Electronic Supplementary Material (ESI) for RSC Advances.

Study on the mechanism of laccase-catalyzed polydopamine rapid dyeing and modification of silk

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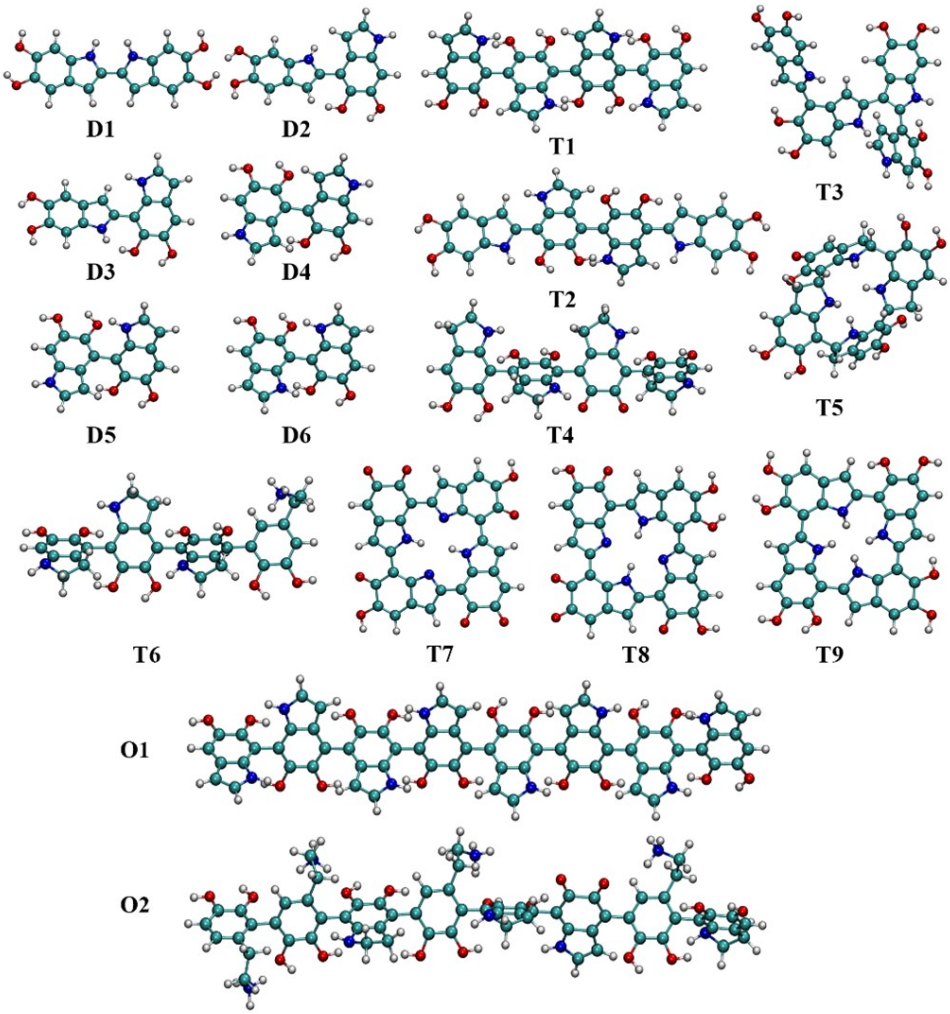

Fig. S1 The molecular structures of dopamine oligomers; D: Dimer, T: Tetramer, O: Octamer; Red: oxygen atom, Cyan: carbon atom, Blue: nitrogen atom, White: hydrogen atom

The macromolecular chain of silk fibroin contains more than 5000 amino acid residues, so it was not feasible to study the interaction between dopamine oligomers and the natural structure of the entire silk fibroin by molecular dynamics simulation. However, there was no simple representative silk protein structure in the protein database. Therefore, referring to the method of Cheng Yuan et al.,[1] a representative silk fibroin structure model of silk fibroin peptide sequence with both crystalline and amorphous regions was established. The structure model included two antiparallel peptide chains with the same amino acid sequence. The peptide chain included three

parts: Linker 5, Domain 6.5 and Linker 6.[2] Two of the Linker parts belonged to the amorphous region, the Domain part belonged to the crystal region, and the crystal region had typical GAGAGA and GAGAGS sequences. The specific sequence of the three parts is as follows:

Linker 5：GLY ALA GLY ALA GLY ALA GLY ALA GLY ALA GLY THR GLY SER SER GLY PHE GLY PRO TYR VAL ALA ASN GLY GLY TYR SER GLY TYR GLH TYR ALA TRP SER SER GLH SER ASH PHE GLY THR GLY;

Domain 6.5：GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY SER GLY ALA GLY ALA GLY TYR GLY ALA GLY ALA GLY SER GLY ALA ALA SER;

Linker 6：GLY ALA GLY ALA GLY ALA GLY ALA GLY ALA GLY THR GLY SER SER GLY PHE GLY PRO TYR VAL ALA ASN GLY GLY TYR SER GLY TYR GLH TYR ALA TRP SER SER GLH SER ASH PHE GLY THR GLY SER.

The ABTS substrate was scanned by UV spectrophotometer. As shown in Fig. S2, it has the maximum absorption wavelength at 415nm. All subsequent experiments on the determination of laccase activity were measured at this wavelength. Three different buffers with a concentration of 0.05mol/l were used to evaluate the enzyme activity of laccase. It could be seen from table S1 that the effects of the three buffers on laccase activity were not significant. Among them, the acetic acid-sodium acetate buffer had

the highest laccase activity. Therefore, in subsequent experiments, this buffer was selected as the buffer used to adjust the pH value of the reaction.

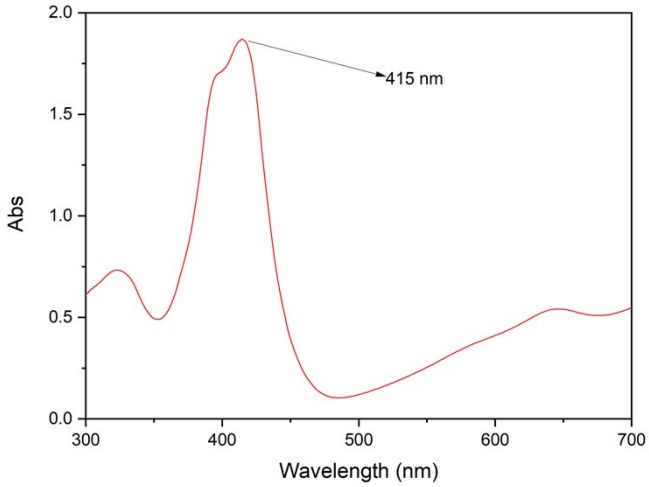

Fig. S2 UV-Vis spectra of ABTS

Table S1 Effect of buffer solution on laccase activity

Type of buffer solution	Laccase activity (U/mg)
$C_6H_8O_7$ - $Na_3C_6H_5O_7$	0.875
PB，Phosphate Buffer	0.894
CH_3COOH - CH_3COONa	0.955

The effect of pH value (2.5-7.5) on laccase activity was also explored. It could be seen from Fig. S3a that laccase showed the highest activity when pH = 3.5, laccase was gradually inactivated as pH value increases, while laccase activity was also inhibited when acidity was too strong. In addition, the effect of temperature (25-85 ℃) on laccase activity was measured. It was found that the activity was the highest when the temperature was 55 ℃ (Fig. S3b). However, silk belongs to protein fiber, and high temperature was not friendly to protein, so the enzymatic dyeing temperature in this work was 50 ℃. When the temperature was 25-55 ℃, the activity of laccase gradually increased with the increase of temperature, but when the temperature was higher than

65 ℃, the activity would decrease sharply, and the laccase had been completely inactivated at 85 ℃. Finally, the effect of buffer concentration on laccase activity was explored. It was found that (Fig. S3c) different concentrations of the buffer had little effect on laccase activity, and the optimal concentration was 0.1mol/l.

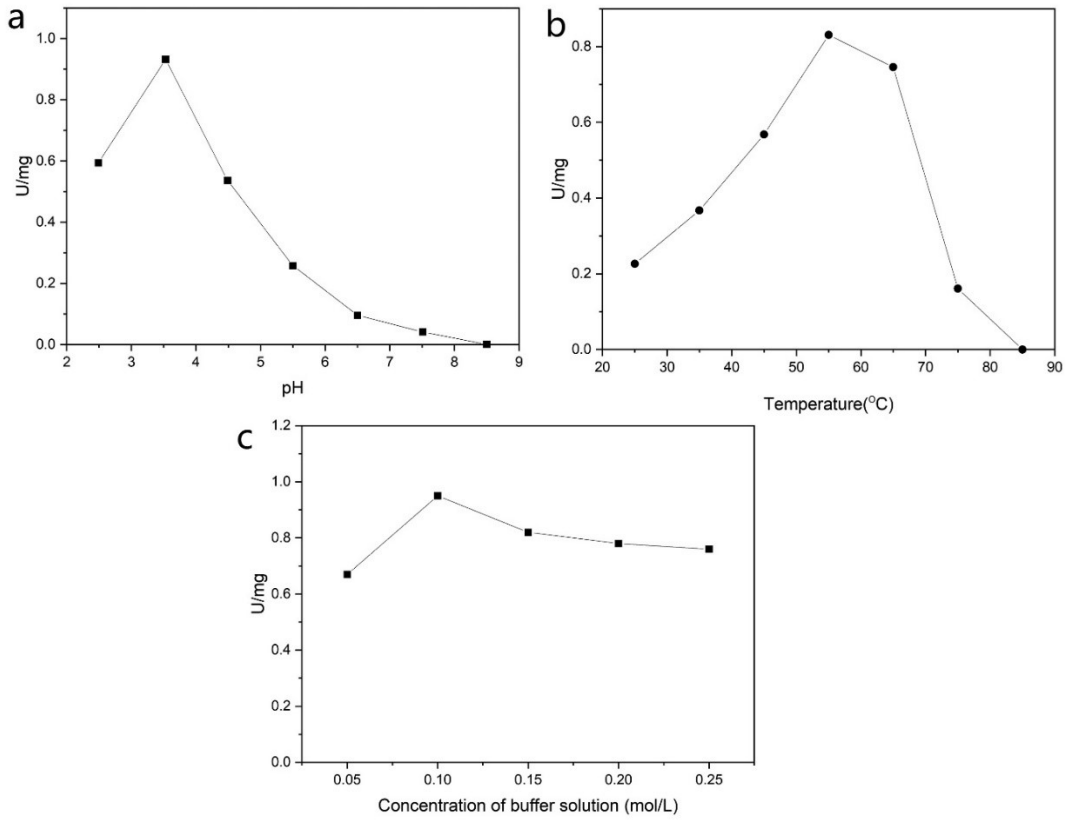

Fig. S3 The influence of various factors on laccase activity: (a) the influence of pH value on laccase activity; (b) the influence of temperature; (c) the influence of buffer concentration

The rubbing fastness of dyed fabrics was tested according to ISO 105-X12:1993 and evaluated by gray sample card for assessing staining. The sample size was 20 cm × 5 cm, and one square cotton lining fabric (5 cm × 5 cm) was used to wrap the circular rubbing head. During the test, the rubbing head completed 10 rubbing tests with a reciprocating range of 100 mm within 10 s, and its vertical pressure was 9 N. For this

color fastness test, the wet rubbing cloth was soaked with tertiary water and its water content was 95% - 105%.

According to ISO 105-C01:1989 standard, the color fastness to washing was tested at 40 ℃ for 30 min. The sample size was 10 cm × 4 cm, stitched along a short edge with a multi-fiber lining fabric of the same size. The preparation standard of soaping solution was: Standard synthetic detergent 4 g/L. After the combined cloth sample was washed and dried, it was evaluated by gray sample card for discoloration and staining.

The color fastness to light of dyed fabric was tested according to ISO105-B02:1994 standard. After being exposed to xenon arc lamp for 10 h, the fabric was evaluated according to the fading grade (1 ~ 8) of blue wool standard samples exposed at the same time.

Notes and references

1. Y. Cheng, L.-D. Koh, D. Li, B. Ji, Y. Zhang, J. Yeo, G. Guan, M.-Y. Han and Y.-W. Zhang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21787-21796.

2. C.-Z. Zhou, F. Confalonieri, M. Jacquet, R. Perasso, Z.-G. Li and J. Janin, *Proteins: Struct., Funct., Bioinf.*,2001, **44**, 119-122.