

Supporting Information for

## Robust Mussel-inspired Coatings for Controlled Zinc Ion Release

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## 1. Materials

Polyvinyl alcohol (PVA) (PVA1788, average molecular weight ( $M_w$ ) ~85,000, hydrolysis degree 87.0-89.0 mol %; Mowiol® PVA203,  $M_w$  ~31,000, hydrolysis degree 86.7-88.7 mol % ; Mowiol® PVA210,  $M_w$  ~67,000, hydrolysis degree 86.7-88.7 mol % ; Mowiol® PVA224,  $M_w$  ~205,000, hydrolysis degree 86.7-88.7 mol %), *n*-butyraldehyde (BA), *n*-octyl aldehyde (OA), zinc nitrate hexahydrate, zinc acetate dihydrate, anhydrous dimethyl sulfoxide (DMSO) and *p*-toluenesulfonic acid monohydrate (TsOH) were purchased from Aladdin Industrial Co. The other PVA (Mowiol® 1888,  $M_w$  ~130,000, hydrolysis degree 86.7-88.7 mol %) was purchased from Sigma-Aldrich Co. LLC. 3,4-Dihydroxybenzaldehyde (DBA) was purchased from Linhai Xinghua Chemical Co., LTD.

## 2. Synthesis of PVA-based Biomimetic Polymers

The PVA-based biomimetic polymer with pendent catechols and alkyl groups (PVA-*g*-DBA/BA) was synthesized by choosing three cheap commercially available materials: PVA, DBA and BA. A typically procedure using Mowiol® PVA210 as start material with around 20 mol % degree of grafting (DG) of DBA and 12 mol % DG of BA was shown below: 10 g of PVA210 was added in 100 mL of DMSO and stirred at 80 °C until fully dissolved. After being cooled down to room temperature (rt), DBA (7.0 g) and TsOH (0.75 g) were added and the solution was heated to 80 °C again and stirred at this temperature for 12 h under Ar atmosphere. After cooling to rt, BA (3.6 g) was added and stirred for 4 h under Ar atmosphere. Then the reaction mixture was precipitated in water twice and washed with massive water. The resulting grey white solid was dried under vacuum at 45 °C to yield 15.8 g of PVA-*g*-DBA/BA.

### 3. Characterizations

$^1\text{H}$  NMR spectra were recorded on a Bruker AV600 MHz spectrometer using TMS as an internal standard. Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of the samples were recorded on a Fourier-transform infrared spectrometer (1600, Perkin-Elmer Co., Wellesley, MA, USA). The data were collected at rt over 16 scans with a resolution of  $4\text{ cm}^{-1}$ . UV-vis spectra were recorded in a quartz cuvette with an optical path length of 1 cm or on a quartz slide using a Varian Cary 50 UV-vis spectrophotometer. AFM measurements were performed on an Agilent 5400 instrument using tapping mode. SEM measurements were performed on a Hitachi S-4800 with an accelerating voltage of 3.0 kV on freshly cleaved mica and the samples were coated with gold before imaging. Adhesion test was performed using a cross-cutter, model Erichsen 295/II. Wear resistance was done by using a Taber Abrasion tester with 1000 g loading and 60 rpm rotate speed. The hardness of the coating was tested by using pencil hardness tester, model Elcometer 501.

### 4. The Formula of ASW

**Table S1** The components of ASW

<b>Component</b>	<b>Mass concentration [g·L<sup>-1</sup>]</b>
NaCl	23.0
MgCl <sub>2</sub> ·6H <sub>2</sub> O	9.8
Na <sub>2</sub> SO <sub>4</sub>	3.9
CaCl <sub>2</sub>	1.2

## 5. The DG of Catechol of PVA-g-DBA with Different $M_w$ of PVA

**Table S2** The calculated DGs of catechol of PVA-g-DBA with different  $M_w$  of PVA

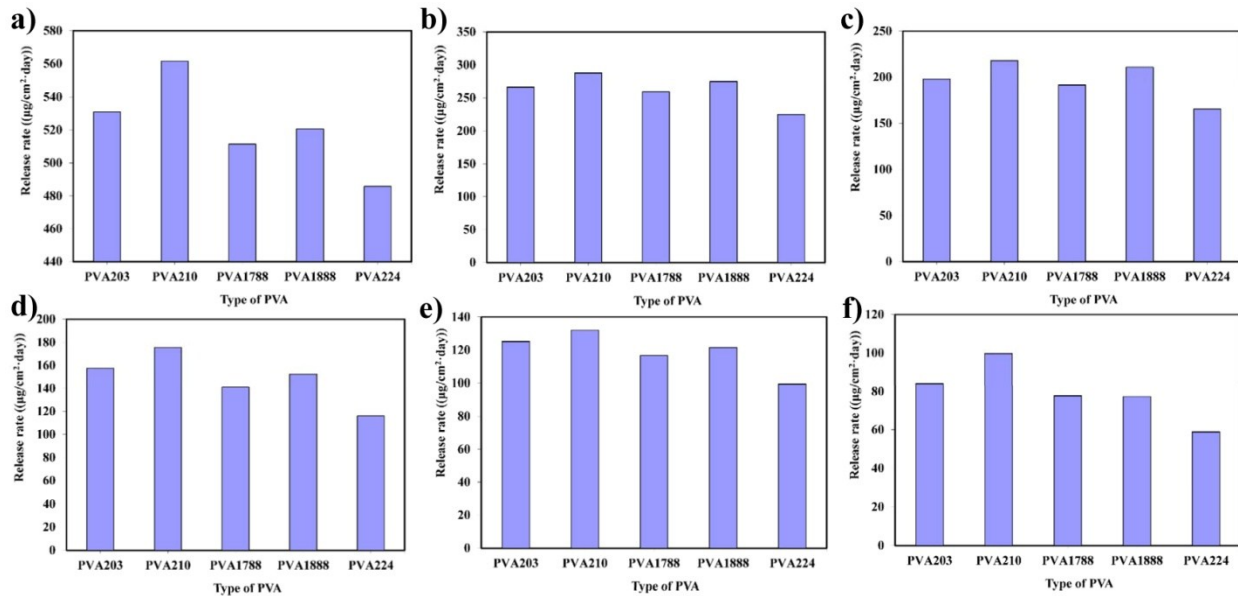
PVA	DG of catechol [mol %]
PVA203 ( $M_w$ : ~31000)	20.1
PVA210 ( $M_w$ : ~67000)	20.3
PVA1788 ( $M_w$ : ~85000)	19.8
PVA1888 ( $M_w$ : ~130000)	19.3
PVA224 ( $M_w$ : ~205000)	18.9

## 6. The Effect of $Zn^{2+}$ Dosage on Adhesion of Obtained Coating

**Table S3** The adhesion of coating at different  $Zn^{2+}$  dosage

$n_{Zn^{2+}}:n_{catechol}$	Adhesion (ASTM D3359)
1:3	5B
1:2	5B
1:1	3B
1.5:1	2B
2:1	2B

## 7. The Effect of $M_w$ of PVA on Release Rate of $Zn^{2+}$ of PVA-g-DBA-based Coating at Different Immersion Time



**Fig. S1** The release rate of  $Zn^{2+}$  of PVA-g-DBA-based coating driven from different  $M_w$  of PVA at the certain immersion time, a) 5 days, b) 10days, c) 15days, d) 20days, e) 25days, f) 35days.

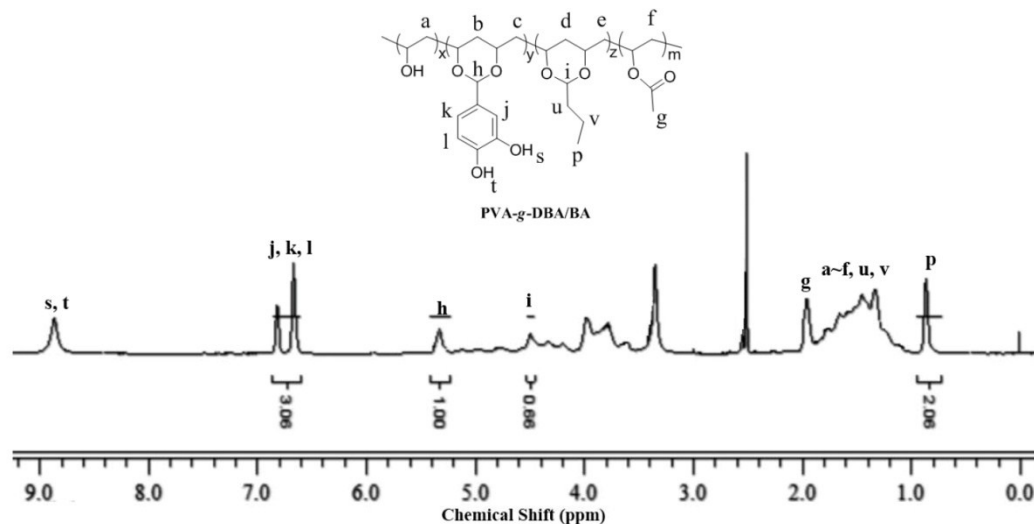
## 8. The Chemical Structure of PVA-g-DBA/BA

A typical  $^1\text{H}$  NMR spectrum of the resultant polymer (PVA-g-DBA/BA) is shown in Figure S2. The peak h at 5.30 ppm is assigned to the proton on the acetal group formed by the DBA and PVA, and the peaks between 6.60-6.90 ppm are assigned to the three protons on the phenol ring. The integrals of the acetal and aromatic protons match well, indicating that DBA was incorporated into the polymer. The peak i at 4.50 ppm is assigned to the proton on the acetal group formed by the BA and PVA, and the peak p at 0.80 ppm is assigned to the proton on the terminal methyl group. The integrals of the acetal and methyl protons match well, also indicating that BA was incorporated into the polymer. The peaks between 1.0-1.80 ppm (a-f,u,v) are assigned to the methylene groups on the polymer backbone and propyl side chain, and the peaks between 3.40-4.50 ppm are assigned to other protons on the polymer backbone. The DG was determined by  $^1\text{H}$  NMR spectroscopy according to equation (1, 2) shown below:

$$DG_{DBA} = \frac{I(h)}{I(a-f,u,v) - \frac{4}{3}I(p)} \quad (1)$$

$$DG_{BA} = \frac{\frac{1}{3}I(p)}{I(a-f,u,v) - \frac{4}{3}I(p)} \quad (2)$$

where  $I$  refers to the integral of the peak(s).



**Fig. S2**  $^1\text{H}$  NMR spectrum of PVA-*g*-DBA/BA in  $\text{DMSO-}d_6$

In order to investigate the effect of  $M_w$  of PVA on coating properties, a series of PVA-*g*-DBA/BA with different  $M_w$  of PVA were synthesized and the calculated DGs were shown in Table S3.

**Table S4** The DGs of DBA and BA of PVA-*g*-DBA/BA

PVA	DG [mol %]	
	DBA	BA
PVA 203 ( $M_w$ : ~31000)	19.6	13.1
PVA 210 ( $M_w$ : ~67000)	19.1	12.8
PVA 1788 ( $M_w$ : ~85000)	18.6	12.1
PVA 1888 ( $M_w$ : ~130000)	18.6	11.6
PVA 224 ( $M_w$ : ~205000)	17.8	11.5

## 9. The Effect of Reaction Time on DG of BA

**Table S5** The DG of BA at different reaction time

Reaction time	DG of BA <sup>a)</sup> [mol %]
1 h	5.2
2 h	9.6
4 h	12.8
8 h	15.1
12 h	15.1
20 h	15.1

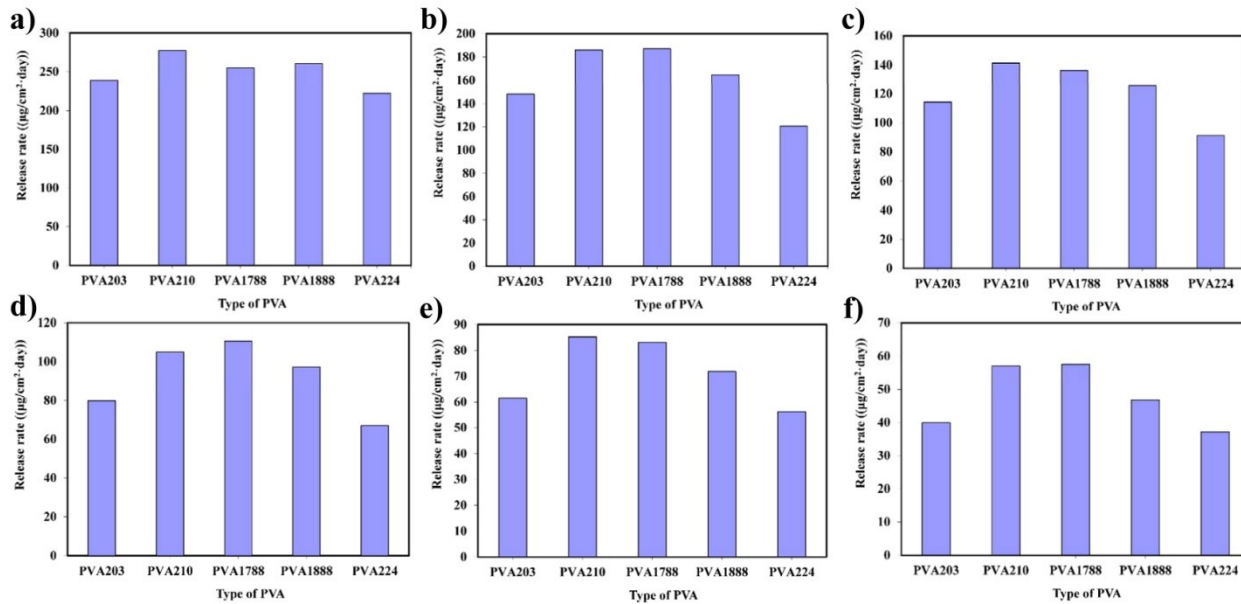
a) The polymer was obtained from the PVA210.

## 10. The Effect of Zn<sup>2+</sup> Dosage on Adhesion of PVA-g-DBA/BA-based Coating

**Table S6** The adhesion of PVA-g-DBA/BA-based coating at different Zn<sup>2+</sup> dosage

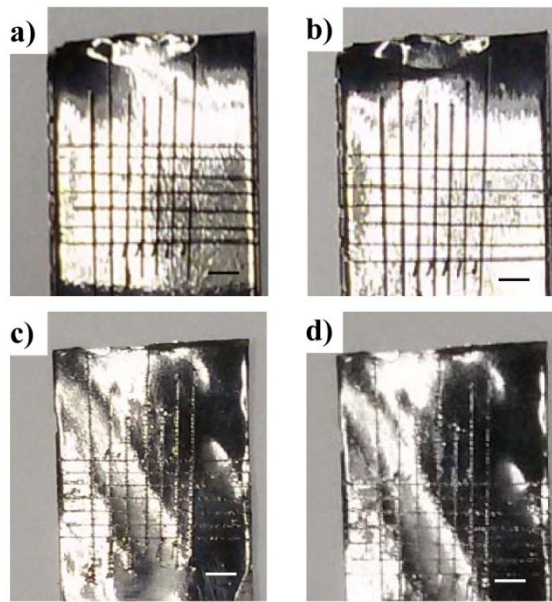
$n_{Zn^{2+}} : n_{catechol}$	Adhesion (ASTM D3359)
1:3	5B
1:2	5B
1:1	2B
1.5:1	2B

## 11. The Effect of M<sub>w</sub> of PVA on Release Rate of Zn<sup>2+</sup> of PVA-g-DBA/BA-based Coating at Different Immersion Time

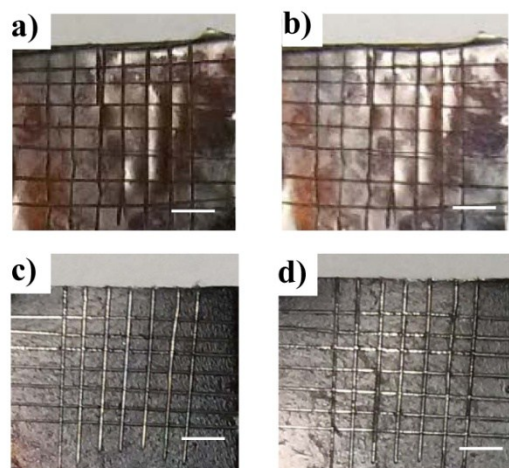


**Fig. S3** The release rate of Zn<sup>2+</sup> of PVA-g-DBA/BA-based coating derived from different M<sub>w</sub> of PVA at the certain immersion time, a) 5 days, b) 10 days, c) 15 days, d) 20 days, e) 25 days, f) 35 days.

## 12. The Contrastive Photos of Adhesion Test for PVA-g-DBA-based and PVA-g-DBA/BA-based Coating



**Fig. S4** The photo images of before (a, c) and after (b, d) the adhesion test based on the cross-cut method. a, b) The pristine PVA-g-DBA -based coating. c, d) The coating was immersed into ASW for 35 days. Scale bar is 2mm.



**Fig. S5** The photo images of before (a, c) and after (b, d) the adhesion test based on the cross-cut method. a, b) The pristine PVA-g-DBA/BA -based coating. c, d) The coating was immersed into ASW for 35 days. Scale bar is 2mm.



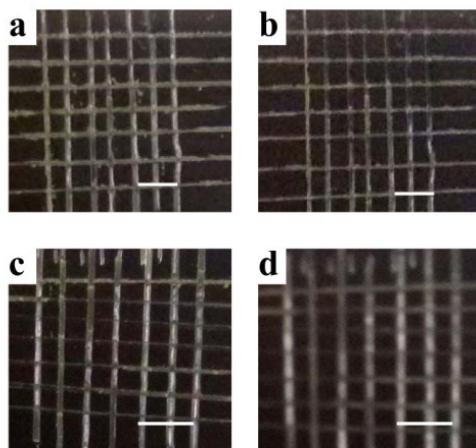


Fig.S6 The photo images of before (a, c) and after (b, d) the adhesion test based on the cross-cut method on glass substrate. a, b) The PVA-g-DBA-based coating. c, d) The PVA-g-DBA/BA -based coating. Scale bar is 2 mm.

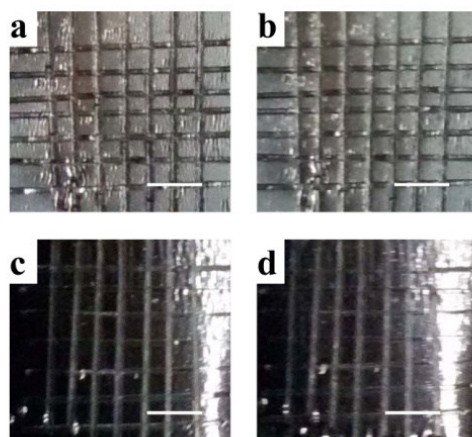
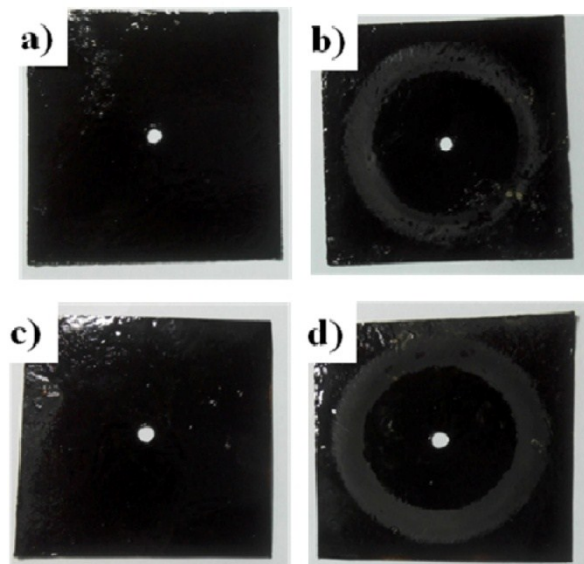


Fig.S7 The photo images of before (a, c) and after (b, d) the adhesion test based on the cross-cut method on PVC substrate. a, b) The PVA-g-DBA-based coating. c, d) The PVA-g-DBA/BA -based coating. Scale bar is 2 mm.

### 13. The Contrastive Photos of Abrasive Resistance Test for PVA-g-DBA-based and PVA-g-DBA/BA-based Coating



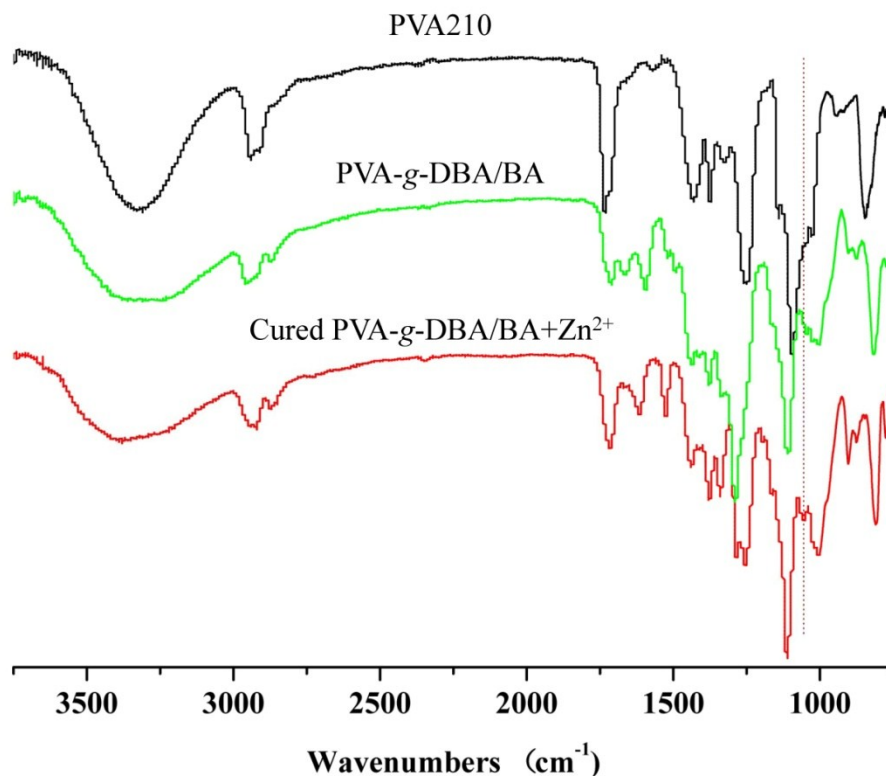
**Fig. S8** The photo images of before (a, c) and after (b, d) the adhesion test of the PVA-g-DBA-based(a, b) and PVA-g-DBA/BA-based(c, d) coating

#### 14. The Color of PVA-g-DBA/BA, PVA-g-DMB/BA and PVA-g-PHB/BA



**Fig. S9** Photo images of a) PVA-g-DBA/BA, b) PVA-g-DMB/BA and c) PVA-g-PHB/BA. For the PVA-g-DMB/BA and PVA-g-PHB/BA, no color change was observed before (b and c) and after (**Figure 4c B and C**) curing.

#### 15. FT-IR Spectra of PVA, PVA-g-DBA/BA and Cured PVA-g-DBA/BA

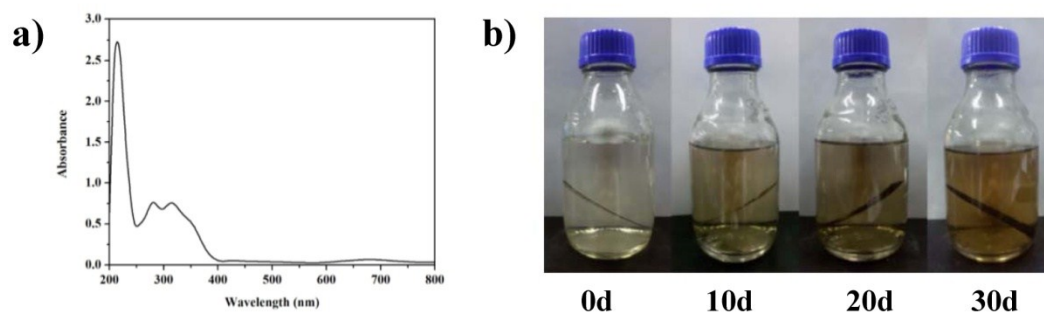


**Fig. S10** FT-IR spectra of PVA, PVA-g-DBA/BA and cured PVA-g-DBA/BA+Zn<sup>2+</sup>. Cured PVA-g-DBA/BA+Zn<sup>2+</sup> was obtained directly from the polymeric residue on the SS. The molar ratio of Zn<sup>2+</sup> to catechol was 1:2.

## 16. The Color and UV-vis Spectrum of ASW After Immersion of PVA-g-DBA/BA Coated SS Foil

The UV-vis spectrum of the ASW after immersing was shown in Figure S9 a. The absorption bands at 227 nm and 281 nm are assigned to the benzene ring on catechol group, and the absorption band at 693 nm is assigned to the Zn<sup>2+</sup>-catechol complexes. These typically absorption bands indicated that the chelated Zn<sup>2+</sup> had been released from the polymeric coating. The absorption band that appear at 326 nm is assigned to quinone formation (oxidation of catechol), which might derived from 1) the oxidized catechol moieties dropped from the polymeric coating, 2) the cleaved catechol-derived moieties that were further oxidized in basic ASW. Moreover, the color change of the ASW before and after immersion gives visual and indirect evidence. The ASW before immersion is colorless, and the ASW was gradually became darker after immersion (Figure S9 b).

These evidences testifies that the occurrence of hydrolysis of acetal at weak alkaline aqueous solution.



**Fig. S11** a) UV-vis spectrum of the ASW after immersion 35 days. b) Photo images of the ASW during the process of immersion.