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Electronic Supplementary Information

Superlattice Assembly of Graphene Oxide (GO) and Titania Nanosheets:

Fabrication, In Situ Photocatalytic Reduction of GO and Highly Improved

Carrier Transport

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Supplementary information 1--- Synthesis of GO and Ti_{0.87}O₂^{0.52-} Nanosheets

GO was prepared from natural graphite flake (Wako, 99.999% purity, 100 mesh) using a modified Hummers' method.¹ Briefly, 1 g of graphite, 1.2 g of KNO₃ and 50 cm³ of H₂SO₄ were mixed in a 1000 cm³ beaker. Then, 6 g of KMnO₄ was slowly added. The solution was maintained at room temperature and stirred for 6 h. Subsequently, 30 cm³ of water was slowly added, and the temperature of the suspension was maintained less than 80 °C. Then, 200 cm³ of water was added to further dilute the suspension, followed by the slow addition of 6 cm³ of H₂O₂. The resulting mixture was diluted to 1000 cm³ with water, and the dilution was repeated several times until the pH of the solution was greater than 5.

Ti_{0.87}O₂^{0.52-} nanosheets were prepared according to previously reported procedures.² Weighed powders of TiO₂, K₂CO₃, and Li₂CO₃ were mixed at a molar ratio of 10.36:2.40:0.81 and finely ground together. The mixture (10 g) was placed in a Pt crucible and heated at 1173 K in air for 30 minutes to be decarbonated. After cooling, the powder was ground and calcined at 1273 K for 20 h. Phase purity as K_{0.8}Ti_{1.73}Li_{0.27}O₄ was confirmed by XRD data. Next, acid exchange was performed by stirring 10 g of K_{0.8}Ti_{1.73}Li_{0.27}O₄ in 1 dm³ of a 1 M HCl solution at ambient temperature for 3 days. The HCl solution was replaced daily with fresh solution by decantation. The product was recovered by filtration, washed with copious amounts of water, and dried in air. The resulting protonated phase of H_{1.07}Ti_{1.73}O₄·H₂O was exfoliated by treatment with a tetrabutylammonium hydroxide solution (C₄H₉)₄NOH (hereafter TBAOH); the molar ratio of H⁺ in H_{1.07}Ti_{1.73}O₄·H₂O: OH⁻ in TBAOH = 1:1. Finally, the mixture was reciprocally agitated for one week at a speed of 180 rpm. The resulting suspension contained monodispersed unilamellar nanosheets with an average lateral size of ~300 nm.



Fig. S1 AFM images and height profiles for GO (a) and $Ti_{0.87}O_2^{0.52}$ nanosheets (b).



Fig. S2 Typical AFM images GO films fabricated using different concentrations of GO suspensions: (a) 0.005, (b) 0.01, (c) 0.02, (d) 0.03, (e) 0.04 and (f) 0.05 g dm⁻³.



Fig. S3 Coverage and film quality versus the GO concentration. Height profiles of the AFM images were used to estimate the coverage. Three discrete peaks attributable to the uncovered surface, monolayer, and overlapped region were used to estimate their proportion by peak deconvolution.



Fig. S4 UV-visible absorption spectra in the multilayer buildup process for (**a**) (PDDA/Ti_{0.87}O₂^{0.52-})₁₀, (**b**) (PDDA/GO)₁₀, and (**c**) (PDDA/GO)₅. Experimental conditions: deposition time of 20 min and nanosheet concentrations of 0.08 g dm⁻³ for Ti_{0.87}O₂^{0.52-} and 0.04 g dm⁻³ for the GO suspension.



The basal spacings for $(PDDA/GO)_{10}$ and $(PDDA/Ti_{0.87}O_2^{0.52})_{10}$ are 1.25 nm and 1.46 nm, respectively. We therefore assume that the thickness of one unit cell of $(PDDA/GO/PDDA/Ti_{0.87}O_2^{0.52})_5$ is 2.7 nm, which is the summation of the two individual components. The 2θ positions for the first- and second-order peaks of this hetero-structure are expected to occur at approximately 3.27° and 6.54°, respectively. The XRD patterns of the superlattice films were simulated based on the following equations:

 $F_{001} = \sum m_i f_i \exp\{2\pi i Z_i (2\sin\theta/\lambda)\};$

 $I = L_p \times (F_{001}F_{001}^*) \times \text{Laue function};$

Lorentz polarization factor $L_p = (1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta);$

Laue function = $(1/n) \times [\sin^2(2\pi nc\sin\theta/\lambda)/\sin^2(2\pi c\sin\theta/\lambda)]$.

where m_j , f_i , θ , Z_j , n, and λ are the site occupancy, atomic scattering factor, scattering angle, atomic site coordinates, repeated number of (GO/Ti_{0.87}O₂^{0.52-}) bilayers and X-ray wavelength, respectively.

Fig. S5 Structural model of the superlattice film of (PDDA/GO/PDDA/Ti $_{0.87}O_2^{0.52}$)₅.



Fig. S6 Simulated XRD pattern (blue) and experimental data (red) of the (PDDA/GO/PDDA/Ti_{0.87} $O_2^{0.52}$)₅ film. The broad hump at approximately 23° is due to the amorphous halo from the glass substrate.



Fig. S7 UV-visible absorption spectra of (PDDA/GO/PDDA/Ti_{0.87}O₂^{0.52-})₅ (**a**), (PDDA/Ti_{0.87}O₂^{0.52-})₁₀ (**b**) and (PDDA/GO)₅ (**c**) under UV light irradiation ($\lambda = 270-400$ nm, approximately 2.5 mW cm⁻²).

	(PDDA/GO/PDDA/Ti _{0.87} O ₂ ^{0.52-}) ₅		(PDDA/GO) ₅	
	Before	After UV treatment	Before reduction	After thermal
	reduction			annealing
С-С, С=С, С-Н	58.7 %	65.0 %	43.9 %	63.8 %
(285.0 eV)				
C-N (285.9 eV)	7.1 %	5.8 %	8.7 %	6.5 %
C-OH (286.4 eV)	16.6 %	11.4 %	18.6 %	14.4 %
C-O-C (287.2 eV)	11.1 %	6.9 %	20.7 %	5.5 %
C=O (287.7 eV)	3.4 %	5.2 %	3.1 %	3.7 %
COO (288.8 eV)	3.0 %	5.8 %	4.9 %	6.1 %
O/(C+O)	34.1 %	29.2 %	47.3 %	29.7 %

Table S1. The percentage of different functional groups

XPS was used to characterize the change in functional groups on GO before and after the reduction process. The peak positions follow those of previous reports.³⁻⁵ Compared with the (PDDA/GO)₅ film, the reason for the considerably lower oxygen content in the heteroassembly before UV treatment is still unclear, which may be due to the influence of titania nanosheets on the XPS analysis of the functional groups.



Fig. S8 XRD data of $(PDDA/Ti_{0.87}O_2^{0.52})_{10}$ (**a**), $(PDDA/GO/PDDA/Ti_{0.87}O_2^{0.52})_5$ (**b**) and $(PDDA/GO)_5$ (**c**) under UV light illumination. The broad hump at approximately 23° is due to the amorphous halo from the glass substrate.



Fig. S9 *G-V* curve of the $(Ti_{0.87}O_2^{0.52})_{10}$ film after removing PDDA via UV illumination for 48 h.

Calculation of carrier mobility and intrinsic carrier concentration

The carrier mobility is defined by the derivative of the Drude formula $\mu = [L/(V_{ds} \times C_i W)](dI_{ds}/dV_{gs})$, where I_{ds} , V_{ds} , L, and W are the current, voltage, channel length and width between drain and source electrodes. C_i is the specific capacitance of the silicon dioxide dielectric layer. For our devices, Land W is 40 and 400 µm, V_{ds} is set to 1 V; and C_i equals 17.7 nF cm⁻².

The minimum conductance in the neutral point can be expressed as follows: $G_{\min} = (I_{ds})_{\min}/V_{ds} = \sigma_{\min} E S/V_{ds} = \sigma_{\min} t W/L$, where $(I_{ds})_{\min}$, σ_{\min} , E, S, and t are the drain and source currents at the neutral point, the conductivity at the neutral point, the electric field between drain and source electrodes, the cross section area and the thickness of the channel materials, respectively. The minimum conductivity can be estimated using the following formula: $\sigma_{\min} = e n_i (\mu_e + \mu_h)$, where n_i, μ_e and μ_h are the intrinsic carrier concentration, electron and hole carrier mobility, respectively.⁶ We consider the area carrier concentration here; therefore, t = 1, and consequently, the intrinsic carrier concentration here; therefore, t = 1, and be between the G-V curves shown in Figure 4, and the values of μ_e and μ_h can be estimated from the derivative of the Drude formula.



Fig. S10 (a) Temperature dependence of the minimum conductance (G_{\min}) of $(rGO)_{10}$ and $(rGO/Ti_{0.87}O_2^{0.52})_{10}$ when the gate voltage sweeps; (b) the temperature dependence of the on/off ratios of $(rGO)_{10}$ and $(rGO/Ti_{0.87}O_2^{0.52})_{10}$.

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