Grafting-through functionalization of graphene oxide with cationic polymers for enhanced adsorption of anionic dyes and viruses

Ryota Kimura,[a] *Pilar Ferré-Pujol,*[b†] *Yuta Nishina*[a,b,c*]

[a] Graduate School of Environmental, Life, Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan.

[b] Research Core for Interdisciplinary Sciences, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

[c] Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

E-mail: nisina-y@cc.okayama-u.ac.jp

Chemicals

A carbon black (CB) was obtained from The Association of Powder Process Industry and Engineering, JAPAN, standard test powder 1 (JIS Z8901) (class 12, Carbon black). Carbon nanotube (CNT) was provided from Zeon Nano Technology Co., Ltd., ZEONNANO^{TM} SG101.

Methods

Fourier Transform Infrared Spectroscopy (FT-IR) was measured with Shimazu, IRTracer-100. Each sample was measured by ATR. X-ray diffraction (XRD) measurement was performed on PANalytical, Aeris (40 kV, 15 mA) with Cu ($\lambda_{\text{k-alpha1}}$ = 1.540598 Å, $\lambda_{\text{k-alpha2}}$ = 1.544426 Å, $\lambda_{\text{kalpha2}}/\lambda_{\text{k-alpha1 = 0.5}}$) in the 2θ range of 5-60°. Raman spectroscopy was performed on Jasco, NRS-3100 at room temperature using a laser (532 nm). Each sample was analyzed as a powder basis in 3 positions in a Raman shift interval within 500 to 4000 cm^{-1}. STEM analysis was performed on Hitachi High Tech SU9000 (30 kV).

Preparation of CB-AA and CNT-AA

100 mg of CB or CNT was dispersed in 50 mL water. Then, 100 mg allylamine was added to carbon dispersion under stirring. The mixture was stirred at room temperature for 24 h (synthesis of CB-AA or CNT-AA). After finishing the reaction, CB-AA or CNT-AA was recovered by filtration.

Table S1. (a) Result of the reaction for optimization reaction during initial modification of GO by allylamine. (b) Results of allylamine modification on CB and CNT under the same conditions as for conditioning GO-AA 1:1.

(a)

material	C 1s (at%)	N 1s (at%)	O 1s (at%)
GO-AA 1:0.25	67.62	1.74	30.64
GO-AA 1:0.5	68.18	2.01	29.91
GO-AA 1:1	71.22	2.01	26.76
GO-AA 1:2	70.66	1.93	27.41

(b)

material	C 1s (at%)	N 1s (at%)	O 1s (at%)
CB	97.79	0.16	2.05
CNT	95.34	0.15	4.51
CB-AA	97.31	0.32	2.37
CNT-AA	94.51	0.59	4.89

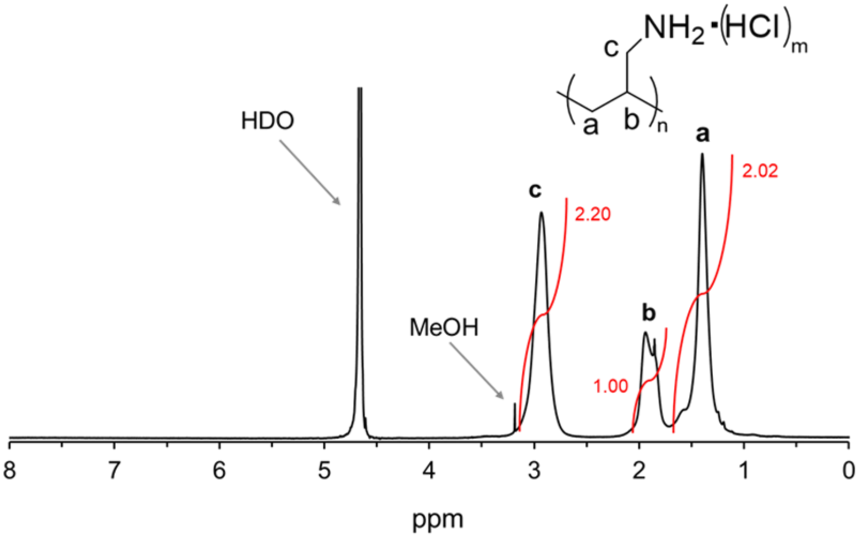


Figure S1. ^{1}HNMR of the product recovered from the supernatant of the GO-PAAm solution (PAAm·HCl). 600 MHz in D_2O.

Figure S2. (a) Picture of a solution in which PAAm-HCl was added to GO under the same conditions as in section 2.5 and then diluted.

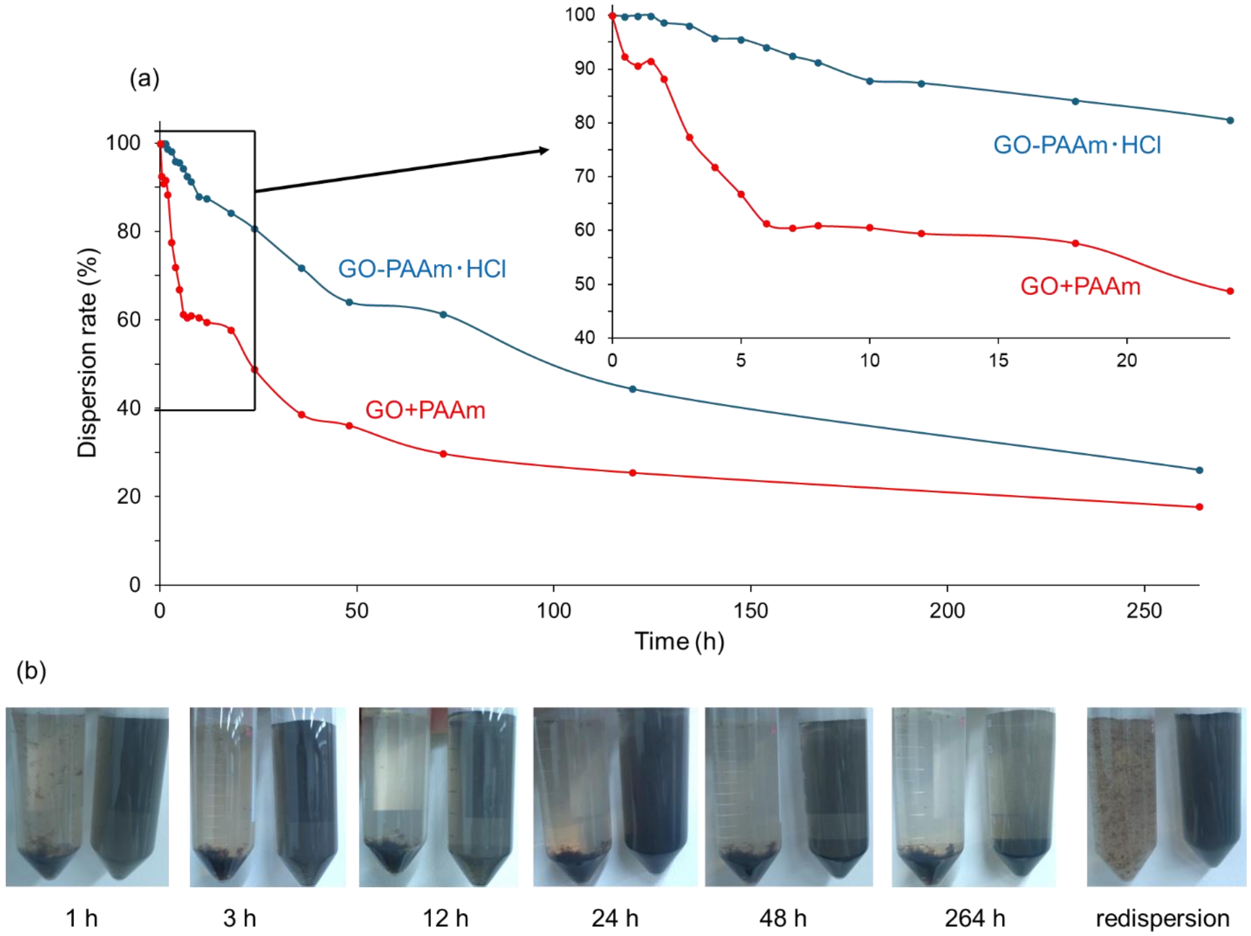


Figure S3. (a) Confirmation test of dispersibility of **GO-PAAm·HCl** and **GO+PAAm** using UV-Vis. Samples adjusted to appropriate concentrations (0.0025 wt% for **GO-PAAm·HCl** and 0.005 wt% for **GO+PAAm**) were placed in quartz cells and measured at regular intervals.

$$\text{Dispersion rate} = \frac{A_0 - A_t}{A_0} \times 100 \quad (\%)$$

A_0 is the absorbance of the sample at 0 h (initial absorbance), A_t is the absorbance of the sample at each time (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 18, 24, 36, 48, 120, 264 h)
(b) Picture to confirm the dispersibility of **GO-PAAm·HCl** (right) and **GO+PAAm** (left). After adding the prepared sample for test (a) to a centrifuge tube, photographs were taken at arbitrary time points. Redispersion was taken after 264 h, redispersed by shaking, and left to stand for 5 min.

Table S2. Result of elemental analysis by XPS of GO, **GO-AA 1:1**, **GO-PAAm·HCl**, **GO+PAAm**, PAAm·HCl.

entry	material	C 1s (at%)	N 1s (at%)	O 1s (at%)	Cl 2p (at%)
1	GO	68.4%	0.5%	31.1%	—
2	GO-AA 1:1	71.2%	2.0%	26.8%	—
3	GO-PAAm·HCl	75.8%	4.0%	18.6%	1.7%
4	GO+PAAm	70.2%	4.0%	24.9%	0.9%
5	PAAm·HCl	70.6%	13.7%	—	15.7%

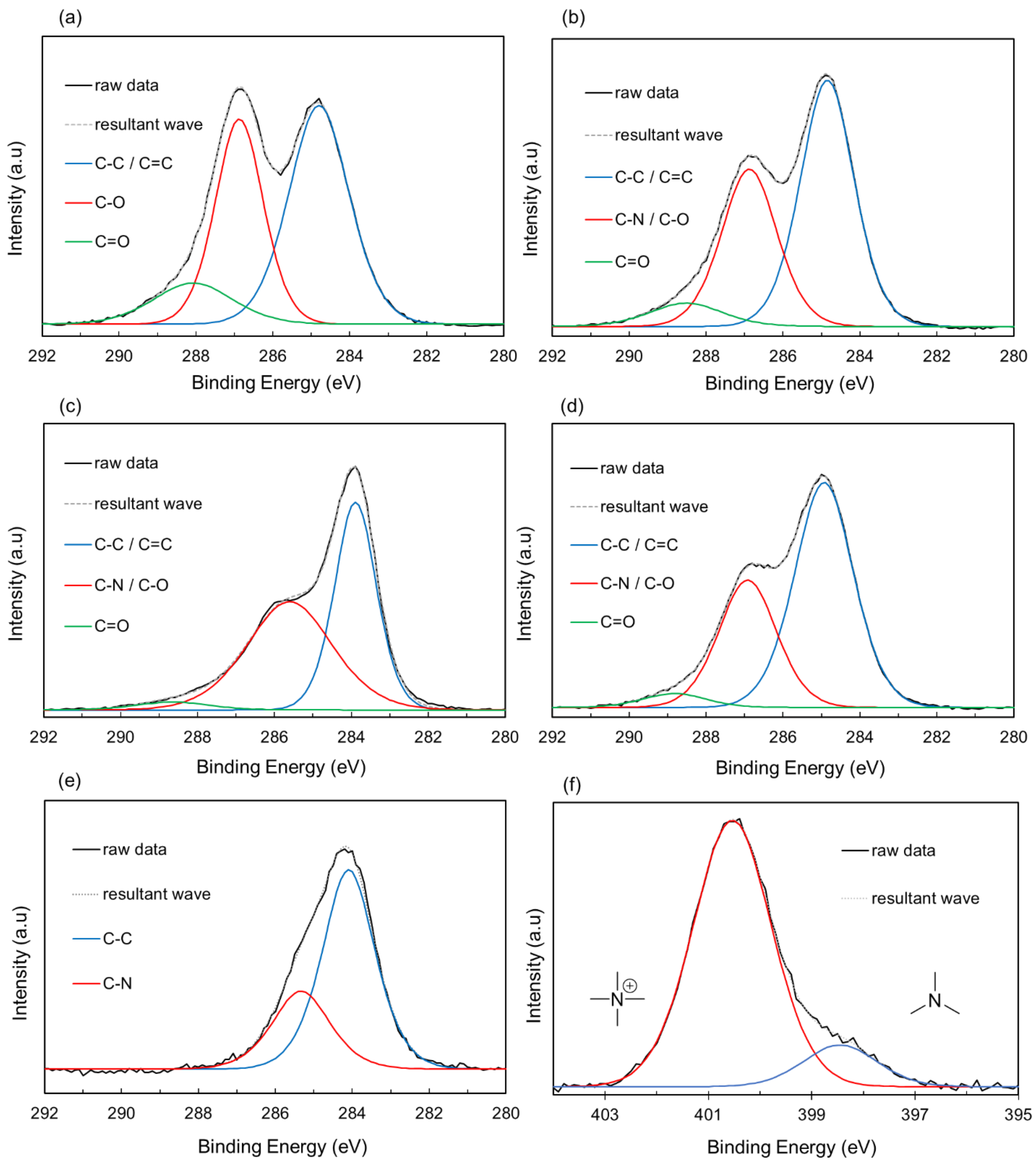


Figure S4. XPS analysis at C 1s region of (a) GO (b) **GO-AA 1:1** (c) **GO-PAAm·HCl** (d) **GO+PAAm** (e) PAAm·HCl, N 1s region of (f) PAAm·HCl.

Table S3. Result of CHN elemental analysis of PAAm·HCl, **GO-AA 1:1**, **GO-PAAm·HCl**, **GO+PAAm**.

material	C (%)	H (%)	N (%)	Remain(%)
PAAm·HCl	35.5	9.0	13.6	41.9 (Cl)
GO-AA 1:1	48.2	2.8	2.4	46.6 (O)
GO-PAAm·HCl	58.0	6.3	4.5	31.2 (O, Cl)
GO+PAAm	48.1	4.3	4.4	43.2 (O)

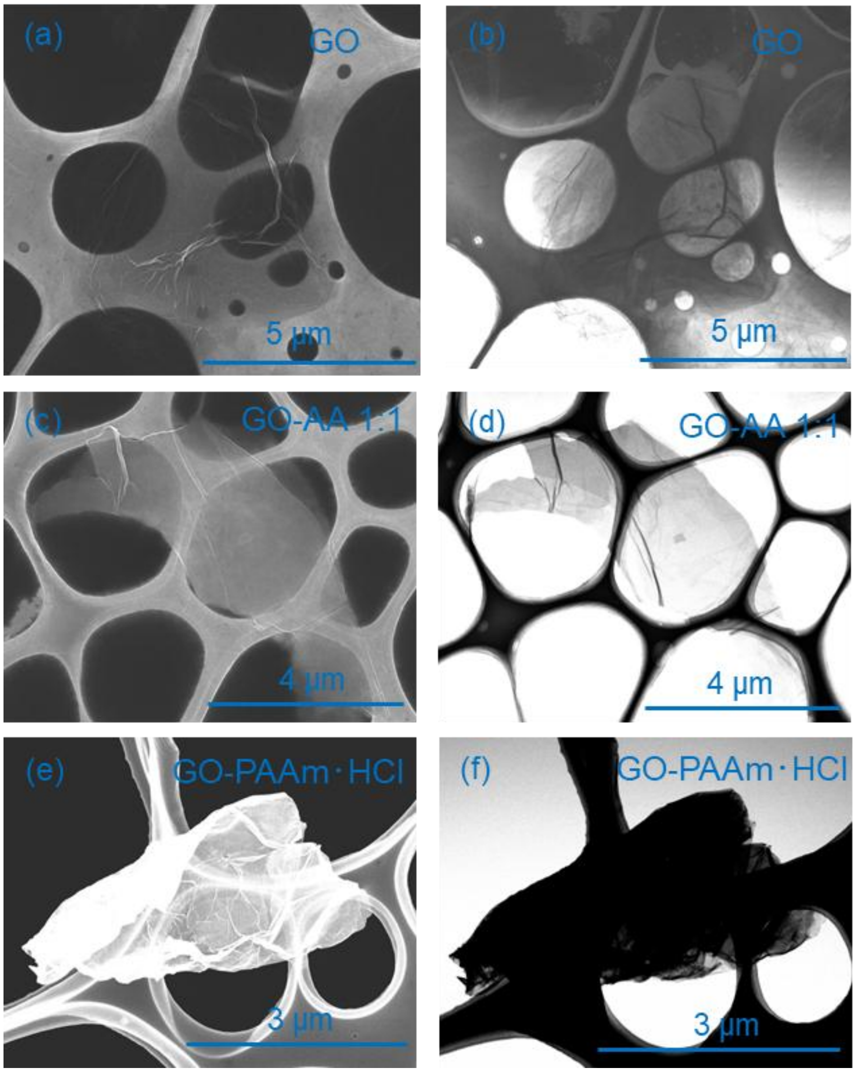


Figure S5. SEM image of (a) GO (c) GO-AA 1:1 (e) GO-PAAm·HCl and STEM image of (b) GO (d) GO-AA (f) GO-PAAm·HCl.

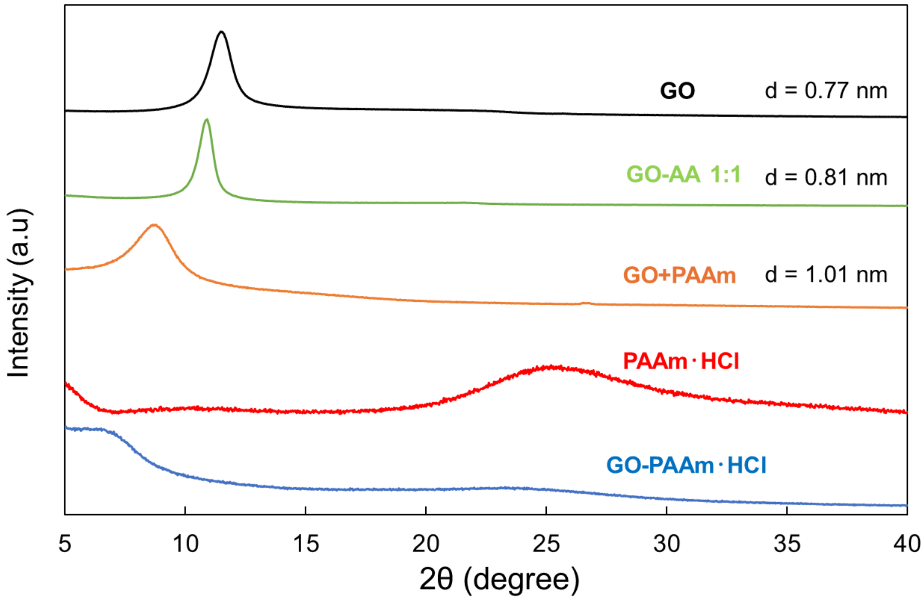


Figure S6. XRD analysis results for GO, **GO-AA 1:1, GO+PAAm**, PAAm·HCl, **GO-PAAm·HCl**

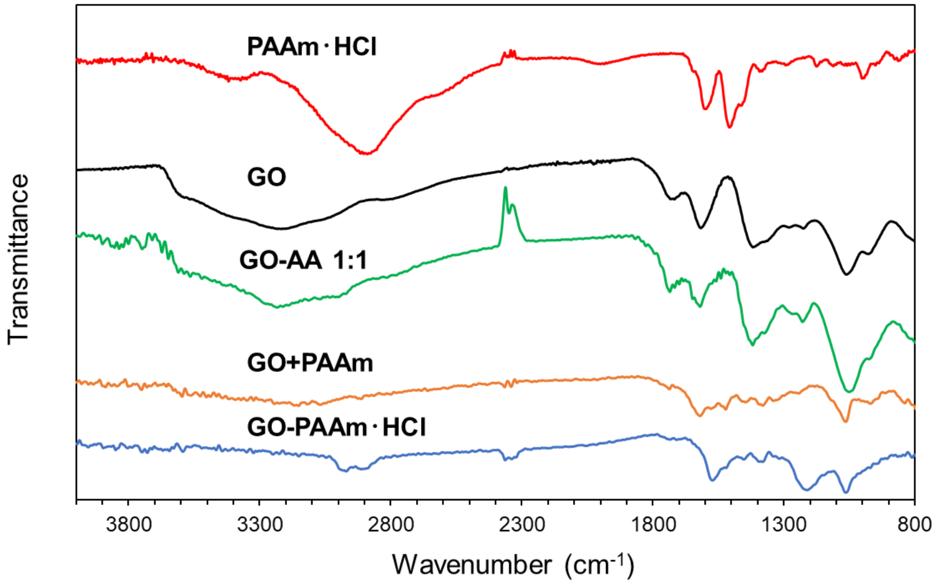


Figure S7. FT-IR analysis of PAAm·HCl, GO, **GO-AA 1:1**, **GO+PAAm**, and **GO-PAAm·HCl**.

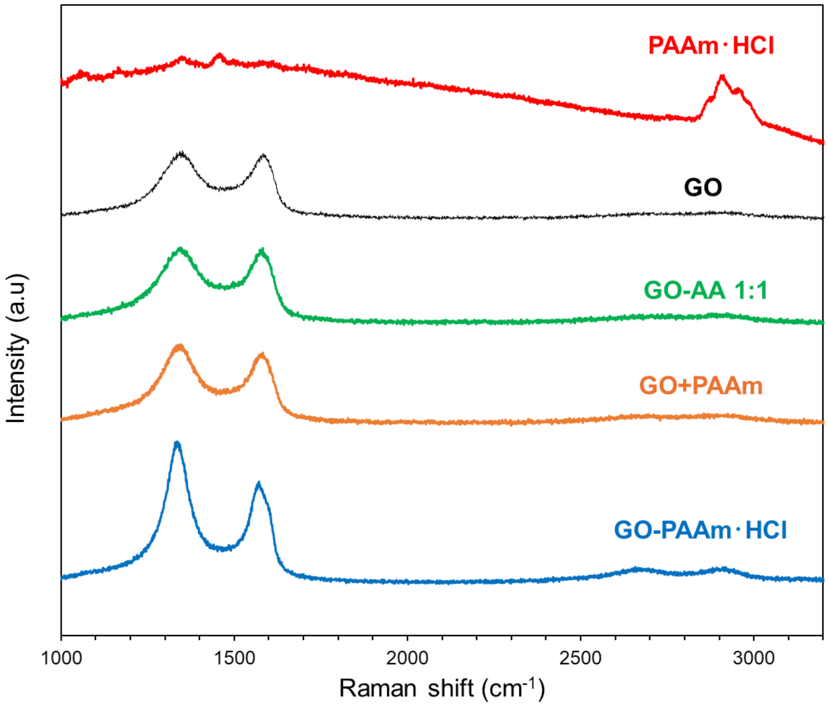


Figure S8. Raman spectrum of PAAm·HCl, GO, **GO-AA 1:1, GO+PAAm** and **GO-PAAm·HCl**

Table S4. Adsorption experiments of (a) MB and (b) MO. Concentration of dyes was 50 mg/L, adsorption time was 4 days, temperature was 25 °C, n= 3.

(a)

material	removal efficiency (% ± SEM)	
	pH 2	pH 7
GO	78.5 ± 2.3	99.5 ± 0.2
GO-PAAm·HCl	25.4 ± 1.8	34.2 ± 0.7
GO+PAAm	11.3 ± 1.9	26.6 ± 2.3

(b)

material	removal efficiency (% ± SEM)	
	pH 7	pH 10
GO	3.0 ± 0.4	2.8 ±1.1
GO-PAAm·HCl	74.4 ± 2.2	20.6 ± 1.5
GO+PAAm	22.0 ± 2.5	6.9 ± 2.7

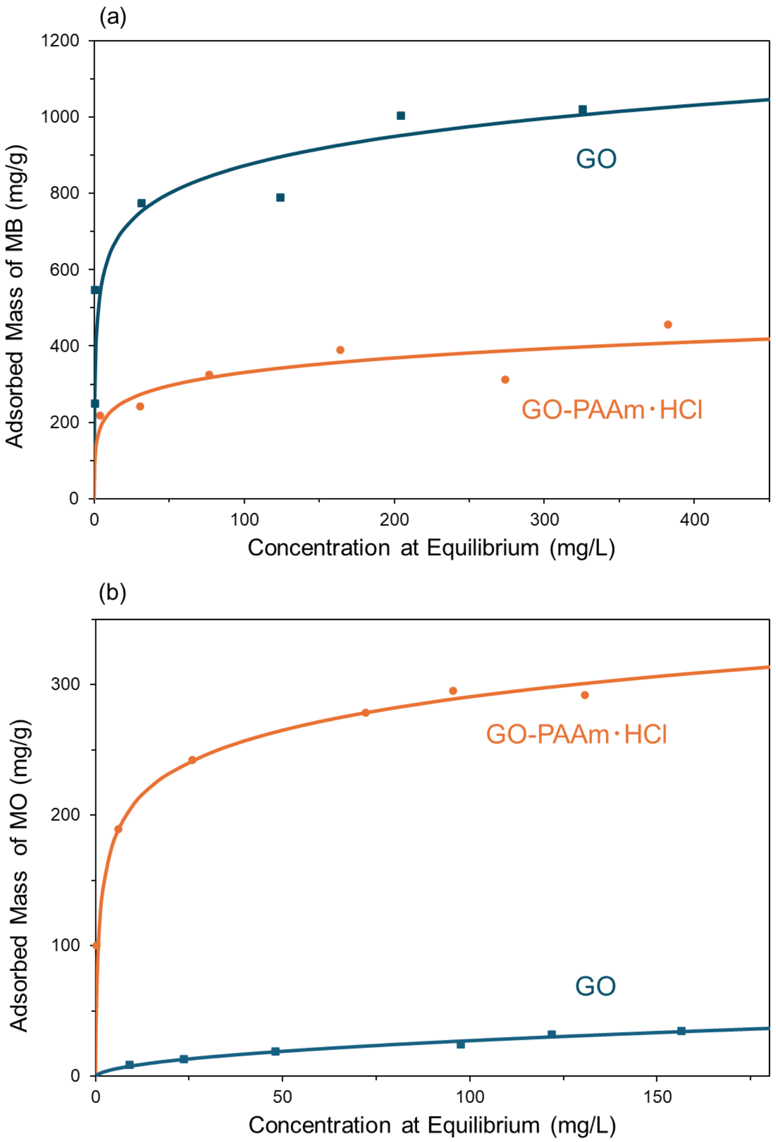
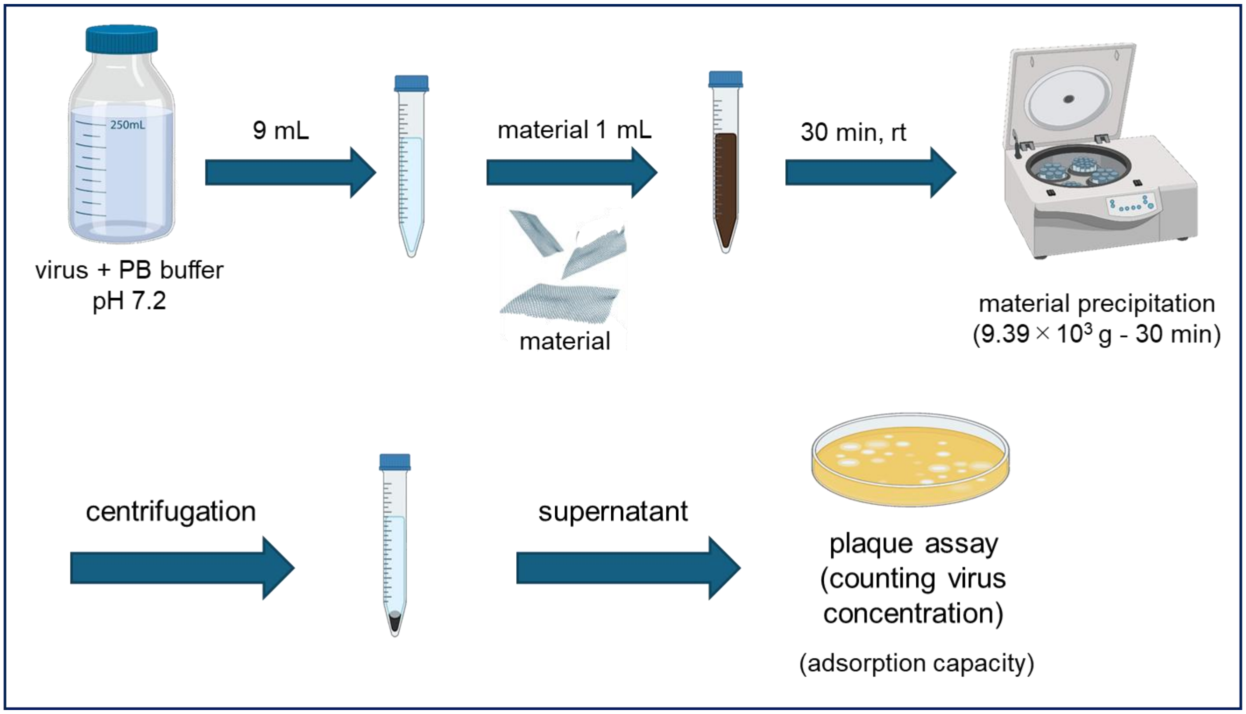


Figure S9. Adsorption isotherms of (a) MB and (b) MO onto GO and **GO-PAAm･HCl** at 25°C, pH7, adsorption time is 4 days.



Scheme S1. Schematics of the methodology employed for the virus adsorption experiments.

Table S5. Adsorption experiments of virus under different concentrations.

Material (w/v %)	Average virus concentration [(PFU/mL) ± SD]	Average virus adsorption (% ± SEM)
original virus concentration	$3.20 \times 10^7 \pm 2.03 \times 10^7$	-
GO (0.01)	$1.01 \times 10^5 \pm 0.938 \times 10^5$	99.6847 ± 0.1172
GO (0.001)	$1.29 \times 10^6 \pm 1.61 \times 10^6$	95.9804 ± 1.965
GO-PAAm·HCl (0.01)	$2.64 \times 10^3 \pm 1.24 \times 10^3$	99.9917 ± 0.0024
GO-PAAm·HCl (0.001)	$9.90 \times 10^5 \pm 2.3.71 \times 10^5$	96.9076 ± 2.107
original virus concentration	$1.82 \times 10^8 \pm 0.677 \times 10^8$	-
GO (0.01)	$7.76 \times 10^5 \pm 13.6 \times 10^5$	99.5743 ± 0.3285
GO (0.001)	$1.05 \times 10^7 \pm 1.03 \times 10^7$	94.2222 ± 2.238
GO-PAAm·HCl (0.01)	$3.03 \times 10^5 \pm 5.83 \times 10^5$	99.8339 ± 0.1445
GO-PAAm·HCl (0.001)	$2.47 \times 10^7 \pm 1.07 \times 10^7$	86.4394 ± 3.8194

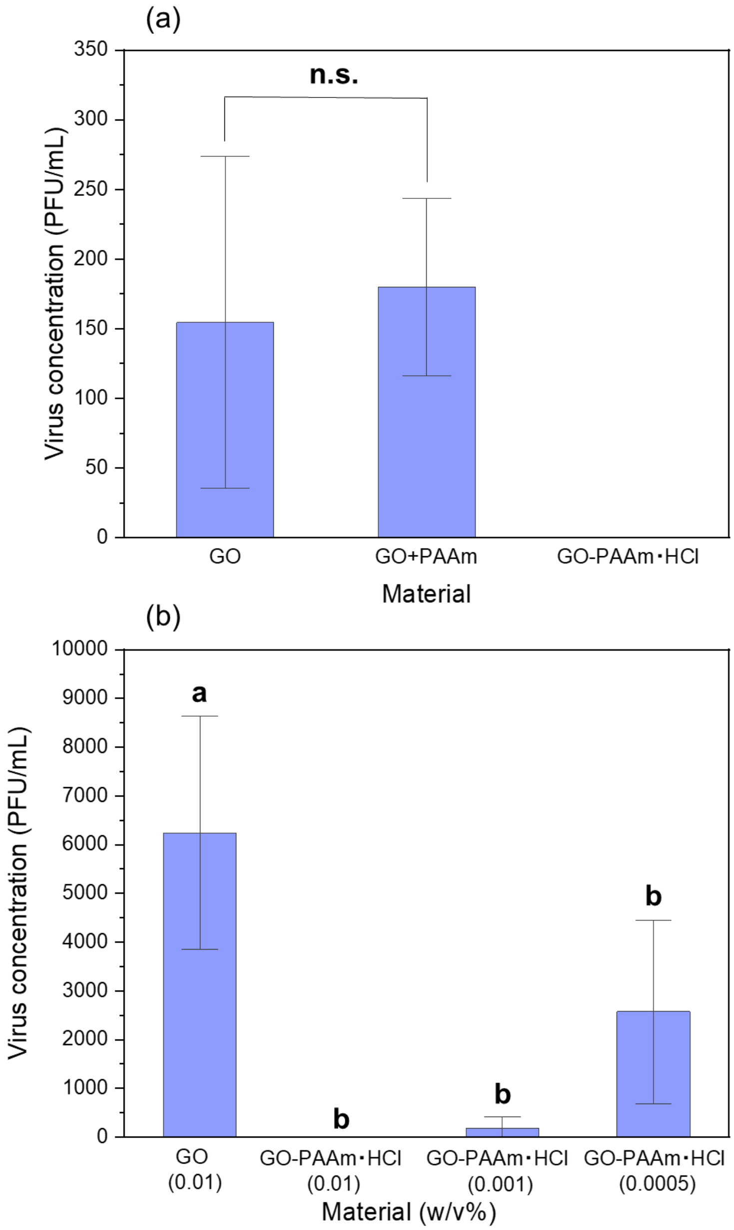


Figure S10. The concentration of the remaining virus present in the supernatant after adsorption with the following materials, (a) GO, **GO+PAAm**, **GO-PAAm·HCl** (0.01 w/v%) when an initial concentration of 5.07×10^5 PFU/mL was used and, (b) GO at 0.01 w/v% **vs GO-PAAm·HCl** at decreasing concentrations of 0.01, 0.001 and, 0.0005 w/v% when employing an initial virus concentration of 1.89×10^6 PFU/mL.: ^{a,b}Different letters indicate significant differences amongst the groups analyzed ($P < 0.05$). The experiment was replicated 4 times.