

23 from Aladdin Chemical Co. (Southern California, USA). N,N-dimethylformamide
24 (DMF) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. Sodium
25 borohydride (NaBH₄, 98%) was purchased from Tianjin great chemical reagent
26 factory. All other reagents were of analytical grade. All aqueous solutions were
27 prepared with deionized water (DW, 18 MΩ cm).

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29 *SI.2. Apparatus*

30 The morphologies of the prepared samples were characterized by a JEM 2100
31 transmission electron microscopy (TEM, Japan). Fourier transform infrared (FTIR)
32 study was performed over the wavenumber, range of 4000–400 cm⁻¹ by a Thermo
33 Fisher SCIENTIFIC Nicolet IS10 (Massachusetts, USA) FTIR impact 410
34 spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was carried
35 out on a Q50 TGA (TA Instruments, New Castle, USA), from 25 to 800 °C in argon
36 at a heating rate of 5 °C min⁻¹. Electrochemical impedance spectroscopy (EIS), cyclic
37 voltammetry (CV), and differential pulse voltammetry (DPV) experiments were
38 performed with a CHI 660E Electrochemical Workstation from Shanghai Chen-hua
39 Instrument (Shanghai, China) and conducted using a three-electrode system, with the
40 modified GCE as working electrode, a platinum wire as the counter electrode, a
41 saturated calomel electrode (SCE) as the reference electrode.

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43 *SI.3. Synthesis of carboxyl silicon carbide (CSiC)*

44 CSiC was synthesized according to a previous study.¹ Firstly, SiC-OH was

45 prepared through a hydrothermal reaction of glucose. Briefly, 50 mg of SiC and 200
46 mg of glucose were dispersed in 60 mL of DW *via* sonication, the suspension was
47 transferred to an autoclave and kept at 180 °C for 8 h. After reaction, the autoclave
48 was cooled naturally. The suspension was centrifuged and washed with DW and
49 alcohol for 3 times, respectively. SiC-OH was obtained by freeze-drying. Secondly,
50 the obtained SiC-OH was dispersed in 30 mL of ethanol *via* sonication, and then 1.0
51 mL of APTES was added to the suspension with vigorous stirring. After stirring for
52 12 h, the resulting mixture was cleaned with ethanol for 3 times. SiC-NH₂ was
53 obtained by freeze-drying. Thirdly, a dispersion of SiC-NH₂ in 20 mL DMF was
54 added dropwise to a flask containing 20 mL of 0.1 M succide anhydride in DMF. The
55 mixture was stirred for 24 h, the resulting SiC nanoparticles with carboxylic-function
56 groups at their surface (CSiC) were washed with DMF, alcohol, and DW for 3 times.
57 Finally, CSiC was obtained by freeze-drying.

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59 *S1.4. Preparation of Au@CSiC-SH/NH₂-CD composite material*

60 Au@CSiC-SH/NH₂-CD composite material was synthesized according to a
61 previous work ^{1,2} with some modifications. Briefly, 5 mg of CSiC was dissolved in 5
62 ml of DMF, and 130 μL of chloroauric acid was added. Similarly, 10 mg of SH-CD
63 and 0.9 mg of sodium borohydride were dissolved in 5 mL of DMF, and then the
64 mixture of CSiC and chloroauric acid was added quickly dropwise to the above
65 solution under stirring for 6 h. The resulted suspension was centrifuged and washed
66 with DW for 3 times followed by freeze-drying to obtain Au@CSiC-SH-CD. The

67 Au@CSiC composite was prepared using the similar process of Au@CSiC-SH-CD in
68 the absence of SH- β -CD. Then 20 mg of Au@CSiC-SH-CD, the carboxyl groups on
69 which have been activated by 10 mL of EDC/NHS (0.5 mM) under stirring for 2 h,
70 was added into the above mixture and stirred for another 5 h. After that, the mixture
71 was centrifuged and washed with DW for 3 times. The final Au@CSiC-SH/NH₂-CD
72 composite product was obtained by freeze-drying.

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74 *S1.5. Fabrication of the modified electrodes*

75 A glassy carbon electrode (GCE, 3 mm in diameter) was polished with 0.3 and 0.05
76 μm Al₂O₃ powder respectively and subsequently sonicated in ethanol and DW to
77 remove the physically adsorbed substance and dried in air. The CSiC, Au@CSiC,
78 Au@CSiC-SHCD, or Au@CSiC-SH/NH₂-CD was dissolved in DW respectively at a
79 concentration of 1.0 mg/mL with the aid of ultrasonic agitation for 20 min, resulting
80 in a homogeneous suspension. To prepare the materials modified electrode, 5 μL
81 of the suspension was dropped onto the electrode surface and dried at room
82 temperature. The obtained electrode was noted as the CSiC/GCE, Au@CSiC/GCE,
83 Au@CSiC-SHCD/GCE, and Au@CSiC-SH/NH₂-CD/GCE electrode.

84

85 *S1.6. Electrochemical measurements*

86 CV was carried out in 0.1 M PBS (pH 6.0) containing 1 mM o-NP and p-NP. DPV
87 was performed in 0.1 M PBS (pH 6.0) containing different concentrations of o-NP
88 and p-NP by scanning the potential from -0.2 to 1.2 V with a pulse amplitude of 0.05

89 V and a pulse width of 0.05 s. EIS was recorded in the frequency range from 10^{-1} to
90 10^{-5} Hz with an amplitude of 5 mV using 2.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple (1:1)
91 with 0.1 M KCl as supporting electrolyte. All the measurements were carried out at
92 room temperature.

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94 *S1.7. Molecular docking*

95 Crystal structure of β -CD (ID: IHEGEL) was obtained from Crystallography Open
96 Database (<http://www.crystallography.net/>). The structures of nitrophenol isomers were
97 constructed by the UCSF Chimera software. The β -CD and nitrophenol isomers
98 structures were fully optimized by the UCSF Chimera software. Hydrogen atoms
99 were added using the Dock Prep module. The GAFF force field and the AM1-BCC
100 charges were used. The optimized structures were used as a starting structure in the
101 docking study. For the molecular docking study, the molecular surface of the β -CD
102 molecule was generated using the DMS tool with a probe radius of 1.4 Å. The sphgen
103 module was applied to generate spheres surrounding the binding site. The Grid
104 module of DOCK6 was employed to generate Grid file which was used in scoring in
105 the subsequent docking procedure. The flexible docking method was utilized
106 producing 1000 different conformational orientations for the guest molecule. The
107 electrostatic interactions and van der Waals forces were calculated based on the grids.
108 Finally, clustering analysis with root-mean-square deviation (RMSD) threshold of 2.0
109 Å was performed to retain the best results.

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112 **References**

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