# **Supporting information**

## Highly stable single Pt atomic sites anchored on aniline-stacked graphene for the

### hydrogen evolution reaction

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# Table

Table S1. EXAFS fitting parameters for the Pt L<sub>3</sub>-edges of the Pt SASs/AG and Pt/C.

| Sample     | path  | Ν    | R (Å) | $\Sigma/10^{-3}\text{\AA}^2$ | $\Delta E_0 (eV)$ | R factor/10 <sup>-3</sup> |
|------------|-------|------|-------|------------------------------|-------------------|---------------------------|
| Pt SASs/AG | Pt–N  | 4.3  | 2.03  | 7.4                          | 14.7              | 4.0                       |
| Pt/C       | Pt–Pt | 12.0 | 2.76  | 5.0                          | 8.5               | 2.4                       |

Table S2. EXAFS fitting parameters for the Pt L3-edges of the Pt SASs/AG before and after durability testing.

| Sample                              | path | Ν   | R (Å) | $\Sigma/10^{-3}\text{\AA}^2$ | $\Delta E_0$ (eV) | R factor/10 <sup>-3</sup> |
|-------------------------------------|------|-----|-------|------------------------------|-------------------|---------------------------|
| As-prepared Pt<br>SASs/AG           | Pt-N | 4.3 | 2.03  | 7.4                          | 14.7              | 4.0                       |
| Pt SASs/AG after<br>durability test | Pt–N | 4.5 | 2.03  | 7.4                          | 14.7              | 4.0                       |

# Figures



Fig. S1 (a) TEM image, and (b) Raman spectrum of graphene.

The low I<sub>D</sub>/I<sub>G</sub> and intensive 2D peaks with narrow FWHM indicate that low defect and high quality of graphene.



The oxygen in graphene is as low as 1.69 at%, and the binding energy of O 1s is located at ~532 eV, which suggests that the oxygen is originated from absorbed  $H_2O$  on the surface. Moreover, the content of nitrogen is negligible from the spectra of survey and N 1s, indicates that the graphene is pure without doping of heteroatom.



Fig. S3 Water-contact angle of (a) graphene and (b) aniline-stacked graphene.



Fig. S4 Photos of (a) graphene-water suspension and (b) aniline-stacked graphene dispersion.



Fig. S5 (a) TEM, (b) HRTEM images, and (c) elemental mapping images of C and N of AG.



Fig. S6 XRD patterns of Pt SASs/AG and Pt/C (PDF#65-2868).



Fig. S7 XPS spectra of (a) survey, (b) C1s, (c) O1s, and (d) N 1s of AG.



Fig. S8 XPS spectra of (a) survey, (b) C1s, (c) O1s and (d) N 1s of Pt SASs/AG.



Fig. S9 XPS spectra of (a) survey, (b) C1s, (c) O1s, (d) N 1s, (e) Pt 4f and (f) Cl 2p of Pt SASs/AG before microwave irradiation.



Fig. S10 Extended XAFS spectra of Pt SASs/AG and Pt/C.



Fig. S11 LSV curves of Pt SASs/AG prepared by different volumes of H<sub>2</sub>PtCl<sub>6</sub> solution with iR corrction.



Fig. S12 (a) LSV curves of Pt SASs/AG and Pt/C before the iR correction; LSV curves of (b) Pt SASs/AG, and (c) Pt/C before and after the iR correction.



Fig. S13 TEM images of Pt/C (a) before and (b) after durability testing.



Fig. S14 (a) TEM image, (b) HAADA-STEM images and corresponding elemental mapping of (c-f) C, N, Pt and (g) AC HAADA-STEM images of Pt SASs/AG after durability testing.



**Fig. S15** (a) XANES and (b) FT-EXAFS of the Pt L<sub>3</sub>-edge of Pt SASs/AG before and after durability testing (without phase correction); (c) Corresponding EXAFS fitting curve of Pt SASs/AG after durability testing.



Fig. S16 LSV curves of Pt SASs/AG and Pt/C with current density normalized to the (a) geometry area and (b) mass of Pt in 1 M KOH at 2 mV s<sup>-1</sup> respectively; (c) Tafel plots of Pt SASs/AG and Pt/C in 1 M KOH



Fig. S17 DFT calculation models (side views) of (a) Pt (111), (b) Pt<sub>ab</sub>/G and (c) Pt SASs/AG.



Fig. S18 Total DOS of (a) Pt (111), (b) Pt<sub>ab</sub>/G and (c) Pt SASs/AG.



Fig. S19 (a, d) Pt (111), (b. e) Pt<sub>ab</sub>/G and (c,f) Pt SASs/AG with the H absorption model for the DFT calculations.