Supporting Information

Application of Composite Film Containing Polyoxometalate Ni25 and Reduced Graphene Oxide for Photoelectrocatalytic Water Oxidation

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Experimental Section

Materials and instruments

The purified water which was employed in the whole experiment was obtained from Millipore Milli-Q system. The infrared spectra were recorded on Nicolet iS5 Fourier transform infrared spectrometer. The buffer solutions of pH 4–6 were made by 1M NaAc + HAc. All other chemicals used in this

experiment were available from commercial sources without further purification.

Synthesis of Ni25

$Na_{50}[Ni_{25}(H_2O)_2OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]\cdot 85H_2O$ was synthesized according to the published

paper.[1] $NiCl_2\cdot 6H_2O$ (0.3 g, 1.26 mmol) was dissolved in 40 mL of distilled water. $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$ (1.0 g, 0.34 mmol) was added, and the mixture was stirred until a clear green solution formed. Then, $Na_3PO_4\cdot 12H_2O$ (0.80 g, 2.1 mmol) and Na_2CO_3 (0.05 g, 0.47 mmol) were added, and the pH adjusted to 8.0−9.0 with 255−325μL 4.0 M HCl(aq). The resulting green mixture was stirred at 60°C−70°C for 2 h, and the green precipitate was removed by filtration. The filtration rate was maintained in a 50 mL beaker to allow for slow evaporation at room temperature. After 3 weeks, separate green block crystals suitable for X-ray crystallography formed, and washed with cold distilled water.

Synthesis of GO.

GO was synthesized according to the literature.[2] Then, it was modified in this experiment.[3] The oxidized graphite powder (20 g) was put into cold (0 °C) concentrated H_2SO_4 (460 mL). $KMnO_4$ (60 g) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20 °C. The mixture was then stirred at 35 °C for 2 h, and distilled water (920 mL) was added.

In 15 min, the reaction was terminated by the addition of a large amount of distilled water (2.8 L) and 30% H_2O_2 solution (50 mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with 1:10 HCl solution (5 L) in order to remove metal ions.

Synthesis of PDDA/rGO

Graphite oxide was dispersed in 100mL deionized water by ultrasonic vibration for 2 h at concentration of 1 mg/mL, then 2.5 g PDDA (5 wt.% in water) was added. The above suspension was stirred for 12 h at room temperature and 1 mL hydrazine hydrate was added. Then the mixture was heated at 100 °C and stirred for 24h to reduce graphite oxide. After the temperature decreased to room temperature, the mixture was separated by centrifugation, and washed three times with deionized water.

Electrochemical measurements

The electrochemical characterization of the solution and composite films were tested on the (Chenhua, Shanghai) CHI660E electrochemical workstation, with a three-electrode system. The three electrodes include a working electrode (ITO and the modified ITO electrode), a counter electrode (platinum wire), and a reference electrode (Ag/AgCl, 3 M KCl). Before each experiment, the ITO electrode was ultrasonically cleaned in a mixed solution containing 1 M NaOH and alcohol solution with 1:1 mass ratio for 5 min, then rinsed repeatedly with distilled water, and blow-dried with high-purity N_2.

UV–Visible (UV–vis) absorption spectra

UV–vis absorption spectra were tested on the UV-2700 spectrophotometer, which was used to record the assembly process of the composite films. The quartz sheet is used as the substrate

for assembling composite films. Before each experiment, the mixture of H_2SO_4 and H_2O_2, at a 7:3 volume ratio, was heated to 80°C, then the quartz slide was immersed in the solution for 1 h. After that, the cleaned quartz slide was rinsed repeatedly with distilled water and blow-dried with high-purity N_2.

Scanning electron microscope (SEM)

Morphology of the two films were characterized by the field-emission scanning electron microscope (FE-SEM, Hitachi S-4800), operated at 1.0 kV.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out on a MULTILAB2000 with Al K_α radiation.

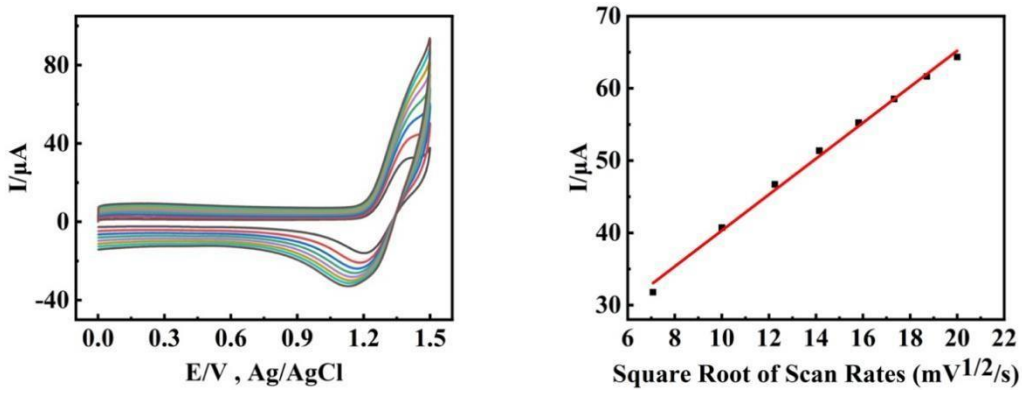


Figure S1. CVs of 0.1mM Ni25 in 1M NaAc+HAc (pH 6) solutions at different scan rates of 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mV/s, using ITO electrode. (right) The relationships of square root of scan rates vs. the oxidation peak currents of Ni^{2+}

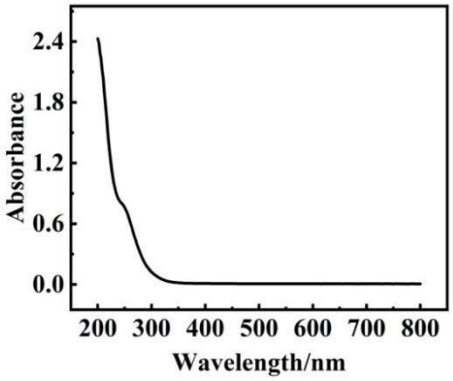


Figure S2. UV–vis spectrum of Ni25 (1×10^{-6} M) in solution.

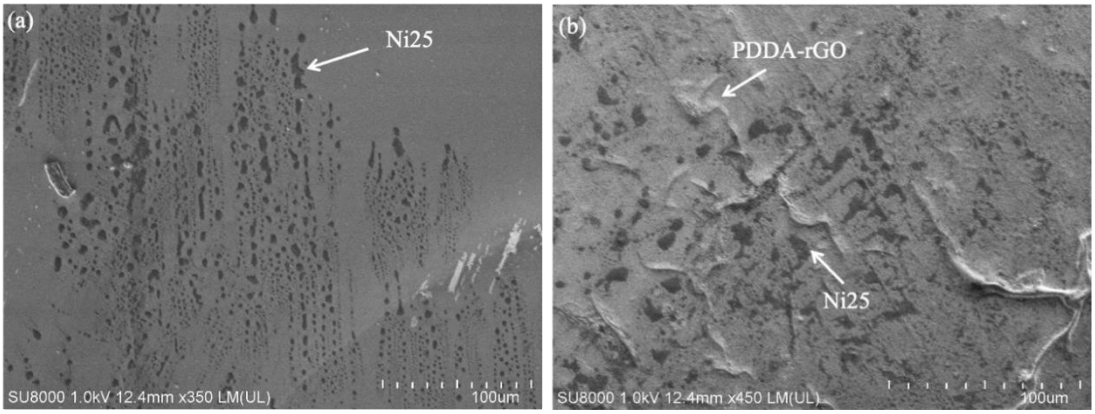


Figure S3. SEM images of (a) $[PDDA/Ni_{25}]_6$/ITO and (b) $PDDA/[Ni_{25}/(PDDA–rGO)]_6$/ITO.

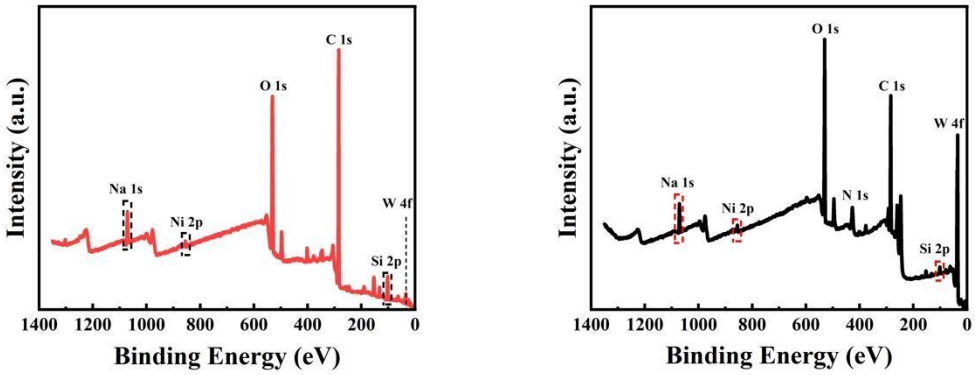


Figure S4. XPS spectra of $[PDDA/Ni_{25}]_6$/ITO (red curve) and PDDA/[Ni25/(PDDA–rGO)]$_6$/ITO (black curve).

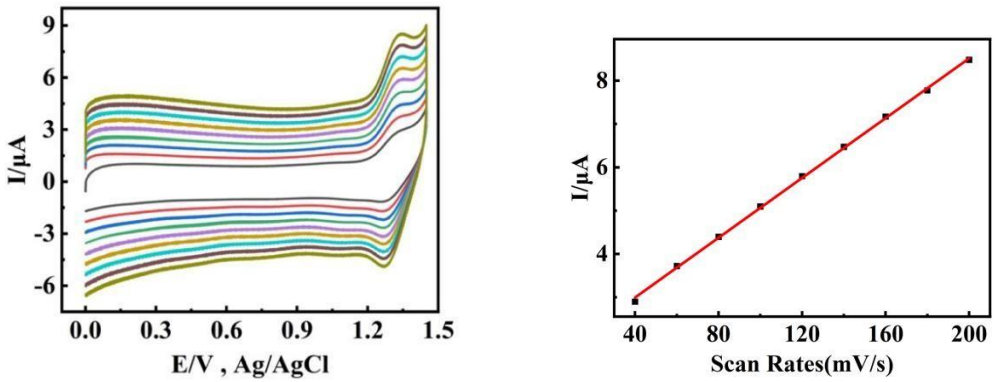


Figure S5. (left**)** CVs of PDDA/[Ni25/(PDDA–rGO)]$_6$/ITO in 1M NaAc + HAc (pH 6) solutions at different scan rates of 40, 60, 80, 120, 140, 160, 180, and 200 mV/s. (right) The relationships of scan rates vs. the oxidation peak currents of Ni^{2+}.

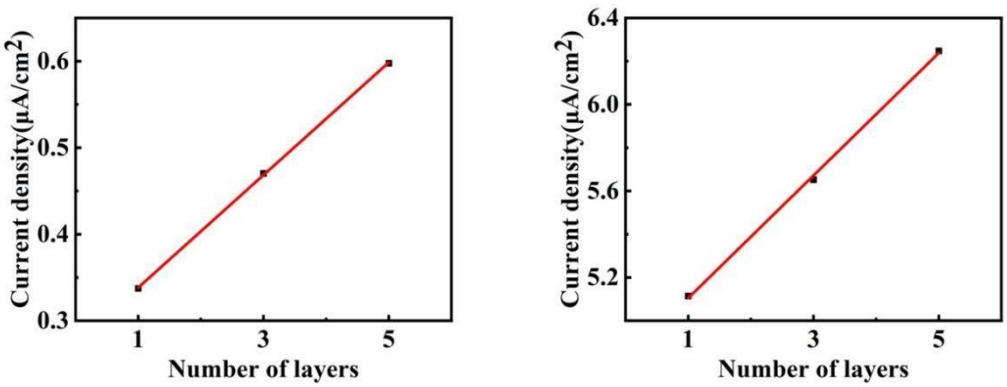
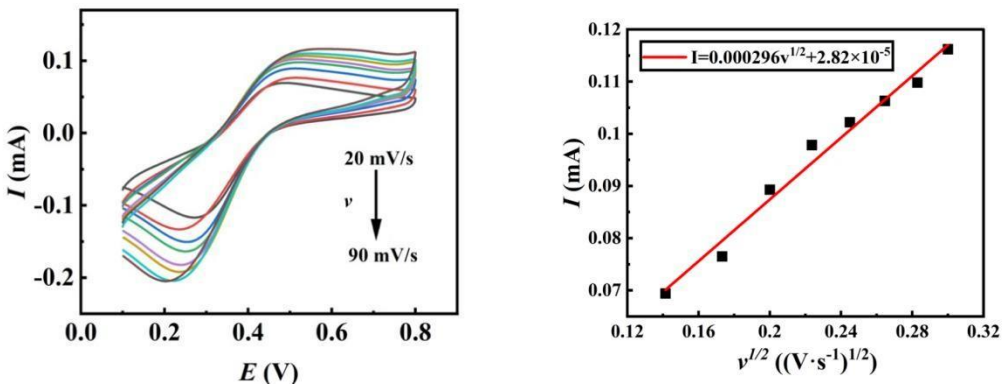


Figure S6. The relationship of the photogenerated currents vs. the different number of layers. (left) [PDDA/Ni25]$_n$ (n = 1, 3, 5) and (right) PDDA/[Ni25/(PDDA–rGO)]$_n$ (n = 1, 3, 5).



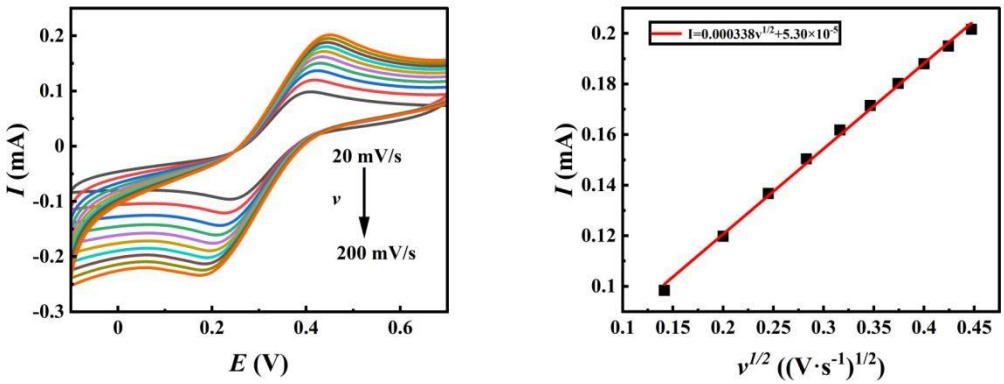


Figure S7. (left) Typical CVs of PDDA/[Ni_{25}/(PDDA–rGO)]$_4$/ITO (top) and [PDDA/Ni_{25}]$_4$/ITO (bottom) in 1 mM $[Fe(CN)_6]^{3-}$ solution containing 0.1 M KCl at increasing scan rates, and (right) corresponding plots of I_{pa} vs. $\upsilon^{1/2}$, PDDA/[Ni_{25}/(PDDA–rGO)]$_4$/ITO (top) and [PDDA/Ni_{25}]$_4$/ITO (bottom)

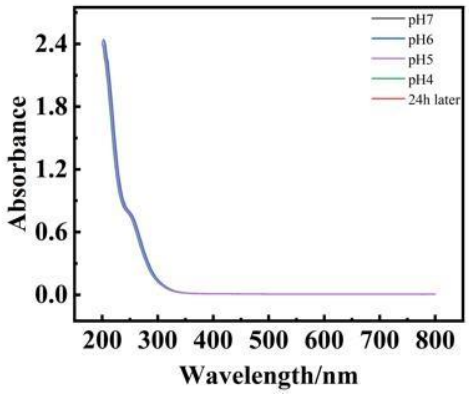


Figure S8. UV–vis spectra of Ni25 at different pH and after being stored for 24 h.

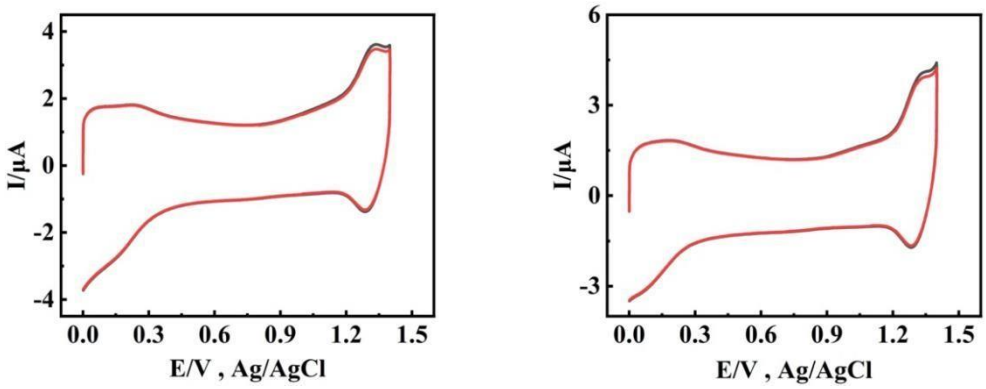


Figure S9. Films [PDDA/Ni_{25}]$_3$ (left) and PDDA/[Ni_{25}/(PDDA–rGO)]$_3$ (right) were deposited on the ITO electrode during the 1st and 100th CV cycles in 1 M NaAc + HAc solution (pH 6), at a

scan rate of 50 mV s^{-1}. Black lines represent the 1st CV cycle, and red lines represent the 100th CV cycle.

Table S1. Comparison of the catalytic activities of Ni25 in two films

	$[PDDA/Ni_{25}]_6$	$PDDA/[Ni_{25}/(PDDA–rGO)]_6$
Γ(mol/cm^2)	0.278×10^{17}	1.03×10^{17}
I_{cat} (A)	4.5×10^{-5}	2.25×10^{-4}
I'_{cat} (per mol.)	1.62×10^{-21}	2.18×10^{-21}

Reference

1 X. B. Han, Y. G. Li, Z. M. Zhang, H. Q. Tan, Y. Lu and E. B. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 5486–5493.

2 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

3 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771–778.

4 L. Cui, T. Pu, Y. Liu and X. He, Electrochim. Acta, 2013, **88**, 559–564.