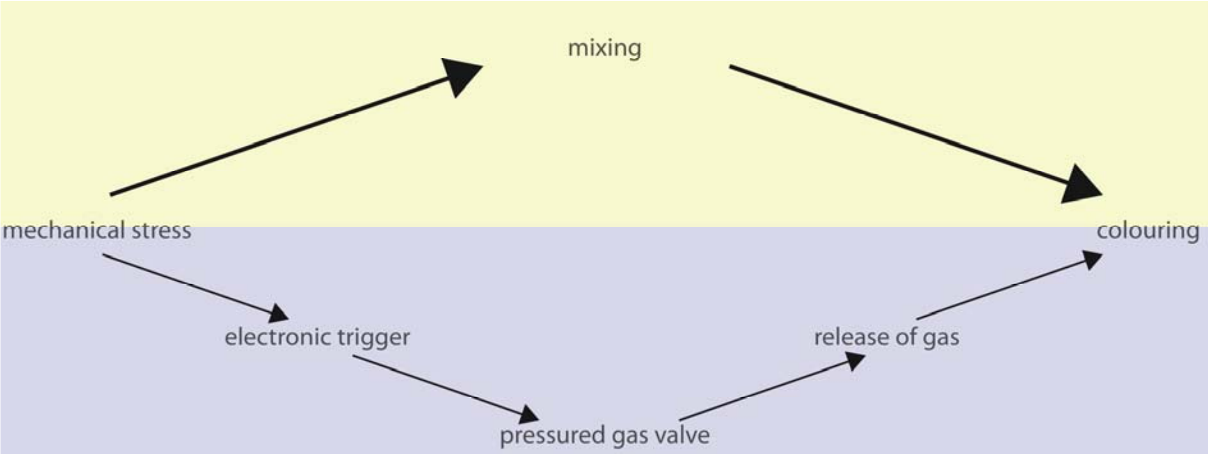
Table S4.2 Theoretical life time of the surface system as a function of dehydration. The durability was calculated with a surface of 0.01 m^2, a liquid mass of 10 g and a maximal loss of 5 weight percents.

Material	Thickness (µm)	Permeability (g / (m^2 day))	Durability of reactive surface (days)
PVdC	14-20	2.8-2.0	18-25
PVdC	100	0.4	125
aluminium foil	50	0.09	556
aluminium foil	100	0.045	1112

S5 Comparison

S5.1 Complexity

While existing security systems of ATMs and money transportation container often use complex activation mechanism including electronics and pressured ink and gas tanks, the presented foil only needs a mechanical trigger. Scheme S3 depicts the activation path of both systems.



Scheme S3 Steps from mechanical stress to spoilage of bank notes.

S5.2 Durability

While ink cartages and gas bombs of existing ATM security systems have to be replaced every 4 years, the durability of the novel reactive surface can be enlarged up to 3-4 years as explained in section S4.

S5.3 Colouring efficiency

The colouring efficiency of existing systems is in fact nearly 100%. A smart placement of the reactive surface plates in the money container, *e.g.* on the walls the bottom and the top, would result in an appropriate disfiguration of the bank notes. It is possible, that the whole interior of the money cassette will be filled with colouring foam when physical attack happened.

S5.4 Cost analysis

The cost for the material of a large scale application of the reactive surface was estimated and is shown in table S5.4. A cost of 41 $/m^2$ was determined. A money cassette has typical dimensions of 10 cm x 20 cm x 50 cm which results in a surface of 0.34 m^2. This means that the material cost to entirely equip a money cassette is about 14 $. The cost of the mechanical trigger is not included in this number as it has a much higher life span. The calculation of the cost is a worst case scenario, where a thick aluminium foil (100 µm) was used instead of the PVdC which would be cheaper. For the aramid comb, which is normally used in aerospace, a lower priced alternative is believed to be found.

Table S5.4 Conservative cost analysis of the reactive surface.

Material	Cost/ton	g/m2	Cost/m2
H_2O_2 (30%)	500 $[a]	1000	0.5 $
MnO_2	500 $[a]	50	0.025 $
H_2O	negligible	950	negligible
Nile blue		negligible	negligible
DNA/SiO_2 particles		negligible	negligible
aluminium	3000 $[a]	270	0.81 $
aramid comb			39 $[b]
clear coat	3000 $[a]	100	0.3 $
reactive surface			41 $

[a] Alibaba.com (www.alibaba.com; 26.02.2014)

[b] Swiss Composites catalogue (www.swiss-composite.ch; 26.02.2014), calculated from CHF (1 CHF = 1.127 $)

S6 Additional literature

1. M. Lopez, ATM anti-theft device, US 5598793, 1997.
2. T. K. Abe, H. K. Minamishin and M. K. Koike, Theft-prevention ink pack device, and treasure safe having the same, US 7100520, 2006.
3. A. R. Searle and G. K. Hill, Security system, US 7428873, 2008.
4. P. Chirita, *Chem. Biochem. Eng. Q.*, 2007, **21**, 257-264.
5. M. D. Steven and J. H. Hotchkiss, *Packag. Technol. Sci.*, 2002, **15**, 17-27.