Supporting Information

Mussel-Inspired Direct Immobilization of Nanoparticles and Application for Oil-Water

Separation

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Figure S1. XRD patterns of Fe₃O₄ (a) and SiO₂ (b) nanoparticles used in this study.



Figure S2. Optical image (a) and UV-Vis spectra (b) of aqueous dopamine solutions (10.5 mmol L^{-1}) at different pH values.

Figure S2 shows the optical image and UV-Vis spectra of aqueous dopamine solutions at pH 1-11. The solutions are colorless, pink and black after storage at pH 1-3, 5-7 and 9-11 for 12 h, respectively (Figure S2a). UV-Vis spectra in Figure S2b show a characteristic peak of catechol at ~280 nm for the solutions at pH 1 and pH 3. Then this peak shifts to ~295 nm and a new band appears at ~450 nm as pH value changes from 5 to 11, indicating the oxidation of dopamine to o-quinone.¹ The spectra also suggest that dopamine starts to oxidize under moderate acidic conditions of pH 5, as evidenced by the weak band at 300-320 nm (Inset of Figure S2b).



Figure S3. SEM images of the sponges treated in aqueous dopamine/Fe₃O₄ dispersions at pH 9 (a) and pH 11 (b).



Figure S4. Optical image (a) and UV-Vis spectra (b) of aqueous dopamine solutions (2.6 mmol L^{-1}) containing different concentrations of *n*-dodecanethiol at pH 11. The solutions were stored in air for 24 h at ambient temperature.

To investigate the effect of thiol on the oxidation of dopamine, optical image and UV-Vis spectra were recorded on aqueous dopamine solutions (2.6 mmol L⁻¹) containing different amounts of *n*-dodecanethiol at pH 11. For the solutions containing low content of *n*-dodecanethiol (< 0.132 mmol L⁻¹), they quickly turned black at ambient temperature, indicating the oxidation of catechol. The solutions kept colorless over 24 h when the concentration of *n*-dodecanethiol was higher than 0.265 mmol L⁻¹ (Figure S4a). UV-Vis spectra show that the intensities of the peaks at ~326 nm and the bands at ~450 nm reduce continuously as increasing the content of *n*-dodecanethiol from 0.066 to 0.53 mmol L⁻¹ (Figure S4b), suggesting anti-oxidation effect of the thiol on catechol moiety. Indeed, the peaks and the bands diminish completely when the concentration of *n*-dodecanethiol is higher than 0.265 mmol L⁻¹, indicating that the oxidation of dopamine into *o*-quinone is significantly retarded by the thiol even under strong alkaline conditions. Notably, the sharp and asymmetric peaks at \sim 326 nm might relate to the rearrangement of *o*-quinone.¹



Figure S5. XPS spectra of the superhydrophobic sponge prepared in dopamine/Fe₃O₄ dispersion containing n-dodecanethiol at pH 7; (a) Survey scan, (b) Fe 2p, (c) O 1s, (d) C 1s, (e) S 2p and (f) N 1s.

Figure S5 shows the XPS spectra of the superhydrophobic sponge fabricated in dopamine/Fe₃O₄ dispersion containing 2.1 mmol L^{-1} of *n*-dodecanethiol at pH 7. Survey scan reveals the elements of Fe, C, O, N and S on the

sponge (Figure S5a). Fe 2p spectrum in Figure S5b shows typical Fe 2p_{3/2} (711 eV), Fe 2p_{1/2} (725 eV) and satellite (718.8 eV) peaks for iron oxides. The Fe 2p_{3/2} peak can be deconvoluted into two components of Fe³⁺ (711 eV) and FeOOH (713.1 eV).² The satellite peak indicates the coordination of Fe³⁺ with catecholic moiety.^{3,4} This conclusion is also supported by O 1s and C 1s spectra. There are signals at 530.6, 531.2 and 533.2 eV in the O 1s spectrum (Figure S5c), corresponding to iron oxide, quinone C=O and phenolic hydroxyl C-OH, respectively. The C 1s spectrum in Figure S5d shows the components of C-C (284.4 eV), C-N (285.4 eV), C=C-S (286 eV), C=N (286.5 eV), phenolic hydroxyl C–OH (287.1 eV) and quinone C=O (288.2 eV).^{5,6} Clearly, these phenolic hydroxyl and quinone peaks partly originate from the catecholic moiety anchored on Fe_3O_4 nanoparticles. The existence of the C=<u>C</u>-S and C=N components implies the reactions of mercapto and amino groups with quinone,¹ which is further supported by S 2p and N 1s spectra. In the S 2p spectrum (Figure S5e), S 2p_{3/2} and S 2p_{1/2} peaks for free *n*-dodecanethiol locate at 163.7 and 164.7 eV, while those of the bound thiolate species are centered at 161.9 and 162.9 eV, respectively.^{7,8} We ascribe the peaks at 161.9 and 162.9 eV to the S atom of C=C-S species, which is consistent with the C 1s signal at 286 eV. These C=C-S species indicate the grafting of *n*-dodecanethiol molecule to o-quinone via Michael addition.¹ Notably, the C=C-S species exhibit lower binding energies compared alkanethiol bound to a gold surface⁹ (~162 and 163.1-163.5 eV for S 2p_{3/2} and S 2p_{1/2} peaks, respectively). A possible explanation for the lower values is that electron-rich phenyl ring of catecholic moiety reduces the energy needed to abstract an electron from S atom.¹⁰ The N 1s spectrum can be deconvoluted into four components at 398.2, 399.2, 399.9 and 401.5 eV (Figure S5f), corresponding to the N atoms of C=N, 11 –NH-, 12 –NH₂ and hydrogen bonded amine,13 respectively. The presence of C=N and -NH- species suggests the reactions between -NH₂ and *o*-quinone through Schiff base reaction and/or Michael addition.¹

To further investigate possible reactions of *o*-quinone with –NH₂ and –SH groups, we conducted gas chromatography-mass spectrometry (GC-MS, Angilent Technologies 7890A GC system) on an ethanol solution

containing 10.5 mmol L⁻¹ of dopamine and 2.1 mmol L⁻¹ of *n*-dodecanethiol. The resulting spectra in Figure S6a show signals at 355 and 281, the mass/charge ratio (m/z) of these signals are closed to compounds **3** and **4** produced through Michael addition and Schiff base reaction. We attribute the signals at 91, 117, 207 and 405.1 to the fragments of dopamine (91 and 117), compound **4**, and disulfide **5**, respectively. A possible formation route of these compounds is illustrated in Figure S6b.^{1,14-16} Although the structural characteristics of these compounds should be further identified, the MS results provide an alternative evidence for the appearance of –NH–, C=N and C=C–S species in Figure S5.



Figure S6. Mass spectrometry results (a) of the ethanol solution of dopamine/n-dodecanethiol at the elute time of

13 min. (b) A proposed formation route for the compounds detected in the MS.



Figure S7. SEM images of the nickel (a) and copper (b) foams treated in aqueous dopamine/Fe₃O₄ dispersions at

pH 1.



Figure S8. SEM images and water contact angles for the nickel (a) and copper (b) foams treated in aqueous dopamine/Fe₃O₄ dispersions containing 2.1 mmol L^{-1} of *n*-dodecanethiol at pH 11.

(a) (C) Wt 42.28 52.65 39.87 СК 05.46 05.83 NK NK. 04.50 34.00 31.79 ок ОК 24.79 18.26 09.73 30.84 FeK

Figure S9. SEM image (b) of the PU sponge treated in aqueous dopamine/Fe $_3O_4$ /SiO $_2$ dispersion at pH 1. (a) and

(c) are the EDX plots of SiO_2 and Fe_3O_4 nanoparticles, respectively.

7.00

1.00 2.00

3.00 4.00 Energy-keV



Figure S10. SEM images of the Fe₃O₄ nanoparticles anchored sponge after ultrasonication in ethanol for (a) 5 min,

(b) 10 min, (c) 15 min and (d) 20 min. The sponge was treated in aqueous dopamine/Fe₃O₄ dispersion at pH 1.

57.80

05.60-

26.99-

09.62

2.00

3.00 4.00 Energy - keV 5.00 6.00 7.00



Figure S11. SEM images of the Fe_3O_4 nanoparticles anchored nickel foam after ultrasonication in ethanol for (a) 5 min, (b) 10 min, (c) 15 min and (d) 20 min. The nickel foam was treated in aqueous dopamine/Fe₃O₄ dispersion at pH 1.





Figure S12. XPS spectra of dopamine-anchored Fe₃O₄ nanoparticles. (a) Survey scan, (b) Fe 2p, (c) C 1s, (d) N 1s,(e) O 1s.

In this study, Fe₃O₄ nanoparticles were incubated in an aqueous dopamine solution (10.5 mmol L⁻¹) at pH 1 for 12 h to obtain dopamine-anchored nanoparticles. Then XPS was used to characterize the surface chemistry of the resulting nanoparticles (Figure S12). Survey spectrum in Figure S12a shows the elements of C, O, N and Fe. In the Fe 2p spectrum, besides the characteristic signals of iron oxide at 710.8 (Fe 2p_{3/2}) and 712.8 eV (Fe 2p_{1/2}), it also displays a satellite peak of Fe³⁺ coordinates with dopamine at 719.9 eV (Figure S12b). The C 1s spectrum in Figure S12c shows five components of C–C (284.6 eV), C–N (285.3 eV), C=N (286.3 eV), phenolic hydroxyl C–OH (287.1 eV) and quinone C=O (288.2 eV).² Five peaks are located at 398.3, 399.2, 399.8, 401.4 and 402.3 eV in the N 1s spectrum (Figure S12d), which are assigned to the components of C=N, –NH–, –NH₂, hydrogen bonded amine and protonated amine (–NH₃⁺), respectively.^{12,17} Additionally, the O 1s spectrum in Figure S12e shows the oxygen signals of Fe₃O₄ (530.1 eV), quinone C=O (531.7 eV) and phenolic hydroxyl C–OH (533.1 eV). These results confirm that Fe₃O₄ nanoparticles are modified with dopamine moiety. Notably, the presence of quinone C=O, C=N and –NH– components suggests the oxidation of dopamine to *o*-quinone and subsequent reaction with –NH₂ group through Michael addition and/or Schiff base reaction even in strong acidic conditions of pH 1.



Figure S13. (a) Mass spectrometry data of the aqueous solution of dopamine (10.5 mmol L^{-1} , pH = 1) at the elution time of 3.4 min. (b) A proposed pathway for the formation of compound **6** and **7**. (c and d) Possible fragments of physical self-assembly with a mass/charge ratio of (c) 303.1 and (d) 562.3.

To investigate driving forces for the immobilization of nanoparticles, a control experiment was conducted on an aqueous solution of dopamine (10.5 mmol L⁻¹) at pH 1 by using liquid chromatography-mass spectrometry (LC-MS). The acidity of the solution was tuned by adding acetic acid (HAc). At the elution time of 3.4 min, the MS in Figure S13a shows the signals at 154.1, 150, 303.1, 454.1 and 606.2 (m/z), which are coincident with the structures associated with dopamine, 5,6-dihydroxyindole (DHI) **6** or dopaminechrome, physical dimer of dopamine/DHI, trimer of (dopamine)₂/DHI and tetramer of (dopamine)₂/(DHI)₂, respectively. These results are well consistent with the study conducted by S. Hong *et al.*,¹⁸ indicating the self-assembly of dopamine and DHI molecules *via* noncovalent interactions. Considering the structural characteristics of dopamine and DHI, there are many possible noncovalent interactions between these molecules, including ionic, cation– π , π – π and hydrogen bonding, *etc.*¹⁸ In this case, hydrogen bonding might form between dopaminechrome and dopamine through N–H and O–H bonds, while π – π stacking exists between the phenyl rings of the oxidized and unoxidized species (Figure S13c and 13d),^{18,19} which offers driving forces for the formation of the physical assemblies.

Importantly, a distinct signal locates at 544.4, whose m/z value is closed to a tetramer **7** of dopaminequinone **2**. A similar peak is also observed at 413.3, which might relate to a trimer **8** of dopaminequinone **2**. These tetramer

and trimer might form through intermolecular Schiff base reaction of dopaminequinone (Figure S13b).^{1,14-16} We attribute the signal at 562.3 to a physical self-assembly of trimer **8**/DHI. Although the structure of these compounds needs further identifications, they clearly indicate that covalent bonding also takes place even in strong acidic conditions. This is because that slight oxidation of dopamine to highly reactive *o*-quinone cannot be completely excluded in air atmosphere. Since the immobilization of oxide nanoparticles was performed in the similar dopamine solutions, the present results suggest that both covalent bonding and noncovalent interactions should be considered in order to understand the immobilization mechanism.

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