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1 **Highly-Sensitive SERS Detection of Tetracycline: Sub-**
2 **enhancement Brought by Light Scattering of Nano-diamond**

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15 **Abstract**

16 Antibiotic residues in wastewater cause a serious threat to aquatic environment and
17 human safety, and the development of robust strategies for detecting antibiotic residues
18 becomes critical. In this work, a surface-enhanced Raman scattering (SERS) substrate,
19 consisting of gold nanoparticles/nano diamond/carbon nitride (Au/ND/C₃N₄) hybrid,
20 which features enhanced light utilization and self-cleaning properties, is developed for
21 sensitive sensing of tetracycline. The fabricated Au/ND/C₃N₄ substrate effectively
22 captures target molecules and enhances Raman activities, owing to abundant functional
23 groups and light scattering effect of ND. Moreover, the heterostructure formed by Au
24 NPs, ND and C₃N₄ endows this SERS substrate with superior self-cleaning capability,
25 enabling its reusability. The Au/ND/C₃N₄ substrate exhibits high sensitivity (10⁻¹⁴ M),
26 desirable reproducibility (RSD=13.29%, n=238) and favourable stability (84.8% of
27 initial intensity after 30 days) for crystal violet probe. Also, no significant loss of SERS
28 or catalytic activity is observed during cyclic SERS detection. Likewise, the detection
29 of tetracycline at nanomolar level and cyclic SERS measurement jointly reveals its
30 prospect for recyclable detection of tetracycline. This work proposes a distinctive
31 strategy for enhancing SERS activity, and the developed self-cleaning Au/ND/C₃N₄
32 substrate represents a potential candidate for highly sensitive detection of antibiotic
33 residues in wastewater.

34 **Key words:** Surface-enhanced Raman scattering; nano diamond; sub-enhancement;
35 sensing; tetracycline

36 1. Introduction

37 An increasing concern on monitoring antibiotic residues in wastewater urges
38 the development of high-sensitivity and cost-effective analytical tools to curb
39 environmental pollution. The overuse and delayed metabolism of antibiotics lead
40 to their inevitable residues in water environment, incurring refractory pollution
41 sources [1-3]. From 2000 to 2015, global per-capita consumption of Watch
42 antibiotics experienced a huge increase of 90.9%, and Access antibiotics featured
43 an increase of 26.2% [4]. As an emerging category of pollutants, antibiotics
44 residues in wastewater could induce the emergence of multi-drug resistance
45 (MDR) microbes, antibiotic resistant bacteria (ARB) and antibiotic resistant
46 genes (ARGs) [5, 6]. Bacteria bred by antibiotic residues may sneak into human
47 body and trigger life-threatening infections. A recent report projected about 10
48 million deaths per year by 2050 associated with antibiotic resistance [7].
49 Thereupon, highly-sensitive detection of antibiotic residues in wastewater is
50 becoming more and more imperative for preventing environmental pollution and
51 suppressing production of infectious viruses.

52 Currently, available methods for the detection of antibiotic residues are
53 mainly involved in colorimetric [8], fluorescent [9], chemiluminescent (CL) [10],
54 electrochemical method [11], and electrochemiluminescence (ECL) [12].
55 Colorimetric, fluorescent, CL, and electrochemical suffer from the drawbacks of
56 low sensitivity, short life time, labelling required, and cumbersome pre-treatment
57 respectively [13, 14]. ECL exhibits poor reliability due to its easy vulnerability
58 by external environment [13]. Based on its ultra-sensitive features, compatibility
59 with aqueous solution, and label-free detection, SERS casts light on ultra-trace
60 molecular analysis for detecting antibiotics [15-17]. The enhancement of analyte
61 Raman signal is mainly due to local amplification of electromagnetic field from
62 the interaction between the incident laser beam and SERS substrate.
63 Electromagnetic (EM) enhancement and chemical (charge transfer, CT)
64 enhancement are two widely-accepted Raman enhancement mechanisms of
65 SERS substrates [18-20]. Applying nano-semiconductor to load gold

66 nanoparticles (Au NPs) may acquire satisfactory SERS performance by acting
67 on both EM and CT mechanisms. However, the restrictive effect of scant light
68 utilization on SERS activity of such substrates is seriously ignored.

69 Au NPs can offer long-range EM enhancement for Raman signals by means
70 of their strong localized surface plasmon resonance (LSPR) [21]. Controlling the
71 Au NPs morphology is regarded as a useful method to enhance Raman signals.
72 Constructing nano-tips and adjusting particle size can form SERS hot spots
73 through two SPR effects of lightning rod effect and resonance coupling effect
74 [22, 23]. Various morphologies of Au NPs like nano-needles, nano-stars, and
75 nano-trees have been fabricated and verified to exhibit high SERS sensitivity
76 [24-26]. A combination of nano-semiconductors and Au NPs may enhance
77 Raman signal through CT effect. The heterostructure formed by nano-
78 semiconductors and Au NPs may accelerate charge transfer to induce analyte
79 polarization, and offer short-range chemical enhancement of Raman signals.
80 ZnO, MoS₂, TiO₂, C₃N₄, etc. have been proven to be suited substrate materials
81 for fabricating high-sensitivity SERS substrates [27]. Among them, C₃N₄ is the
82 most promising candidate due to its strong adsorption capacity and superior
83 electronic conductivity [28-30]. Whereas, available works on Au/C₃N₄ substrate
84 ignores the enhancement effect of light utilization efficiency on SERS activity.
85 Increasing utilization efficient of Raman beam may be an efficacious strategy to
86 improve SERS performance. Exploitation of high laser utilization on Au/C₃N₄
87 substrates is a worth strategy to further improve its SERS activity.

88 Adopting effective light utilization to improve SERS performance of
89 Au/C₃N₄ substrate has pivotal matters of finding a suitable light utilization path
90 and revealing its action mechanism. Recent investigations on increasing light
91 absorption efficiency to improve SERS sensitivity focus on the fabrication of
92 light trapping structures [31-34]. A combination of precious metals and special
93 structures such as nano-cavities, nano-spirals, and Si micro-pyramid can achieve
94 superior light trapping effect, and those developed structures generate local
95 electromagnetic enhancement due to resonant cavity effect [35-37]. However, the

96 heavy reliance of the above-mentioned SERS substrates on high-precision
97 manufacturing processes restricts their wide application. Instead, light scattering
98 effect offers a hopeful avenue to improve light utilization. The introduction of
99 nano-diamond (ND) with high light scattering features into the SERS substrate
100 is expected to implement efficient utilization of Raman laser through a handy
101 process. Moreover, the presence of abundant functional groups on ND surface
102 may act as a powerful tool to capture analyte molecules for improving substrate
103 enrichment capacity. Regrettably, it is rare to see a systematic report about
104 adopting light scattering effect of ND to enhance SERS substrate performances.
105 Here, we proposed a strategy to improve SERS activity by means of light
106 scattering, and fabricated Au/ND/C₃N₄ hybrids for SERS detection of a widely
107 used antibiotic tetracycline. A systematic investigation on the microstructure,
108 optical properties and SERS activities of the designed substrate was conducted
109 to reveal improvement mechanism of ND on SERS performance, promoting its
110 application for the detection of antibiotic residues in wastewater.

111 In this work, ND/C₃N₄ hybrid with holey structure was fabricated in one
112 step with the help of Z204 catalyst, and Au/ND/C₃N₄ hybrid with heterohedral
113 Au NPs was produced by introduction of active agent cetyltrimethylammonium
114 bromide (CTAB). A systematic characterization was conducted on optical
115 properties, microstructure and chemical features of the prepared samples. SERS
116 performances of Au/ND/C₃N₄ substrate with self-cleaning features was assessed
117 using crystal violet as a probe molecule, as well as its application for tetracycline
118 assay. Consequently, ND improvement mechanism was revealed via both
119 experimental data and finite difference time domain (FDTD) simulation.

120 **2. Experimental**

121 **2.1 Reagents:** All reagents were of analytical grade. Nitric acid, sulfuric acid,
122 melamine, sodium citrate and CTAB were purchased from Shanghai Aladdin
123 Biochemical Technology Co., Ltd. Crystal violet (CV), tetracycline and chloroauric
124 acid (HAuCl₄, 48~50%) were purchased from Shanghai Maclean Biochemical
125 Technology Co., Ltd. Nano-diamonds (~10 nm, 99%) and Z204 catalyst were

126 purchased from Nanjing Hongde Nanomaterials Co., Ltd. and Sichuan Tianyi
127 Technology Co., Ltd., respectively.

128 **2.2 Characterizations:** Optical properties of the prepared samples were investigated
129 by UV-vis diffuse reflectance spectra (Lambda 750, PE). Microtopography and
130 surface element distribution were observed by scanning electron microscopy (SEM,
131 SUPRA55, Zeiss) and transmission electron microscopy (TEM, Talos F200X,
132 ThermoFisher). Element composition and chemical state of Au/ND/C₃N₄ hybrid were
133 determined by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, ThermoFisher).
134 Phase composition was acquired with an X-ray diffractometer (XRD, D8 Advance,
135 Bruker). Surface functional group composition was assessed with Fourier Transform
136 InfraRed Spectrometer (FT-IR, Specture 100, Peikin Elmer). Surface area were
137 acquired with a specific surface and pore size analyzer (ASAP2020, Micromeritics).
138 Adsorption capacity was investigated by UV-vis absorption spectrophotometry
139 (Lambda 750, PE). SERS performances were recorded by HORIBA Raman microscope
140 (LabRAM HR Evolution, Jobin Yvon; $\lambda_{\text{ex}}=633$ nm). Photocatalytic experiments were
141 conducted using a photoreactor with a xenon lamp (XE-JY500, Beijing Newbit
142 Technology Co., Ltd.).

143 **2.3 Pre-treatment of ND** *Step I*, acid pickling was utilized to remove metal impurities
144 in ND. ND powders (1 g) were dispersed in a mixed solution of nitric acid (5 mL) and
145 sulfuric acid (15 mL), and then the mixture was heated at 40 °C for 1 h under stirring.
146 Subsequently, the ND were washed with ultrapure water to neutral, and grey ND
147 powder was thus obtained after centrifugation and drying. *Step II*, a heat treatment was
148 carried on ND to decompose the *sp*²-C on ND surface. ND powder in *Step I* was
149 calcined at 420 °C for 1 h to produce purified ND.

150 **2.4 Fabrication of ND/C₃N₄ hybrid.** Melamine and purified ND were used as raw
151 materials to prepare ND/C₃N₄ hybrid. A mixture (4 g) of melamine and ND was fully
152 ground (>120 min) and placed in a small crucible, wherein, the mass percentages of
153 ND were set to 1%, 3%, 5%, 7%, and 9%. Afterward, the small crucible was placed in
154 a large crucible containing Z204 catalyst (2 pieces), and the covered crucible was
155 calcined in a muffle furnace. Furnace temperature was raised to 550 °C at a rate of 5

156 °C/min, and held for 4 h. The fabricated ND/C₃N₄ hybrid was washed with ultrapure
157 water and then dried and collected. The colour of ND/C₃N₄ hybrid gradually changed
158 from light yellow to brown upon increasing of ND content.

159 **2.5 Fabrication of Au/ND/C₃N₄ hybrid.** Gold nanoparticles (Au NPs) loading was
160 accomplished through H₂AuCl₄ reduction with sodium citrate in presence of CTAB to
161 induce overgrowth of Au NPs and produce heterohedral morphology. C₃N₄/ND (20
162 mg), CTAB (0.11 g) and H₂AuCl₄ solution (1.5 mL, 5 wt%) were dispersed in ultrapure
163 water (17 mL). The resulting mixture was then sonicated for 10 min and stirred for 1 h.
164 The mixture was transferred to a hydrothermal reactor, and sodium citrate solution (0.1
165 M, 1.5 mL) was added. Thereafter, the reactor was heated and stirred at 110 °C for 5 h.
166 After cooling, the mixture was centrifuged (8000 rpm), and Au/ND/C₃N₄ hybrid was
167 thus collected after drying.

168 **2.6 Photocatalytic activity measurements.** Photocatalytic activities of Au/ND/C₃N₄
169 hybrid were assessed through the degradation of CV and tetracycline. Firstly, the hybrid
170 (50 mg) was immersed in a CV solution (60 mL, 10⁻⁵ M) and kept in dark for 30 min
171 to ensure the adsorption-desorption equilibrium. Subsequently, the suspension was
172 irradiated under a xenon lamp (500 W). CV absorbance at different time intervals was
173 measured to reflect the photodegradation efficiency. Photodegradation of tetracycline
174 was carried out under the same experimental conditions as for CV, except that the
175 amount of used catalyst was 30 mg. Moreover, photocatalytic activities of pure ND and
176 C₃N₄ were measured under the same condition.

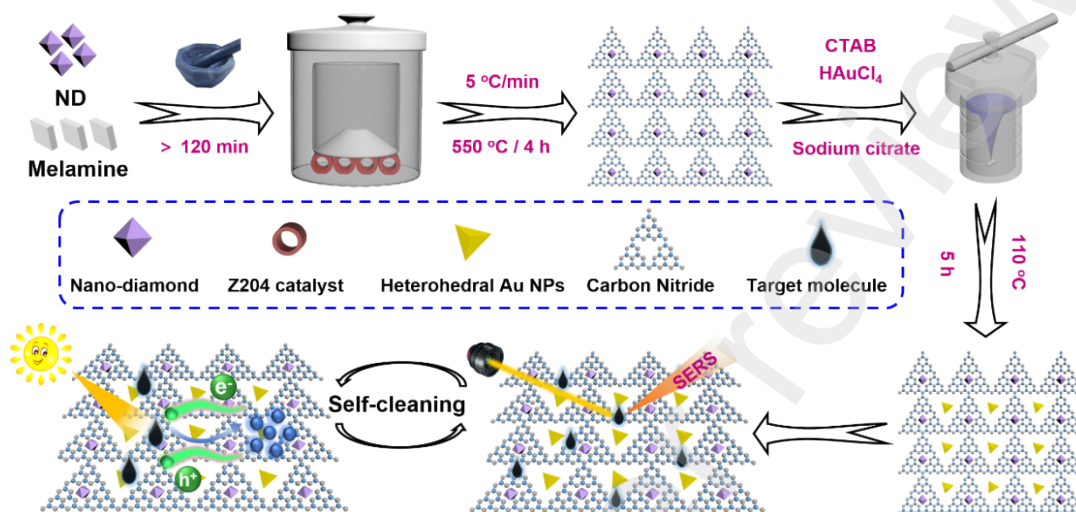
177 **2.7 SERS measurements.** Au/ND/C₃N₄ hybrid (20 mg) was mixed with analyte
178 solution (2 mL) for 30 min to ensure sufficient enrichment of target molecules. The
179 mixture was transferred to a silicon wafer and dried for 5 min to form uniform spots
180 (diameter of 4 mm). During the measurement, the laser power and exposure time were
181 respectively set as 5 mW and 5 s.

182 **2.8 Self-cleaning SERS measurements.** The Au/ND/C₃N₄ hybrid after SERS
183 investigation was collected, washed with deionized water, and irradiated with a xenon
184 lamp (500 W) for 120 min. After that, it was washed with deionized water and

185 centrifuged for 2 times to ensure removal of the residues. After drying, the hybrid was
186 collected and applied for another cycle of SERS detection.

187 3. Results and discussion

188 3.1. Fabrication and characterization

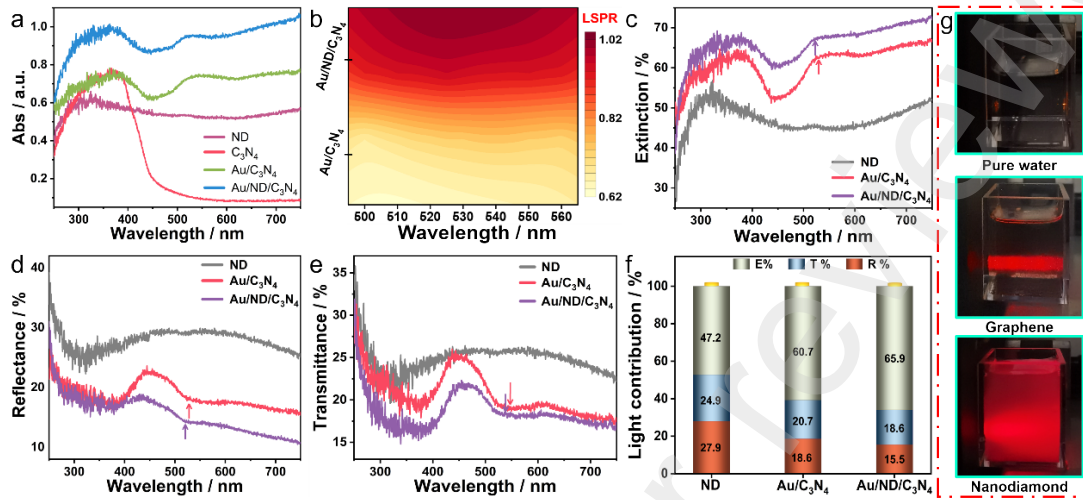


189

190 **Figure 1.** Scheme of the fabrication process and self-cleaning features of the
191 Au/ND/C₃N₄ hybrids

192 Fig. 1 illustrates the fabrication process and self-cleaning features of the
193 Au/ND/C₃N₄ hybrid. The synthesis of Au/ND/C₃N₄ hybrid includes two steps.
194 Step I, the purified ND (Fig. S1a) with a mean size of ~12 nm was thoroughly
195 mixed with melamine, and the mixture was calcined in presence of Z204 catalyst
196 to produce holey ND/C₃N₄ hybrid (Fig. S1b). Z204 catalyst decomposed
197 ammonia gas (NH₃) generated from thermal polymerization of melamine, and
198 accelerated NH₃ escape to generate cavities [38]. Step II, ND/C₃N₄ hybrid was
199 dispersed into a mixed solution of chloroauric acid and sodium citrate, and a
200 hydrothermal reaction was conducted to synthesize Au/ND/C₃N₄ hybrid with an
201 in-situ loading of Au NPs. In this process, CTAB surfactant was introduced to
202 induce overgrowth of Au NPs, forming heterohedral structures with rich tips.
203 Benefiting from abundant functional groups, π - π conjugate and electrostatic
204 interactions of ND and C₃N₄, the analyte can be quickly and efficiently enriched
205 on Au/ND/C₃N₄ substrate [29, 39]. Moreover, the nano-tips of the heterohedral
206 Au NPs can offer more SERS hot spots, which are beneficial for high detection

207 sensitivity. After completing SERS detection, Au/ND/C₃N₄ substrate may have
 208 a self-cleaning property by means of analyte photodegradation under visible light
 209 irradiation.



210
 211 **Figure 2.** (a) UV-vis diffuse reflectance spectra (DRS) of ND, C₃N₄, Au/C₃N₄
 212 and Au/ND/C₃N₄ hybrid. (b) LSPR intensity contrast of Au/C₃N₄ and
 213 Au/ND/C₃N₄. (c-e) Extinction (E), reflectance (R), and transmittance (T) (ERT)
 214 spectra of ND, Au/C₃N₄ and Au/ND/C₃N₄ in 250-750 nm region. (f) Light
 215 contribution variation of ND, Au/C₃N₄ and Au/ND/C₃N₄. (g) Optical images of
 216 pure water, graphene aqueous solution and nanodiamonds aqueous solution
 217 under the irradiation of a 633 nm laser.

218 UV-vis DRS was conducted to investigate the optical properties of samples,
 219 as displayed in Fig. 2a. ND exhibits a broad absorption range from 300-700 nm,
 220 confirming its positive effect on improving light utilization. C₃N₄ has an
 221 absorption edge at ~453 nm, and exhibits a scant light absorption especially in
 222 visible range. Au/C₃N₄ behaves an obviously red-shift of absorption edge and
 223 enhanced light absorption than that of C₃N₄. A new absorption peak can be
 224 observed at 534 nm, assigned to resonance peak of Au NPs. The improved optical
 225 properties of Au/C₃N₄ may be ascribed to the strong LSPR effect of Au NPs [40].
 226 For Au/ND/C₃N₄, the absorption edge continues to red-shift and light absorption
 227 is further enhanced. In addition, Au NPs absorption peak of Au/ND/C₃N₄ blue-
 228 shifts to 531 nm and features a stronger intensity than that of Au/C₃N₄, as shown

229 in Fig 2b. These results offer direct evidences that the introduction of ND can
230 enhance light utilization and strengthen LSPR effect of plasma in Au/ND/C₃N₄
231 hybrid.

232 Subsequently, ERT spectra were determined to assess the light utilization of
233 fabricated samples, wherein E+R+T=100%, as depicted in Fig. 2c-e. ND
234 acquires the highest reflectance than that of Au/C₃N₄ and Au/ND/C₃N₄,
235 indicating its superior light scattering capability (Fig. 2d). In Fig. 2c, the
236 extinction of Au/ND/C₃N₄ exhibits a huge hoist than that of Au/C₃N₄, proving
237 an effective enhancement of ND on light utilization. Moreover, the extinction of
238 Au NPs for Au/C₃N₄ has a resonance peak at~534 nm, while Au/ND/C₃N₄
239 exhibits the Au NPs resonance peak at~531 nm. The blue-shift of Au NPs
240 resonance peak may be due to the variation of Au NPs morphology and size [41].
241 Transmittance spectra of ND, Au/C₃N₄ and Au/ND/C₃N₄ are shown in Fig. 2f.
242 In general, the transmittance drop corresponds to the extinction peak position
243 [42]. The transmittance spectra show a blue shift of Au NPs resonance peak as
244 expected. Hereafter, mean ERT are estimated to reflect light contribution
245 variation of ND, Au/C₃N₄ and Au/ND/C₃N₄, as displayed in Fig. 2f. It is apparent
246 that Au/ND/C₃N₄ acquires the highest extinction and is 1.09 times of that
247 Au/C₃N₄. Such enhancement of extinction reveals favourable function of ND on
248 light utilization. Fig. 2g shows the optical images of pure water, graphene
249 aqueous solution and ND aqueous solution under the irradiation of a 633 nm
250 laser. The observed scattered light area in ND aqueous solution illustrates its
251 distinctive light scattering characteristic, different from other carbon materials
252 like graphene. The same results can also be observed in UV-vis spectra of the
253 above samples, as shown in Fig. S2. More commendably, the light-scattering
254 property of ND remains after ND are hybridized with other materials (Fig. S3).
255 Thus, it is reasonable to speculate that the light scattering of ND may improve
256 light utilization of samples for a better SERS activity.

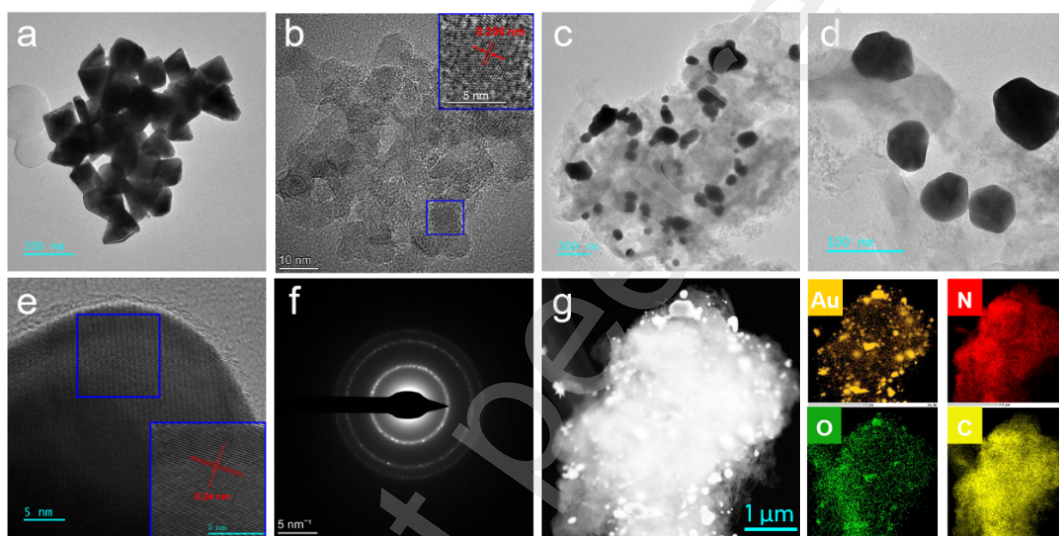
257 Effect of ND content was further considered on optical properties of
258 Au/ND/C₃N₄ hybrid. Fig. S4 depicts the UV-vis DRS of Au/ND/C₃N₄ hybrids

259 with five ND contents, as well as resonance peak variation of Au NPs. As shown
260 in Fig. S4, LSPR intensity initially enhances and then lowers with the increase
261 of ND content, and the resonance peak gradually blue-shifts. Au/ND/C₃N₄ hybrid
262 with a ND content of 5% features the strongest resonance peak intensity, and is
263 most promising to acquire superior SERS activity. Fig. S5- Fig.S7 depict the
264 ERT spectra and mean ERT values of the five samples. Au/ND/C₃N₄ hybrid with
265 a ND content of 7% has the biggest extinction, and is slightly higher than that of
266 5% ND content. Excessive ND content (9%) may induce an increase in
267 reflectance, and reduces the extinction ratio of Au/ND/C₃N₄ hybrid, as shown in
268 Fig. S7.

269 ND content for Au/ND/C₃N₄ substrate was optimized to acquire a better
270 SERS signal response with crystal violet (CV) probe. Fig. S8 depicts the SERS
271 activity variation of Au/ND/C₃N₄ substrates prepared with five ND contents. The
272 peak at ~1174 cm⁻¹, assigned to C-H in-plane bending mode of CV molecule, is
273 selected as a fingerprint signal of CV [43]. SERS activity initially raises then
274 drops with the increase of ND content. Au/ND/C₃N₄ substrate with 5% ND
275 exhibits the strongest SERS signal. Excess ND content induces an attenuation of
276 the SERS activity due to the strong fluorescence of ND. Considering the optical
277 properties and SERS activity, Au/ND/C₃N₄ with 5% ND is selected as optimal
278 substrate to conduct the following measurements.

279 TEM was used to observe the microstructure and morphology of the
280 prepared samples. Fig. 3a and Fig. S9 show TEM images of Au NPs with
281 heterohedral morphology. Such heterohedral morphology with nano-tips could
282 enhance EM efficacy by mean of "lightning rod" effect [44]. Micromorphology
283 of ND/C₃N₄ hybrid is depicted in Fig. S1b and Fig. 3b. ND are incorporated into
284 C₃N₄ nanolayers in form of small agglomerates and form strong interactions with
285 C₃N₄ (Fig. S1b). The formation of agglomerates is due to the interaction of
286 abundant functional groups on ND [45]. Different from pure ND (Fig. S1a), ND
287 agglomerates in ND/C₃N₄ hybrid exhibit a smaller mean size. This may be that
288 C₃N₄ acts as a stabilizer and inhibits ND agglomeration during the thermal

289 polymerization [46]. HRTEM image of ND/C₃N₄ reveals a tight bonding of ND
 290 agglomerates with C₃N₄ (Fig. 3b). In Fig. 3b, clear lattice fringes with an
 291 interplanar spacing of 0.206 nm can be observed, corresponding to the (111) facet
 292 of ND [47]. This provides direct evidence for occurrence of ND on C₃N₄
 293 nanosheets. ND incorporation introduces rigid materials into C₃N₄ stacked
 294 layers, expands lamellar spacing of C₃N₄ layers and broadens the nanochannels,
 295 which could enhance the enrichment of analyte and accelerate charge transfer
 296 during SERS process.

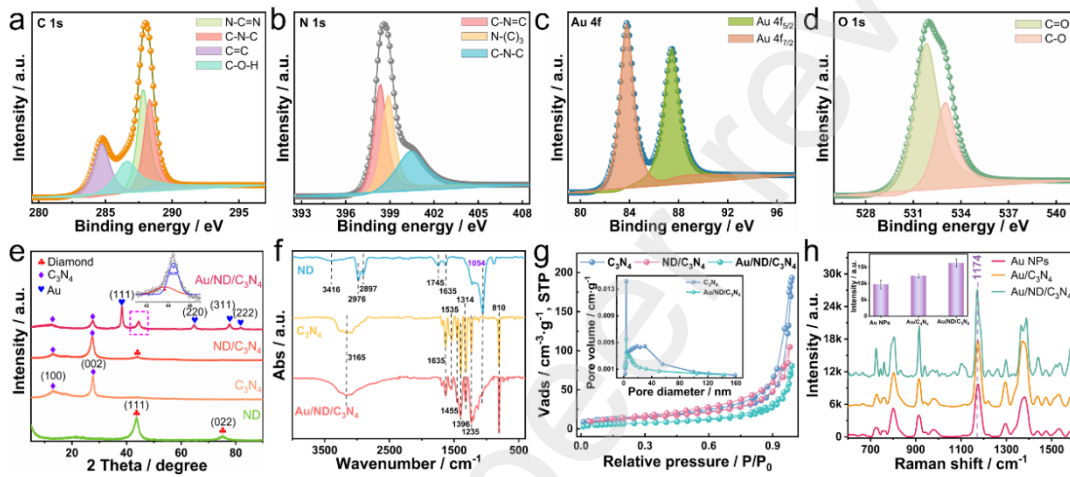


297

298 **Figure 3.** (a) TEM image of heterohedral Au NPs. (b) HRTEM image of
 299 ND/C₃N₄ hybrids. (c-e) TEM images of Au/ND/C₃N₄ hybrids at three different
 300 magnifications. (f) Selected area electron diffraction pattern of Au/ND/C₃N₄. (g)
 301 Elemental mapping images of Au/ND/C₃N₄.

302 Fig. 3c-e display the TEM images of Au/ND/C₃N₄ hybrid. As shown in Fig.
 303 3c, Au NPs with a mean size of 96 nm are uniformly decorated on the surface
 304 and stacked layers of ND/C₃N₄, whereas, the particle size difference between Au
 305 NPs is large. At a higher magnification, abundant cavities can be observed on
 306 C₃N₄ nanosheets (Fig. S10). The produced cavities may enlarge adsorption
 307 capacity of the hybrid. Fig. 3d reveals that Au NPs in Au/ND/C₃N₄ hybrid retain
 308 heterohedral morphology with nanotips. And the nanotips display lattice fringes
 309 with an interplanar spacing of 0.24 nm, corresponding to the (111) facet of Au

310 NPs, as shown in Fig. 3e. Selected area electron diffraction pattern of
 311 Au/ND/C₃N₄ hybrid manifests three ring-shaped diffuse diffraction patterns,
 312 corresponding to the (111), (220) and (311) facets of ND, respectively (Fig. 3f).
 313 The diffraction ring also confirms the tight binding of ND and C₃N₄. The uniform
 314 distribution of Au, C, and N element in Fig. 3g indicates successful synthesis of
 315 Au/ND/C₃N₄ hybrid. The presence of O element may be assigned to oxygen-
 316 containing functional groups of ND and moisture adsorbed by the hybrid.



317
 318 **Figure 4.** (a-d) XPS high-resolution spectra of the C 1s, N 1s, Au 4f and O 1s of
 319 Au/ND/C₃N₄ hybrid. (e) XRD patterns of ND, C₃N₄, ND/C₃N₄ and Au/ND/C₃N₄
 320 hybrid. (f) FT-IR spectra of ND, C₃N₄ and Au/ND/C₃N₄ hybrid. (g) Nitrogen
 321 adsorption-desorption isotherms of C₃N₄, ND/C₃N₄ and Au/ND/C₃N₄, the insert
 322 is the pore size distribution profiles of C₃N₄ and Au/ND/C₃N₄. (h) SERS spectra
 323 of 10⁻⁴ M CV adsorbed onto the Au NPs, Au/C₃N₄ and Au/ND/C₃N₄ substrates
 324 accordingly.

325 XPS was employed to analyse chemical composition and surface chemical
 326 state of Au/ND/C₃N₄ hybrid. XPS survey spectrum reveals four distinct peaks
 327 corresponding to C 1s, N 1s, Au 4f and O 1s (Fig. S11), indicating successful
 328 synthesis of Au/ND/C₃N₄ hybrid. The high-resolution spectrum of the C 1s is
 329 shown in Fig. 4a. It can be deconvoluted into four characteristic bands located at
 330 284.7, 286.6, 287.8, 288.3 and 286.6 eV, assigned to pure graphitic sites in the
 331 CN matrix (C=C), *sp*²-C attached to NH₂ group in the aromatic ring (N-C=N),
 332 *sp*²-C bonded to N in an aromatic ring (C-N-C) and *sp*³-C of C-O-H group,

333 respectively [48, 49]. The emergence of sp^3 -C concretely confirms successful
334 residing of ND. Likewise, the high-resolution spectrum of N 1s can be
335 deconvoluted into three bands of 398.3, 398.9 and 400.4 eV (Fig. 4b),
336 corresponding to C-N=C, N-(C)₃, and C-N-C coordination accordingly [50]. In
337 Fig. 4c, the spectrum of Au 4f comprises two peaks ascribed to Au 4f_{5/2} (83.7
338 eV) and Au 4f_{7/2} (87.4 eV) [51]. The high-resolution plot of O 1s could be curve-
339 fitted with two bands due to C=O (531.8 eV) and C-O (533.0 eV) (Fig. 4d),
340 revealing that ND addition introduces new functional groups into Au/ND/C₃N₄
341 hybrid [52].

342 XRD was used to characterize the phase structure of ND, C₃N₄, ND/C₃N₄
343 and Au/ND/C₃N₄, as shown in Fig. 4e. ND displays two sharp peaks at 2 theta of
344 43.9° and 75.3°, corresponding to the (111) and (220) facets of diamond,
345 respectively [53]. Besides, a broad peak at 2 theta of 26° is attributed to the
346 graphite phase on ND surface. This peak reveal that the purified ND powder
347 consists of diamond and trace graphite [52]. C₃N₄ exhibits two peaks located at
348 13.1° and 27.6° assigned to (100) and (002) facets, respectively. The two peaks
349 are sequentially assigned to in-plane structural packing motif of tri-s-triazine
350 units and stacking of the conjugated aromatic system [54]. For ND/C₃N₄ hybrid,
351 the characteristic peaks of C₃N₄ and ND are well preserved, indicating a
352 favourable interaction of ND and C₃N₄. The absence of the (220) peak of ND
353 may be due to the small amount of used ND. The XRD pattern of Au/ND/C₃N₄
354 hybrid features new peaks at 2 theta of 38.2°, 64.5°, 77.6° and 81.8°,
355 corresponding to the (111), (220), (311) and (222) facets of Au NPs, respectively
356 [29]. The peak at 44.1° can be deconvoluted into (111) facet (43.9°) of ND and
357 (200) facet (44.3°) of Au NPs, as shown in inset of Fig. 4e.

358 Fig. S12 displays the Raman spectra of ND, C₃N₄, ND/C₃N₄ and
359 Au/ND/C₃N₄. A sharp peak at 1332 cm⁻¹ assigned to sp^3 -C of diamond can be
360 observed in the Raman spectrum of ND. The rough baseline is caused by strong
361 fluorescence under laser excitation [55]. Moreover, no characteristic peak of sp^2 -
362 C is evident in the Raman spectrum. This may involve two aspects: (1) the

363 characteristic peak intensity of sp^2 -C is weak due to its trace amount; (2) the peak
364 is annihilated by the strong fluorescence. Four peaks are observed at 683, 775,
365 1215 and 1460 cm^{-1} in the case of C_3N_4 , and are all ascribed to vibration modes
366 of CN heterocycles [56]. For both ND/ C_3N_4 and Au/ND/ C_3N_4 , the characteristic
367 peaks of C_3N_4 are still obvious while the characteristic peak of ND is not seen.
368 The difference lays in that the broad peak at 1317 cm^{-1} of C_3N_4 drifts to 1328
369 cm^{-1} after adding ND. The peak shift may be attributed to interaction of ND and
370 C_3N_4 , in good agreement with XPS data.

371 Furthermore, FT-IR spectra were acquired to analyse the surface functional
372 groups of the prepared samples, as shown in Fig. 4f. It is apparent that ND surface
373 embraces abundant functional groups, and these functional groups are favourably
374 introduced into Au/ND/ C_3N_4 hybrid. Characteristic peaks at 1054, 1635, 1745
375 and 3416 cm^{-1} of ND correspond to C–O stretching vibrations of epoxy groups,
376 O–H deformation vibrations of COOH groups, C=O stretching vibrations of
377 COOH groups and -OH stretching, respectively [57]. The two peaks at 2897 and
378 2976 cm^{-1} are assigned to C-H stretching vibration of saturated carbon [58]. In
379 the FT-IR spectrum of C_3N_4 , the characteristic peaks at 1235, 1314, 1396, 1455,
380 1535, and 1635 cm^{-1} are assigned to typical stretching modes of CN heterocycles.
381 The peaks at 810 and 3144 cm^{-1} correspond to breathing mode of triazine units
382 and stretching vibrations of -NH, respectively [59]. For Au/ND/ C_3N_4 hybrid, the
383 characteristic peaks of C_3N_4 remain clear and the peak at 1054 cm^{-1} of ND can
384 still be observed, suggesting that synthesis process of Au/ND/ C_3N_4 does not
385 break the chemical structure of each component. Copious functional groups of
386 Au/ND/ C_3N_4 hybrid may strengthen its self-cleaning capability and promote
387 analyte enrichment.

388 N_2 physical adsorption isotherm was utilized to discriminate surface area
389 difference among C_3N_4 , ND/ C_3N_4 and Au/ND/ C_3N_4 . Fig. 4g depicts N_2
390 adsorption-desorption isotherms of C_3N_4 , ND/ C_3N_4 and Au/ND/ C_3N_4 . The
391 surface area and pore volume of the prepared samples gradually decrease with
392 loading ND and Au NPs in sequence. C_3N_4 features an IV-type isotherm with

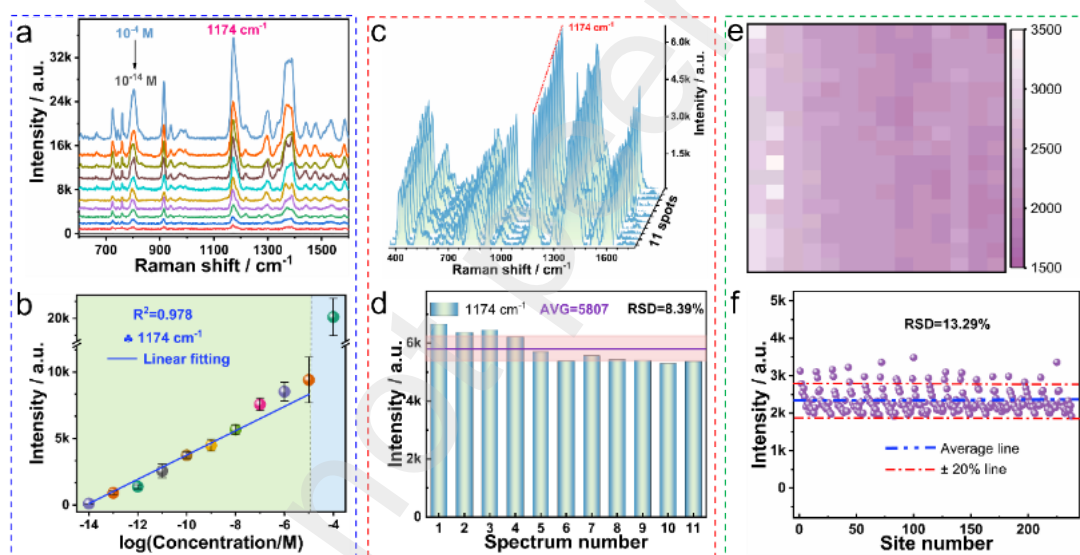
393 H3-type hysteresis loop under high relative pressure, indicating the construction
394 of copious mesopores with the help of Z204 catalyst [60]. Brunauer-Emmett-
395 Teller (BET) surface area of C_3N_4 is $48.39 \text{ m}^2 \text{ g}^{-1}$. S_{BET} of ND/ C_3N_4 hybrid drops
396 to $44.76 \text{ m}^2 \text{ g}^{-1}$. The slight decrease of S_{BET} may be attributed to pore blocking
397 caused by ND embedding in the cavities. S_{BET} of Au/ND/ C_3N_4 hybrid sharply
398 declined to $24.26 \text{ m}^2 \text{ g}^{-1}$, suggesting that numerous Au NPs are embedded in
399 C_3N_4 mesopores. Furthermore, Barrett-Joyner-Halenda (BJH) was applied to
400 deduce pore size distribution (PSD) plots of C_3N_4 and Au/ND/ C_3N_4 , as shown in
401 the inset of Fig. 4g. Pore volume of Au/ND/ C_3N_4 is reduced to $0.125 \text{ cm}^3 \text{ g}^{-1}$, as
402 compared with its counterpart C_3N_4 ($0.299 \text{ cm}^3 \text{ g}^{-1}$). It is reasonable to speculate
403 that Au NPs grow in C_3N_4 mesopores and are embedded in C_3N_4 nanosheets. The
404 holey structure of C_3N_4 is favourable for anchoring Au NPs and inhibiting their
405 agglomeration to improve the reproducibility of SERS signals.

406 To directly identify the effect of ND on SERS activity, SERS signal
407 variation of CV probes on Au NPs, Au/ C_3N_4 and Au/ND/ C_3N_4 substrates were
408 compared. Fig. 4h depicts the Raman spectra of 10^{-4} M CV adsorbed onto the
409 three substrates. Pure Au NPs substrate has the lowest SERS activity, which may
410 be due to its weak enrichment ability [61]. Au/ C_3N_4 substrate exhibits an
411 enhanced SERS activity. This can be attributed to two following facts: (1) the
412 holey C_3N_4 ameliorates substrate enrichment capacity, (2) the heterostructure of
413 Au NPs and C_3N_4 accelerates polarization of CV molecules [62]. Au/ND/ C_3N_4
414 substrate acquires the strongest SERS signal, which provides the most direct
415 evidence for SERS activity improvement upon ND addition. Moreover, the
416 enhancement factor (EF) of the three substrates, which is calculated based on
417 Fig. 4h and Fig. S13, confirms the same result. Au/ND/ C_3N_4 substrate has the
418 highest EF of 6.67×10^6 , which is 2.01 and 1.58 times of that Au NPs (3.32×10^6)
419 and Au/ C_3N_4 (4.21×10^6) substrates, respectively.

420 3.2. SERS performance of self-cleaning Au/ND/ C_3N_4 substrate

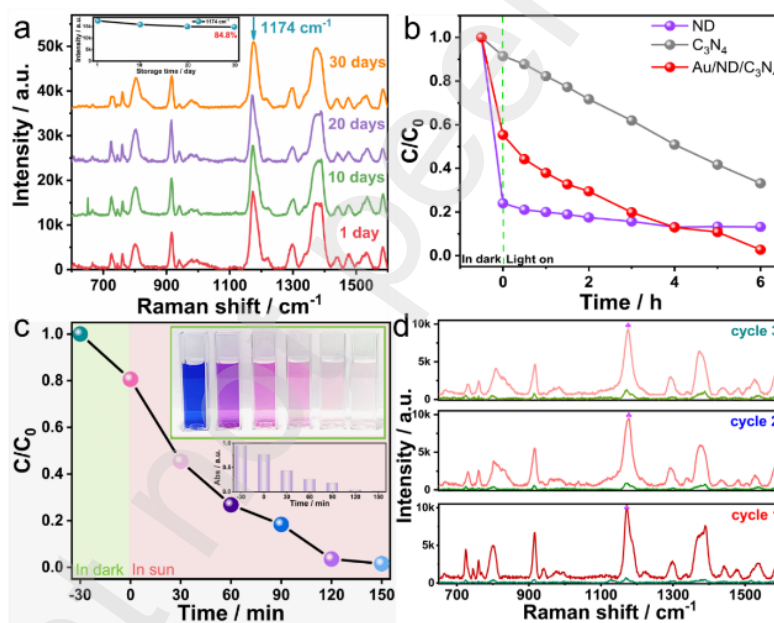
421 A systematic investigation was conducted on sensitivity, reproducibility and
422 stability of the fabricated Au/ND/ C_3N_4 substrate to assess its application prospect.

423 Substrate sensitivity was measured by SERS spectra of CV solutions with different
 424 concentrations, as shown in Fig. 5a, b. In Fig. 5a, the Raman intensity at 1174 cm⁻¹
 425 gradually drops upon decreasing CV solution concentration. Visible characteristic
 426 peaks can be observed even for a CV concentration of 10⁻¹⁴ M, indicating a high
 427 sensitivity of the substrate. Furthermore, logarithmic concentration and Raman
 428 intensity are linearly fitted to determine quantitative SERS detection, as shown in Fig.
 429 5b. The logarithm concentration of CV maintains a good linear relationship with SERS
 430 intensity in a concentration range from 10⁻¹⁴ to 10⁻⁵ M. The calibration equation is:
 431 $I_{SERS}=912 \lg C_{CV}+12874$, and the linear correlation coefficient (R^2) is 0.978. No SERS
 432 signals are recorded when CV concentration is lower than 10⁻¹⁴ M as only very few
 433 molecules lay at the laser spot area.



434
 435 **Figure 5.** (a) SERS spectra of CV in a concentration range from 10⁻⁴ to 10⁻¹⁴ M recorded
 436 from Au/ND/C₃N₄ substrate. (b) Linear calibration plot of the SERS intensity at 1174
 437 cm⁻¹ versus logarithmic CV concentration. (c) SERS spectra of 10⁻⁸ M of CV obtained
 438 on random 11 spots from Au/ND/C₃N₄ substrate. (d) The corresponding histogram of
 439 intensity distribution of the 11 random spots at 1174 cm⁻¹. (e) SERS mappings
 440 (150×170 μm², step size of 10 μm) of the peak value at 1174 cm⁻¹ recorded from
 441 Au/ND/C₃N₄ substrates exposed to 10⁻¹⁰ M CV solution. (f) Intensity distribution at
 442 1174 cm⁻¹ for all the 238 points in SERS mapping.

443 High reproducibility of SERS signals is another indispensable index for practical
 444 quantitative assay. Herein, reproducibility was determined by recording SERS signal
 445 variation of random substrate sites and calculating the relative standard deviation (RSD)
 446 value. Fig. 5c, d depicts SERS spectra of 10^{-8} M CV at 11 random points on
 447 Au/ND/C₃N₄ substrate and the intensity distribution histogram at 1174 cm⁻¹. RSD value
 448 of the 11 points is calculated to be 8.39%. Moreover, 238 random points in 150×170
 449 μm² region were selected to conduct point-by-point measurement for verifying
 450 detection reliability of the SERS substrate using a 10^{-10} M CV solution. Fig. 5e reveals
 451 the mapping diagram of the peak intensity at 1174 cm⁻¹, where the SERS signal is
 452 uniformly distributed. RSD value of the 238 random points is 13.29% (Fig. 5f),
 453 suggesting an acceptable substrate reliability to generate reproducible SERS signals.



454
 455 **Figure 6.** (a) SERS spectra of 10^{-4} M CV collected from Au/ND/C₃N₄ substrate with
 456 different storage times. (b) Photocatalytic degradation curves of 10^{-5} M CV in the
 457 presence of ND, C₃N₄ and Au/ND/C₃N₄ hybrid. (c) Photocatalytic degradation curves
 458 of 10^{-5} M CV in the presence of Au/ND/C₃N₄ hybrid (under sunlight illumination from
 459 12:00 to 14:30). (d) Self-cleaning test of Au/ND/C₃N₄ substrate through three cycles of
 460 SERS detection and photocatalytic degradation of 10^{-5} M CV.

461 Furthermore, stability was assessed by SERS signal variation of CV on
 462 Au/ND/C₃N₄ substrates with different storage times. The storage condition was air

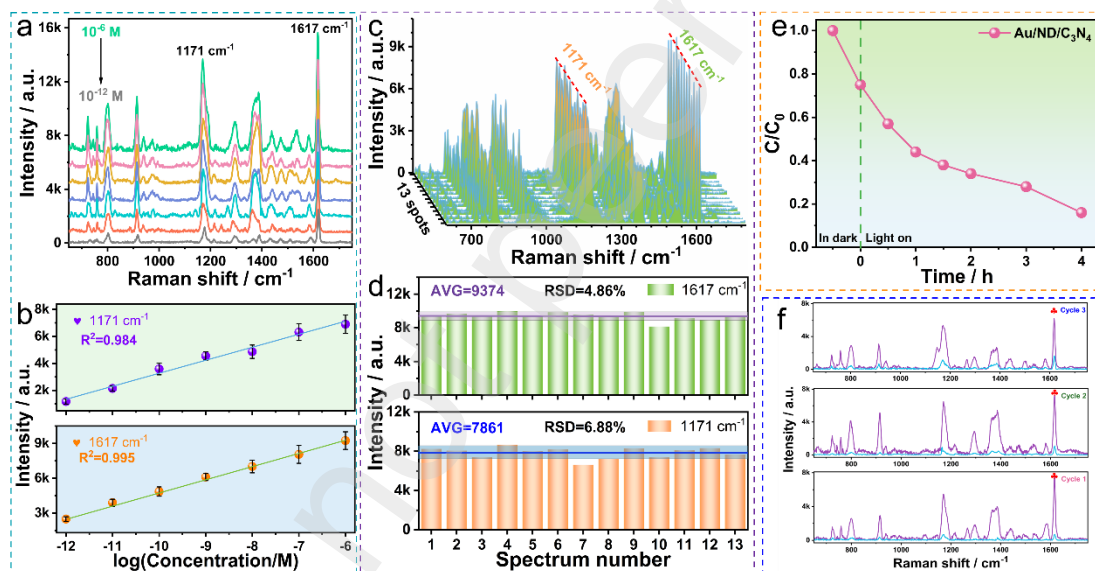
463 environment, and the concentration of CV solution was 10^{-4} M. Fig. 6a depicts SERS
464 spectra of CV on Au/ND/C₃N₄ substrates with 1-, 10-, 20- and 30-days storage. The
465 signal retention is 84.8% after 30 days, indicating a superior environmental stability.
466 Such stability may be attributed to two aspects: (1) good chemical stability of Au NPs;
467 (2) charge transfer between Au NPs and ND/C₃N₄ hybrid [63].

468 Apart from admirable SERS performance, the self-cleaning capability of
469 Au/ND/C₃N₄ is an essential factor for its actual application. To investigate this
470 capability, photocatalytic activities of Au/ND/C₃N₄ hybrid, as well as ND and C₃N₄
471 were assessed for the decomposition of CV under visible light irradiation. The
472 degradation rates were determined by recording the change of UV-vis spectra at 590
473 nm. And C/C_0 was calculated to mirror the degradation rate value, wherein, C_0 and C
474 were the initial absorbance and absorbance at a certain reaction time, respectively. Fig.
475 6b depicts the degradation curves of CV solution in presence of the above three
476 samples. Au/ND/C₃N₄ hybrid exhibits the best photocatalytic activity, and its
477 degradation rate is 97.3% after 6 h visible light irradiation. Degradation rate of
478 Au/ND/C₃N₄ is nearly 1.5 times higher than that of pure C₃N₄ (degradation
479 rate=66.8%). This enhanced photocatalytic activity is mainly ascribed to the formation
480 of a heterojunction, which improves the charge separation efficiency [64]. Specifically,
481 photogenerated electrons excited by C₃N₄ under irradiation will transfer to ND due to
482 the more negative conduction band of C₃N₄ than ND [46]. Au NPs may also take over
483 the electrons from C₃N₄ since its outstanding electron conduction feature [65]. And the
484 LSPR effect of Au NPs is another avenue to excite electrons [66]. Those electrons
485 produce free radical species for decomposing CV molecules. Subsequently, the
486 photodegradation performance of Au/AND/C₃N₄ hybrid is evaluated under sunlight, as
487 shown in Fig. 6c. The results reveal that CV can be degraded almost completely
488 (96.4%) by Au/ND/C₃N₄ hybrid within 150 min. Such photocatalytic activity directly
489 confirms the good self-cleaning ability of Au/ND/C₃N₄.

490 To have a better understanding of self-cleaning features of Au/ND/C₃N₄ substrate,
491 a systematic investigation was conducted on SERS detection and photodegradation of
492 CV for three cycles. Each cycle comprises three steps: (1) the CV solution was mixed

493 with Au/ND/C₃N₄ hybrid for enrichment; (2) SERS detection was executed and the
 494 hybrid was recovered to implement CV photocatalytic degradation after SERS
 495 measurement; (3) the recovered Au/ND/C₃N₄ hybrid was cleaned and dried for the next
 496 cycle. As shown in Fig. 6d, retention rate of SERS intensity at 1174 cm⁻¹ is 92.1% after
 497 three cycles, indicating an acceptable attenuation of SERS detection capability. The
 498 SERS signal of remaining CV molecules gradually raises with increasing the number
 499 of photodegradation cycles. This may be due to the accumulation of residues, as well
 500 as reduction of photocatalytic activity. In brief, fingerprint signal intensity has a small
 501 difference among the three cycles, revealing a good self-cleaning feature of
 502 Au/ND/C₃N₄ substrate and a broad prospect for recyclable detection.

503 3.3. Application of self-cleaning Au/ND/C₃N₄ substrate for tetracycline detection

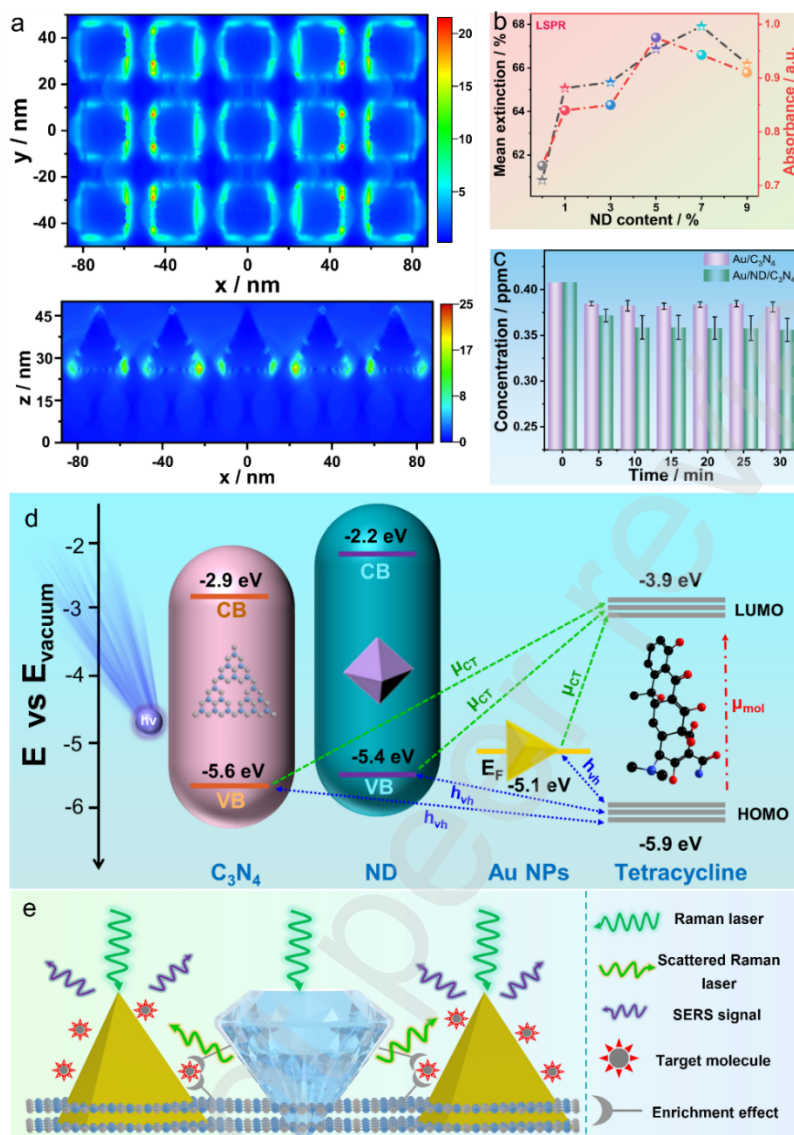


504
 505 **Figure 7.** (a) SERS spectra of tetracycline in a concentration range from 10⁻⁶ to 10⁻¹²
 506 M recorded using Au/ND/C₃N₄ substrate. (b) Linear calibration plots of the SERS
 507 intensities at 1171 and 1617 cm⁻¹ versus logarithmic of tetracycline concentration. (c)
 508 SERS spectra of a 10⁻⁶ M tetracycline solution recorded on random 13 spots using
 509 Au/ND/C₃N₄ substrate. (d) The corresponding histogram of intensity distribution of the
 510 13 random spots at 1171 and 1617 cm⁻¹. (e) Photocatalytic degradation curves of a 10⁻⁵
 511 M tetracycline in the presence of Au/ND/C₃N₄ hybrid (under visible-light
 512 illumination). (f) Self-cleaning test of Au/ND/C₃N₄ substrate through three cycles of
 513 SERS detection and photocatalytic degradation of 10⁻⁷ M tetracycline.

514 In view of the superior performance achieved by Au/ND/C₃N₄ substrate, it is
515 further adopted for tetracycline detection. To begin with, the detection sensitivity of
516 Au/ND/C₃N₄ substrate for tetracycline was assessed. Fig. 7a depicts the SERS spectra
517 of tetracycline in a concentration range from 10⁻⁶ to 10⁻¹² M on Au/ND/C₃N₄ substrate.
518 The attributions of selected peaks (1171 and 1617 cm⁻¹) for tetracycline are listed in
519 Table S1, as well as those of other possible characteristic peaks. Visible selected peaks
520 can be observed even for a tetracycline concentration of 10⁻¹² M, indicating a high
521 sensitivity of Au/ND/C₃N₄ substrate. The linear fitting plot of logarithmic
522 concentration and SERS intensity is shown in Fig. 7b. In a concentration range from
523 10⁻⁶ to 10⁻¹² M, the calibration equation for 1171 cm⁻¹ peak is: $I_{SRES}=1015 \log C_{Tetracycline}$
524 $+13388$, and the R² is 0.984. The calibration equation for the 1617 cm⁻¹ peak is:
525 $I_{SRES}=1143 \log C_{Tetracycline}+16281$, with R²=0.995. The superior sensitivity of
526 Au/ND/C₃N₄ substrate is also been certificated by the performance comparison for TC
527 detection with other SERS substrates, as listed in Table S2. Subsequently, SERS
528 reproducibility of Au/ND/C₃N₄ substrate was determined. Fig. 7c, d display SERS
529 spectra of 10⁻⁶ M tetracycline solution at 13 random points on Au/ND/C₃N₄ substrate,
530 and the histogram of peak intensity distributions at 1171 and 1617 cm⁻¹. The RSD
531 values of peak intensities at 1171 and 1617 cm⁻¹ are respectively 4.86% and 6.88%,
532 proving high SERS signal reproducibility of the substrate.

533 Likewise, the self-cleaning property of Au/ND/C₃N₄ hybrid was evaluated for the
534 decomposition of tetracycline solution under visible light irradiation, as shown in Fig.
535 7e. The degradation rate of tetracycline is 86.1% after 4 h irradiation in presence of
536 Au/ND/C₃N₄, repeatedly confirming its good self-cleaning capability. Furthermore, a
537 systematic investigation was conducted on SERS detection and photodegradation of
538 tetracycline under three cycles. As shown in Fig. 7f, the retention rate of SERS intensity
539 at 1617 cm⁻¹ is 87.1% after three cycles. The small difference of signal intensities
540 suggests that Au/ND/C₃N₄ substrate is suitable for self-cleaning detection of
541 tetracycline.

542 **3.4. Possible mechanism**



543

544 **Figure 8.** (a) Contour plots of the electric field distribution of Au/ND/C₃N₄ substrate
 545 simulated by FDTD. (b) Optical properties variation of Au NPs in Au/ND/C₃N₄ hybrids
 546 upon ND content. (c) The concentration variation of CV solution with adsorption time
 547 in the presence of Au/C₃N₄ (10 mg) and Au/ND/C₃N₄ (10 mg) hybrids, respectively.
 548 (d) Energy-level diagram and possible CT paths between Au/ND/C₃N₄ substrate and
 549 target molecule. (e) Schematic mechanism of Au/ND/C₃N₄ substrate for the enhanced
 550 SERS activity in the presence of ND.

551 To better understand the enhancement effect of ND on SERS signal, electric field
 552 distribution of Au/ND/C₃N₄ substrate under 633 nm laser was simulated by FDTD, as
 553 shown in Fig. 8a. The FDTD result of x-y view mirrors the electric field distribution
 554 for coupling region of Au NPs and ND, while x-z view may mirror the electric field

555 distribution for non-coupling region. The coupling region behaves a stronger field
556 enhancement than that of non-coupling region. This phenomenon is ascribed to the high
557 light utilization brought by ND. On the other hand, the supporting video shows the
558 electric field variation over time of the two views, and the non-coupling region features
559 a delayed field enhancement than coupling region. This delayed electric field
560 enhancement may be attributed to scattering effect of ND for the Raman laser beam.
561 The scattered laser beam irradiates Au NPs again to generate a sub-enhanced electric
562 field. Those results prove well that ND scattering may assist enhancement of electric
563 field and bring EM enhancement. In addition, the edges and tips of Au NPs have the
564 highest electric field strength due to LSPR effect, suggesting that the heterohedral
565 morphology of Au NPs could offer sufficient EM enhancement for analyte.

566 Fig. 8b depicts the optical properties variation of Au NPs in Au/ND/C₃N₄ hybrids
567 with ND content. Obviously, the introduction of ND efficiently strengthens the LSPR
568 effect of Au NPs. The maximum extinction ratio and maximum absorbance of Au NPs
569 are increased by 1.12 times and 1.32 times, respectively. Combined with Fig. 2g and
570 Fig. S3, it is reasonable to speculate that the light scattering properties of ND effectively
571 enhance light utilization of Au/ND/C₃N₄ substrate, thus offering a stronger EM
572 enhancement. This phenomenon may be ascribed to the high optical refractive index of
573 ND (2.42) [46]. Furthermore, concentration variation of CV solution over time was
574 recorded using Au/C₃N₄ and Au/ND/C₃N₄ hybrids to investigate the influence of ND
575 on enrichment capacity, as shown in Fig. 8c. The CV concentration reaches equilibrium
576 after 10 min for both ND/C₃N₄ and Au/ND/C₃N₄ hybrids, but the CV solution in
577 presence of Au/ND/C₃N₄ exhibits a lower residual concentration than that of Au/C₃N₄.
578 This indicates that Au/ND/C₃N₄ substrate has a stronger enrichment capability and may
579 capture more analyte molecules for producing SERS signals. Such superior enrichment
580 capability of Au/ND/C₃N₄ substrate is attributed to a synergistic effect of ND functional
581 groups and the holey C₃N₄ structure on analyte adsorption.

582 Subsequently, possible polarization paths of analyte molecules are analysed from
583 the perspective of energy levels. Fig. 8d displays energy level diagram of charge
584 transfer between Au/ND/C₃N₄ substrate and target molecules. The Fermi level (E_F) of

585 AuNPs is located at -5.1 eV; the valence bands of ND and C₃N₄ are located at -5.4 and
586 -5.6 eV, and conduction bands are at -2.2 and -2.9 eV, respectively [46, 67]. The highest
587 occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital
588 (LUMO) levels of tetracycline are located at -5.9 and -3.9 eV, respectively [68]. Under
589 laser radiation, the energy provided by excitation wavelength at 633 nm (1.95 eV) is
590 not enough to trigger the intramolecular electronic transition between HOMO and
591 LUMO of tetracycline. Instead, energy difference between each component of
592 Au/ND/C₃N₄ and HOMO of tetracycline matches well with the energy of Raman
593 photons. Hence, Au/ND/C₃N₄ may act as a charge transfer medium to push photon-
594 induced CT (μ_{CT}) processes, as illustrated in Fig. 8d. The μ_{CT} with multi-channels could
595 enlarge Raman scattering cross-section to enhance SERS signal. Meanwhile, the
596 excited photothermal electrons of Au NPs may also transfer to LUMO level of
597 tetracycline and induce molecular polarization [67].

598 The above data allow us to propose a ND improvement mechanism for SERS
599 activity, as illustrated in Fig. 8e. The proposed mechanism involves four aspects: (1)
600 **EM effect of heterohedral Au NPs.** Due to LSPR effect, heterohedral Au NPs exhibit
601 a strong electromagnetic field distribution at edges with small curvature radiuses such
602 as nano-tips, and will excite SERS signals. (2) **Enrichment effect.** Abundant functional
603 groups on ND may effectively capture analyte molecules and favour the enrichment of
604 molecules on SERS substrate. More target molecules are enriched on the substrate and
605 receive Raman irradiation, resulting in a stronger SERS signal. In addition, the holey
606 morphology of C₃N₄ and optical plasmons of Au NPs also contribute to the enrichment
607 effect [69]. (3) **CT effect of Au/ND/C₃N₄ heterostructure.** With the help of energy
608 ladder from Au/ND/C₃N₄ heterostructure, analyte molecules may readily undergo a
609 charge transfer from HOMO to LUMO under excitation of Raman photons. Charge
610 transfer process induces polarization of analyte molecules, resulting in SERS
611 enhancement. (4) **Sub-enhancement from light scattering of ND.** ND can scatter
612 Raman laser due to its high refractive index. In coupling region of Au NPs and ND, the
613 laser beam and scattered light jointly excite Au NPs to generate SERS hot spots by
614 means of high light utilization. In non-coupling region, the scattered light excites Au

615 NPs again to contribute an enhanced electric field with a sub-intensity, and offers a
616 SERS signal. More commendably, the enhanced electric field in non-coupling region
617 may boost long-range SERS detection to overcome the poor affinity of Au NPs, thus
618 acquiring high sensitivity [70]. Here, we label those SERS enhancements from the
619 scattered Raman laser as sub-enhancement.

620 **4. Conclusions**

621 In conclusion, Au/ND/C₃N₄ SERS substrate of featuring light-enhancement
622 and self-cleaning properties was successfully constructed by the combination of
623 ND, C₃N₄ and Au NPs. The abundant functional groups and light scattering effect
624 of ND endowed Au/ND/C₃N₄ substrate with excellent enrichment capability and
625 sub-enhancement of SERS signal. Thus, the prepared substrate exhibited a
626 favourable SERS activity and allowed highly sensitive detection of CV and
627 tetracycline at low concentrations of 10⁻¹⁴ M and 10⁻¹² M, respectively. In
628 addition, the hybrid exhibited high catalytic activity due to the enhanced electron
629 separation efficiency, and featured a self-cleaning behaviour. The satisfactory
630 reproducibility and stability of this substrate confirmed its good potential in
631 actual analysis application. Adopting light scattering effect to improve SERS
632 activity provides a good avenue for the fabrication of high-performance SERS
633 substrates. Meanwhile, all the superior performances may allow Au/ND/C₃N₄
634 hybrids to be applied for sensitive assays of antibiotic residues in wastewater.

635 **Declaration of Competing Interest**

636 The authors declare that they have no known competing financial interests or
637 personal relationships that could have appeared to influence the work reported in this
638 paper.

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