

# Electronic Supplementary Information for

## “Substrate Effect on Charging of Electrified Graphene/water Interfaces”

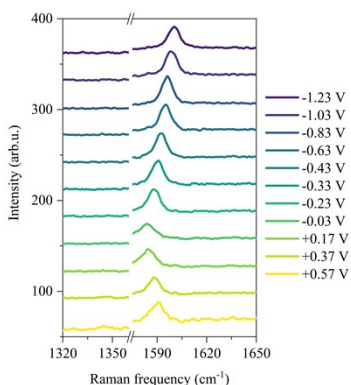
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### S1. Charge density on graphene

We use Raman spectroscopy to independently determine the graphene Fermi level, and thereby its charge carrier density ( $n_g$ ) from the Raman G-band frequency shift.<sup>1,2</sup> The Fermi level in graphene ( $E_F$ ) changes with the density of the charge carriers via  $E_F = \hbar|v_F|\sqrt{\pi n_g}$ , where  $v_F (= 1.1 \times 10^{-6} \text{ ms}^{-1})$  is the Fermi velocity in monolayer graphene,<sup>3</sup> and  $n_g$  denotes the charge carrier density in graphene. Meanwhile, it has been shown that the G-band Raman frequency shifts linearly as a function of the Fermi level,  $E_F = 21\Delta\omega_g + 75 [\text{meV}]$  for electrons and  $E_F = -18\Delta\omega_g - 83 [\text{meV}]$  for holes. Surface charge density on graphene at various electrochemistry potentials can therefore be determined via Raman spectral analysis of the G-band Raman frequency shifts. The Raman spectra of the graphene electrode when changing the applied potentials are shown in Fig. S1, corresponding  $\sigma_g$  as a function of applied potentials is shown in Fig. 1e.



**Fig. S1. Charge density on graphene inferred from Raman G-band frequency.** Raman G-band spectra of the SiO<sub>2</sub>-supported graphene electrode, recorded under various potentials. We used 10 mM NaClO<sub>4</sub>. The data are offset for clarity.

### S2. Self-consistent theory

According to self-consistent theory, the charges ( $n_s = \sigma_s/e$ ) on the substrate could induce a residual charged impurity concentration in graphene ( $n_g$ ), which is given by;<sup>4,5</sup>

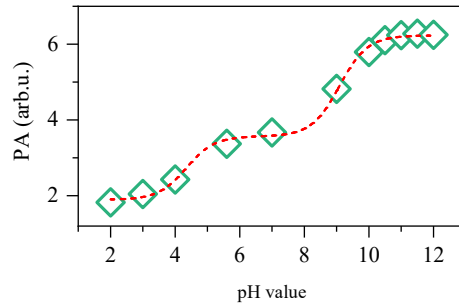
$$n_s = \frac{n_g'}{[2r_s^2 C_0^{RPA}(r_s, a = 4d\sqrt{\pi n_g'})]} \quad \#(S1)$$

where  $r_s = 2e^2/\hbar v_F(\epsilon_1 + \epsilon_2)$ ,  $C_0^{RPA}$  is the correlation function from the random phase approximation (RPA), and  $d$  (~1 nm) is the average distance from the charged impurity to graphene.  $\epsilon_1$  and  $\epsilon_2$  are the dielectric constants of SiO<sub>2</sub> and electrolyte solution, respectively, which gives a value of  $r_s$  of 0.05.  $C_0^{RPA}$  can be calculated according to ref.<sup>5</sup>. Solving the Eq. S1, we obtain  $n_g' = 5 \times 10^{11} \text{ cm}^{-2}$  corresponding to 0.8 mC/m<sup>2</sup> for  $\sigma_s = 100 \text{ mC/m}^2$ .

### 6 S3. Interfacial acid-base equilibria and determination of local pH

We used the Henderson-Hasselbalch equation<sup>6</sup> to describe the relationship between the local pH and the PA under the assumption that the PA is proportional to the density of the charged species on the SiO<sub>2</sub> surface. The fitting yields two  $pK_a$  values of ~4.3 and ~9.0 (Fig. S2), consistent with the previous studies that the SiO<sub>2</sub> surface has two distinct types of silanol surface groups with  $pK_a$  values of ~4.5 and ~8.5 respectively.<sup>7-9</sup>

The fitting equation allows us to infer the local pH using the PA of the  $Im(\chi^{(2)})$  spectra measured at various applied potentials.<sup>10</sup> The inferred local pH value is shown in Fig. 2.



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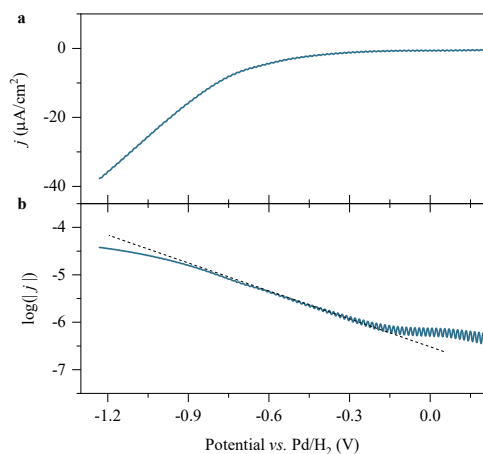
**15 Fig. S2. Interfacial acid-base equilibria at the SiO<sub>2</sub>-supported graphene electrode/aqueous electrolyte**  
**16 interface.** PA of the H-bonded O-H peak as a function of the solution pH at the SiO<sub>2</sub>-supported graphene  
**17 electrode/aqueous electrolyte interface.** We used 10 mM NaClO<sub>4</sub>. The red dashed line is the fitting results using  
**18 the Henderson-Hasselbalch equation.<sup>10</sup>**

### 19 S4. Tafel plots

Tafel plots can quantify the HER kinetics. The plots are shown in Fig.S3. The Tafel slope in the potential range  
 21 of -0.23 V to -0.63 V is 571 mV/decade (dashed line), which is a very large value compared to a metal electrode like  
 22 Pt.<sup>11</sup> Such a large Tafel slope indicates slow HER kinetics and reflects the low catalytic activity of the graphene  
 23 electrode.<sup>12</sup> At potentials below -0.63 V, the slope of the Tafel plots increases, suggesting even slower HER kinetics.  
 24 This explains the saturation of the local pH increase at potentials below -0.63 V. The proton diffusion limits the HER-  
 25 induced pH increase at the graphene/water interface and, in turn, the pH change at the SiO<sub>2</sub>/water interface.

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3 **Fig. S3. HER kinetics.** a. CV of the SiO<sub>2</sub>-supported graphene electrode. The scan rate is 50 mV/s. We used 10 mM  
4 NaClO<sub>4</sub>. For simplicity, only the scan in the negative direction is shown. b. Corresponding Tafel plot.

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## 1 References

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