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Graphical abstract

Surfaces resistant to colouration could be successful dyed via the inducement of dopamine polymerization, thus displayed absolutely different surface properties.

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Dopamine polymerization induced surface colouration on various materials

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Bio-inspired by the melanins and marine mussels' adhesive, a novel method was developed for the material surface colouration. With dopamine polymerization to form an adhesive coating, the surface colouration was easily achieved. This colouration could be succeeded on various materials, including metal, ceramic, polymers and even textile fabrics resistant to colouration through a simple dip-coating procedure. The colour appearance of the dyed materials could be tuned in a controllable way due to the reactivity of dopamine with nucleophiles such as amino acids and heterocycles during its oxidization step. Commercially available colorants could also be used in this procedure to enrich the colour gamut. The surface compositions, morphology and wettability of the dyed surfaces were studied by X-ray photoelectron spectroscopy, scanning electron microscope and water contact angle measurement, respectively. The obtained results showed that the material surfaces were successfully coloured, verified by the obviously changed surface properties compared to the blank samples. For this colouration method, less energy consumption and dyeing auxiliaries were needed, indicating that it is a more environmental friendly approach. It is a promising alternative to the traditional colouration, especially for those materials resistant to colouration.

Introduction

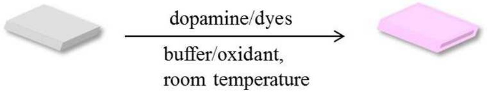
In the natural environment, living organisms are highly optimized due to their evolutionary pressure. Because of their adaptation to the specific environments, they often possess unique and fascinating characteristics. As the gradual disclosure of their underlying mechanisms, it is able to exploit their unique properties and we can be greatly benefited from them.

As well-known, melanins are naturally pigments formed in the hairs and skins of human and many other animals and plants. For example, melanins in human hair share a common biosynthetic pathway related to 3,4-dihydroxyphenylalanine (DOPA),[1,2] which is amino acid formed by post-translational hydroxylation of tyrosine residues. After the enzymatic oxidation, DOPA cyclizes and polymerizes to form melanins. Also, in the tidal environment, marine mussels possess remarkable adhesive ability,[3] which is rapid, permanent and versatile to virtually all types of solid surfaces including organic and inorganic materials.[4] In their adhesive plaques, it was found that this adhesive has a higher content of DOPA, which is believed to play a vital role in the mussel adhesion.[5-7]

In the chemical structure of DOPA, it has two main functional groups of a catechol and an ethylamine, which are also the main functional groups of dopamine. Similar to DOPA, dopamine is also easily oxidized and subsequently self-polymerize when exposing to air, weak lye and oxidants.[8-10] As a result, it is seen as an ideal biomimetic molecule of DOPA. Inspired by this, dopamine was widely reported to prepare various adhesive ad-layers,[10,11] adhesive polymers,[12,13] surface modifications of inorganic materials and nano capsules.[14,15] However, to the best of our knowledge, studies on the dopamine polymerization induced versatile colouration on material surface are few reported.

Materials colouration is also an important functionalization field in modern chemical, biological and material sciences including decoration,[16,17] optical application,[18,19] anti-corrosion,[20,21] fluorescent labelling and fluorescence switch.[22,23] The traditional colouration method can work well on some materials to some extent through strictly complying with the material-dependence rule, but it still lacks the efficacy on broad ranges of materials.

Inspired by the environmental friendship and versatility of melanins and mussels' adhesive in the nature, we achieved in the functionalization of carbon nanotube with polydopamine.[24] With this successful experience, herein, we forward the study of dopamine polymerization induced surface colouration on various materials in a simple way, as indicated in Scheme 1. The materials including metal, ceramic, cellulose, protein fibres and materials resistant to colouration, were studied in detail.



Scheme 1. A description of dopamine polymerization induced surface colouration.

Experimental

Materials

Cotton, wool and polybenzimidazoles (PBI) fabrics were selected as representatives of cellulose, protein fibres and materials resistant to colouration. They were commercially available and were washed in 5‰ sodium dodecyl sulfonate solution for 10 min before use. Then, it was dried in air. Glass and aluminium slides were selected as representatives of ceramic and metal materials. They were commercially available and ultrasonically cleaned firstly in ethanol for 5 min and then in deionized water for another 5 min before use. In addition to dopamine (1), 2,4-dihydroxybenzophenone (2), aniline (3), N-(2-hydroxyethyl)aniline (4), L-histidine (5), Trans-4-hydroxy-L-proline (6) and 1-(4-sulfophenyl)-3-methyl-5-pyrazolone (7) were also investigated as representatives of phenol, amine, amino acid and heterocycle. Rhodamine B was used as a model of commercially available colorant. All chemical reagents were obtained from Sigma-Aldrich and used as received.

Colouration procedure

Wool fabrics were immersed in 10%w.t. dopamine solution overnight at room temperature. Subsequently, it was taken out of the bath and was sprayed with 1%w.t. oxidant solution (potassium periodate, except indicated) and air dried. In order to tune the colour appearance of dyed fabrics, a second component of 2-7 was also respectively added to dopamine solution with the mass ratio of 1:5. The total concentration of the second component and dopamine was kept as 10%w.t. The dyed fabrics were soaped with 5‰ sodium dodecyl sulfonate solution at 60 ^{o}C for 10 min. After dryness, the obtained samples were used for colorimetric analysis and tests.

Other materials were immersed in a solution containing 5 mg mL^{-1} rhodamine B and 5 mg mL^{-1} dopamine hydrochloride at room temperature overnight. The solution was buffered to pH 8.5 with Tris. After the predetermined time, the resulting samples were taken outside. Followed by washing in deionized water for 10 min, the obtained samples were air dried for measurements.

Colouration characterization

From the reflectance values at the λ_{max} of the coloured materials, the colour yield (K/S) was calculated using the Kubelka-Munk equation.[25] Wash fastness was assessed using grey scales according to AATCC Test Method 61-2010 3A at 71^{o}C.[26] Crocking fastness was measured using crockmeter method according to AATCC Test Method 8-2007. Light fastness was obtained according to the Standard Method ISO 105 B02-2013 (Xenon-Arc Lamp). The UV-vis absorption of the coloured materials was tested using a Perkin Elmer Lambda 18 UV/vis spectrometer with the scanning speed of 240 nm/min.

The chemical composition of the material surface was determined by X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out on a SKL-12 X-ray photoelectron spectrometer (Shenyang, China) equipped with a VG CLAM 4MCD electron energy analyzer. XPS is configured with a dual anode source from VG (type XR3E2) and non-monochromatic Mg Kα radiation (1253.6 eV) at a current of 15 mA with an ultrahigh vacuum ($< 8\times10^{-10}$ Torr). To compensate for surface charging effects, all binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV. The morphology of the samples was investigated by scanning electron microscope (SEM) on a TEM 3000 Tabletop Microscope (Hitachi, Japan). The wettability of the samples was investigated by water contact angle measurement using a Model CAM-Micro Contact Angle Meter (Tantec, US).

Results and discussion

Colouration on protein fabrics

Under room temperature, the fresh dopamine solution is colourless and there is no absorption in the visible region, as shown in Fig. 1a. After the addition of oxidant, the solution gradually changed to yellowish brown and an absorption peak centred about 350 nm appeared because of dopamine polymerization induced by oxidation. The polydopamine had the adhesive ability and were used to prepare adhesive coatings and polymers. This feature could be utilized to increase its fixation on the fibres. Thus, dopamine is possible to be used as a precursor molecule for surface colouration.

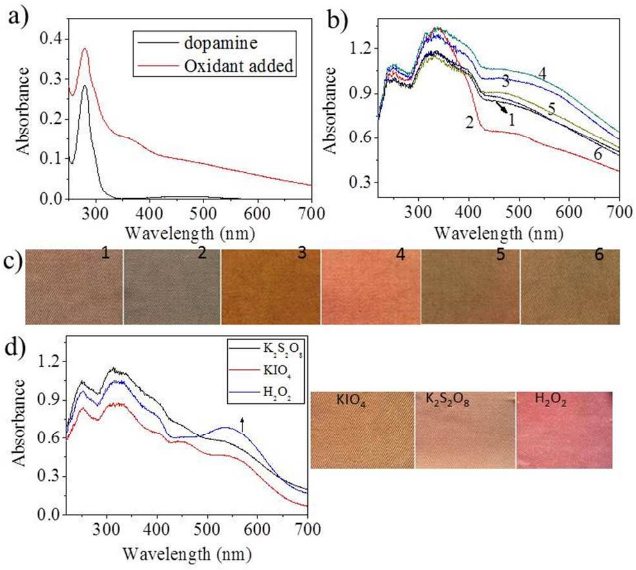


Fig. 1 a) UV-vis absorption spectra of dopamine before and after oxidation; b) UV-vis absorption spectra of the coloured wool fabrics by using dopamine and various components; c) Images of the coloured wool fabrics; d) UV-vis absorption spectra and their images of the coloured wool fabrics using dopamine and component 7 in the presence of different oxidants.

Firstly, dopamine was used to dye protein fibres (wool), which showed a natural-like yellow colour. It was reported that the dopaquinone, formed in the DOPA oxidation, had the ability to react with various nucleophilic species.[2] Based on this understanding, during the oxidation process, it was attempted to tune the obtained colour appearances by adding different kinds of nucleophiles, such as UV absorber (2,4-dihydroxybenzophenone), amino acids (L-histidine and Trans-4-hydroxy-L-proline), heterocycle (1-(4-sulfophenyl)-3-methyl-5-pyrazolone) and aromatic amines (aniline and N-(2-hydroxyethyl)aniline). After colouration, their maximum UV absorptions were centred about 350 nm, but there were differences in their visible absorptions (Fig. 1b). As shown in Fig. 1c, there were noticeable variations in their colour appearances of the dyed fabrics. This tune of the obtained colour appearance was also seen in their colorimetric parameters, as listed in Table 1. Upon the incorporation of different components into the dopamine polymerization process, the L* a* b* values of the obtained colours were obviously changed. And the coloured fabrics had good colour yields with the K/S value of 12-18 (Table 1). In addition, their colour appearances could also be tuned by using the oxidants with different oxidizing ability, as shown in Fig. 1d. By using hydrogen peroxide, pink colour appearance could be obtained.

Table 1. Colour measurements of the coloured wool fabrics and their light and crocking fastness

Compt.	K/S	L*	a*	b*	Light fastness	Crocking fastness	
						Dry	Wet
1	14.9	45.8	7.4	21.3	3	4-5	4-5
2	12.5	52.5	5.9	21.4	2-3	4-5	3-4
3	17.9	37.7	9.0	19.1	2-3	4	3-4
4	15.0	40.8	12.0	18.5	2-3	4-5	4-5
5	15.4	42.0	8.0	19.7	3	4-5	3
6	15.8	42.9	7.8	20.8	2-3	4-5	3-4
7	12.2	59.0	9.5	37.8	3-4	5	4-5

The fastness of the dyed fabrics were also investigated including light fastness, crocking fastness and wash fastness, as listed in Table 1 and 2. Light fastness of the fabrics dyed by histidine and 1-(4-sulfophenyl)-3-methyl-5-pyrazolone was 3 and 3-4 ratings, which was better than those of fabrics dyed by other components. It showed that the incorporation of heterocyclic component was favourable to improving the light fastness, which indicated a useful guide for future work. Their dry crocking fastness was in the range of 4 to 5 ratings, which were a little bit better than their wet crocking fastness. Concerned the wash fastness listed in Table 2, the ratings of their colour change were 4 to 4-5, except the sample dyed by 1-(4-sulfophenyl)-3-methyl-5-pyrazolone in the presence of dopamine. This was possibly due to that its incorporation reduced the polymerization degree of dopamine, leading to higher water solubility. Upon the addition of N-(2-hydroxyethyl)aniline, the dyed fabric showed lower ratings of colour staining, indicating that N-(2-hydroxyethyl)aniline-modified polydopamine derivatives had an adhesive tendency to wool, polyester and nylon fibres. All other samples had colour staining ratings of 5, showing low colour staining to the adjacent fibres.

It was observed that the wash fastness and crocking fastness of the dyed fabrics were better than their light fastness. This was consistent with the fact that underwater mussels' adhesive proteins suffer less direct light radiation and their photostability is possibly not superior to their adhesion. This possibly resulted in the poor photostability of the colorants biomimicked from underwater mussels' adhesion. But, the photostability of dyed fabrics could be improved through the incorporation of photostable heterocyclic compounds according to the light fastness results.

Table 2. Wash fastness of the coloured wool fabrics

Compt.	Colour change	Colour staining					
		Wool	Acrylic	Poly[a]	Nylon	Cotton	Acetate
1	4-5	5	5	5	5	5	5
2	4-5	5	5	5	5	5	5
3	4	5	5	5	5	5	5
4	4-5	3-4	4-5	3	3-4	4-5	4-5
5	4	5	5	5	5	5	5
6	4	5	5	5	5	5	5
7	3-4	5	5	5	5	5	5

[a] Poly, polyester.

Expanding the application ranges, it was found that the colouration approach also works well on silk fabric. But, the results were not so satisfied on the other textile materials, such as cotton, PET and nylon, which were expected. Wool and silk are protein fibres belonging to the same type of human hairs and skins, where natural melanins form. While other fibres cannot provide the similar medium environment, so their colouration only depended on its adhesive ability of the polydopamine derivatives to fibres. Due to the limited disclosure of mussels' adhesive mechanism, its biomimetic adhesion was not so versatile. Based on the fact that mussels can adhere to the anti-sticky Teflon, the developed colouration method would also work well on other fibres, once the mussels' adhesive mechanism is completely discovered.

In addition, the colour spectrum was still not rich, although several methods were used, including changes in the nuleophilic species, oxidant types and ratio of dopamine to nuleophilic specie. In this case, it is proposed to utilize commercial available colorants to take place nuleophilic species to produce a large colour gamut.

Colouration on natural and synthetic fabrics

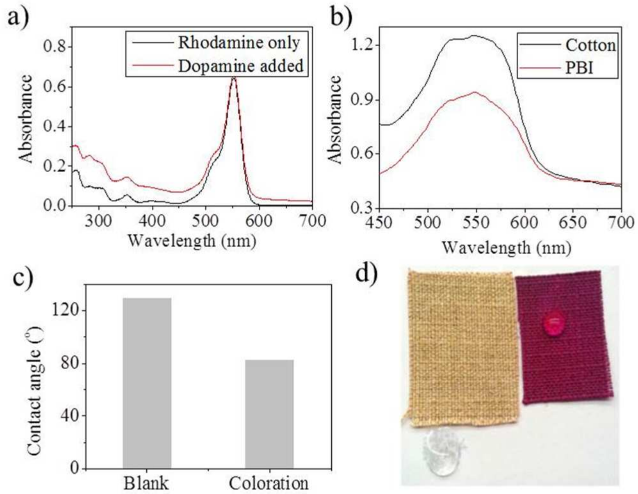


Fig. 2 a) UV-vis absorption spectra of rhodamine B with and without dopamine; b) Visible absorption spectra of fabrics coloured with rhodamine B in the presence of dopamine; c) Water contact angles of PBI before and after colouration with rhodamine B; d) Photography of wetting properties of water droplets on a 45^{o} slope before and after colouration.

Polydopamine has absorption at about 350 nm, perhaps showing some influence on the colour appearance. Thus, a red colorant of rhodamine B was preliminarily chosen as an example to investigate the colouration approach. In order to avoid the influence of oxidants on the colorant chromophore, dopamine polymerization was induced by a typical seawater pH of 8.5 buffered with Tris.

The influence of dopamine polymerization on the colour appearance of rhodamine B was first investigated using UV-vis spectroscopy at room temperature. Fig. 2a shows the absorption spectra of rhodamine B in pH 8.5 Tris solution with and without dopamine. Under the experimental conditions, the presence of dopamine did not cause the obvious changes in the λ_{max} region of rhodamine B solution, although the absorption intensity at other bands had some increases due to the dopamine polymerization. Also, there were no obvious naked-eye-visible changes in the solution colour. Furthermore, there was no precipitation observed in the solution even after centrifugation at a speed of 14000 rpm for 10 min. This indicated that under this condition the presence of polydopamine did not obviously affect the application of rhodamine B.

In the presence of dopamine, cotton and PBI fabrics could also be dyed with red colour by rhodamine B. As shown in Fig. 2b, their visible absorptions were centred at 550 nm, which was similar to that of rhodamine B solution. Their colour measurements were also investigated, as listed in Table 3. Compared with the case in the absence of dopamine, the presence of dopamine caused little colour changes on wool fabric, but larger colour changes on cotton and PBI fabrics. However, the K/S values of the cotton and PBI fabrics were obviously better than those in the absence of dopamine, which showed the improved fabric dyeability.

Table 3. Colour measurements of fabrics dyed by rhodamine

Fabric	Presence of dopamine				Absence of dopamine			
	K/S	L*	a*	b*	K/S	L*	a*	b*
Wool	20.1	33.9	49.4	-16.9	20.0	38.8	57.9	-20.5
Cotton	14.2	32.6	33.5	-3.1	4.2	58.0	47.3	-28.3
PBI	14.3	28.2	22.6	-0.9	5.2	50.2	33.6	-2.0

Moreover, after the colouration, the surface wettability of PBI was obviously changed. Its water contact angle decreased from about 130^o to 83^o (Fig. 2c). The slope test further verified the changes, as shown in Fig. 2d. The water droplets on the un-dyed PBI surface rolled rapidly down a 45^o slope under gravity because of no any adsorption on this super hydrophobic surface; while the water droplet on the dyed fabric surface did not roll down the slope and hung on it. These clearly showed the different interfacial interactions of the PBI surfaces before and after colouration, demonstrating the successful colouration on this hydrophobic surface in the presence of dopamine.

Their surface morphology before and after colouration was further investigated by SEM. In the case of cotton fibres, it can be seen that the pristine fibre surface is more smooth (Fig. 3a, left), while the surface roughness for the dyed fibre increased, showing the obvious contrast results, as shown in Fig. 3a (right). In addition, the dyed layer was composed of the lamellar ad-layer and the aggregated particles. The surface morphology of PBI showed the similar results (Fig. 3b). From these results, obvious changes observed in their surface morphology before and after colouration also indicated the successful colouration.

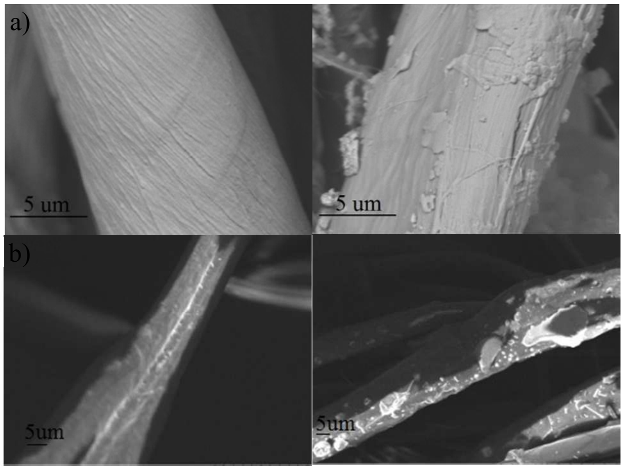


Fig. 3 SEM images of the surface morphology of the fibres before (left) and after (right) colouration; a) cotton, b) PBI.

Colouration on inorganic materials

Using this approach, other kinds of materials, such as metal (Al slide) and ceramic (glass), could also be successfully dyed with red colour by using rhodamine B in the presence of dopamine. Their coloured surfaces were characterized with XPS, SEM and water contact angle measurement.

XPS analysis had been employed to quantitatively determine the chemical composition of the material surface. For the blank materials, the material signals of Si2s and Si2p, Al2s and Al2p were observed; while no nitrogen (N1s) was found in the XPS spectra (Fig. 4, left). However, the XPS spectra of the coloured materials showed no obvious material signal. On the contrary, peaks from the atomic composition of colouration components were clearly observed, especially the nitrogen signal (N1s) (Fig. 4, right).

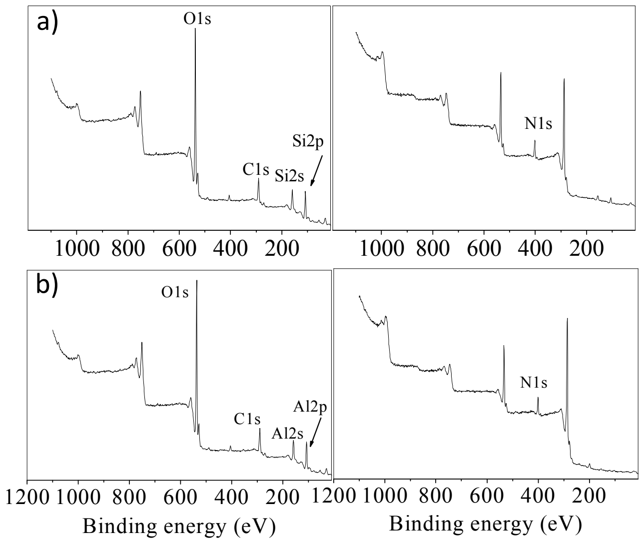


Fig. 4 XPS spectra of glass (a) and Al (b) slides before (left) and after (right) colouration.

Compared to the initial surface, the C1s and O1s XPS spectra signal evidently altered after the colouration (Fig. 5). In the case of glass, two peak species at the binding energy of about 284.6 eV and 287.7 eV, attributable to C-C and C=O species, respectively, were observed in the C1s core-level spectrum of pristine glass. After colouration, the C1s core-level spectrum can be curve-fitted into four peak species at the binding energy of about 284.6 eV, 285.5 eV, 286.5 eV and 287.7 eV attributable to the carbon in C-C/C=C, C-O, C-N, and C=O species, respectively.[27] The colouration of glass surface by rhodamine B/polydopamine system resulted in two additional peak species for C-N and C-O. Both the C-O and C=O signals were existed, which confirmed the carboxyl group in rhodamine B and the catechol and quinone groups in polydopamine. The colouration of glass was further confirmed by the O1s core-level spectra of pristine glass and the dyed glass. In the O1s spectrum of pristine glass, a species at the binding energy of about 532 eV was observed. The O1s spectra of the dyed glass can be curve-fitted into two species at the binding energy of about 532 eV and 533 eV, attributable to C=O and C-O, respectively.[10] The C1s and O1s XPS spectra for the coloured Al surface showed the similar results.

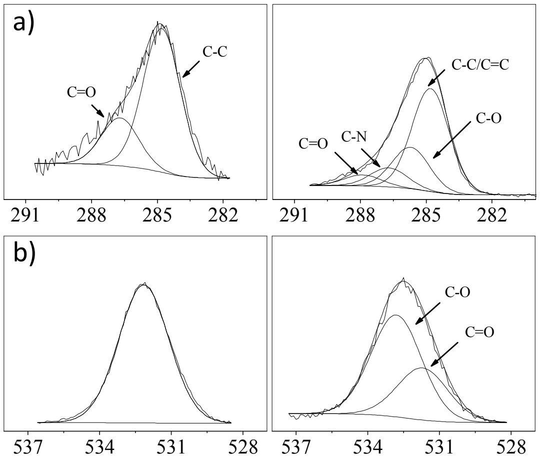


Fig. 5 XPS C1s (a) and O1s (b) core-level spectra for glass before (left) and after (right) colouration.

The changes in their surface morphology before and after colouration further confirmed the successful colouration, as shown in Fig. 6. In the case of the pristine surfaces, it can be seen that they are much smoother. After colouration, the blank surfaces were completely covered by the lamellar ad-layers and the aggregated nano particles. Thus, the coloured surfaces had a higher roughness, showing the obvious contrast results to the blank surfaces.

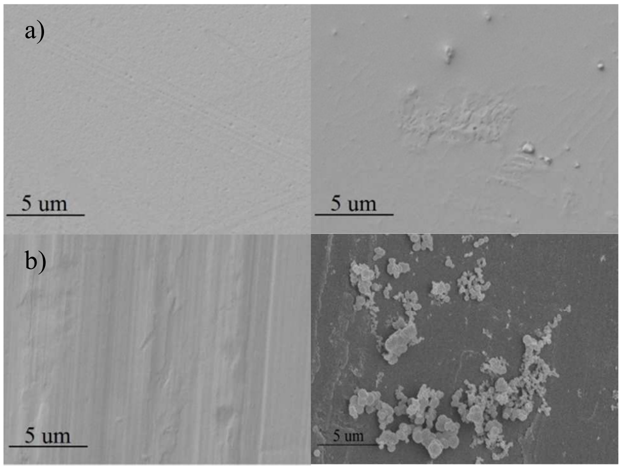


Fig. 6 SEM images of the surface morphology of glass (a) and Al (b) slides before (left) and after (right) colouration.

The wettability of the coloured glass and Al slides was also confirmed using water contact angle measurement. For the pristine surfaces, their water contact angles were about 100^{o}; while after colouration, the contact angles decreased to about 80^{o} (Fig. 7). All these results indicated that the material surfaces were successfully coloured by rhodamine B in the presence of dopamine.

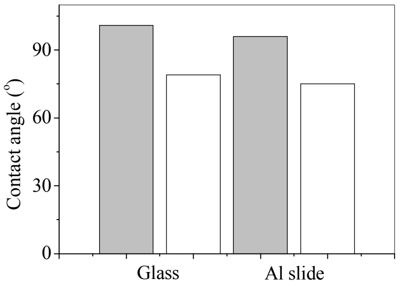


Fig. 7 Water contact angles of glass and Al slides before (grey) and after (white) colouration.

Conclusions

In conclusion, we had developed a simple method for surface colouration on various materials via dopamine polymerization in aqueous media. Induced by the dopamine polymerization, different kinds of materials could be successfully coloured, including textile materials, organic and inorganic materials, and even the materials resistant to colouration. This method showed a material-independence and could be achieved at room temperature, which was completely different from the conventional colouration process. The method expanded the application range of dopamine and proposed a novel colouration idea. It is a promising alternative to the traditional colouration process.

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Notes and references

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1 G. Prota, *Med. Res. Rev.*, 1988, **8**, 525.
2 K. C. Brown, E. Marlowe, G. Prota and G. Wenke, *J. Soc. Cosmet. Chem.*, 1997, **48**, 133.
3 J. H. Waite and M. L. Tanzer, *Science*, 1981, **212**, 1038.
4 J. H. Waite, *Integr. Comp. Biol.*, 2002, **42**, 1172.
5 M. J. Sever, J. T. Weisser, J. Monahan, S. Srinivasan and J. J. Wilker, *Angew. Chem., Int. Ed.*, 2004, **43**, 448.
6 H. Lee, N. F. Scherer and P. B. Messersmith, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 12999.
7 Q. Lin, D. Gourdon, C. Sun, N. Holten-Andersen, T. H. Anderson, J. H. Waite and J. N. Isradlachvili, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 3782.
8 H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426.
9 S. M. Kang, J. Rho, I. S. Choi, P. B. Messersmith and H. Lee, *J. Am. Chem. Soc.*, 2009, **131**, 13224.
10 Q. Wei, F. Zhang, J. Li, B. Li and C. Zhao, *Polym. Chem.*, 2010, **1**, 1430.

11 H. Lee, Y. Lee, A. R. Statz, J. Rho, T. G. Park and P. B. Messersmith, *Adv. Mater.*, 2008, **20**, 1619.

12 H. Lee, J. Rho and P. B. Messersmith, *Adv. Mater.*, 2009, **21**, 431.

13 G. Westwood, T. N. Horton and J. J. Wilker, *Macromolecules*, 2007, **40**, 3960.

14 B. Yu, D. A. Wang, Q. Ye, F. Zhou and W. M. Lin, *Chem. Commun.*, 2009, 6789.

15 J. K. Ryu, S. H. Ku, H. Lee and C. B. Park, *Adv. Funct. Mater.*, 2010, **20**, 2132.

16 O. J. X. Morel and R. M. Christie, *Chem. Rev.*, 2011, **111**, 2537.

17 S. M. Burkinshaw and D. S. Jeong, *Dyes Pigm.*, 2012, **92**, 1025.

18 B. Kahr and R. W. Gurney, *Chem. Rev.*, 2001, **101**, 893.

19 T. Bullard, K. L. Wustholz, E. D. Bott, M. Robertson, P. J. Reid and B. Kahr, *Cryst. Growth Des.*, 2009, **9**, 982.

20 E. E. Oguzie, G. N. Onuoha and A. I. Onuchukwu, *Mater. Chem. Phys.*, 2005, **89**, 305.

21 S. Deng, X. Li and H. Fu, *Corros. Sci.*, 2011, **53**, 760.

22 M. Sameiro and T. Goncalves, *Chem. Rev.*, 2009, **109**, 190.

23 S. Pu, G. Liu, R. Wang and B. Chen, *Dyes Pigm.*, 2013, **98**, 238.

24 B. Fei, B. Qian, Z. Yang, R. Wang, W. C. Liu, C. L. Mak and J. H. Xin, *Carbon*, 2008, **46**, 1795.

25 R. McDonald, *J. Soc. Dyers Colour.*, 1980, **96**, 486.

26 AATCC Test Method 61-2010 Colorfastness to Laundering: Accelerated, Test Condition 3A, AATCC Technical Manual, The American Association of Textile Chemists and Colorists, US, 2011.

27 W. Wang, A. Zhang, L. Liu, M. Tian and L. Zhang, *J. Electronchem. Soc.*, 2011, **158**, D228.