

Supplementary Information

Stacked vanadium pentoxide-zinc oxide interface for optically-chargeable supercapacitor

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1 Digital image of the device



Fig. S1 Digital image of the fabricated symmetric supercapacitor using $V_2O_5/ZnO/FTO$ electrodes.

2 Energy-dispersive X-ray spectroscopy (EDS) analysis of $V_2O_5/ZnO/FTO$

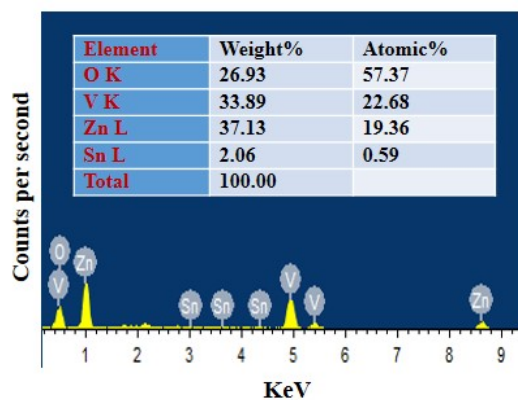


Fig. S2 EDS analysis of the $V_2O_5/ZnO/FTO$ electrode showing atomic and weight percentages of different elements.

3 UV-Visible absorption spectroscopy

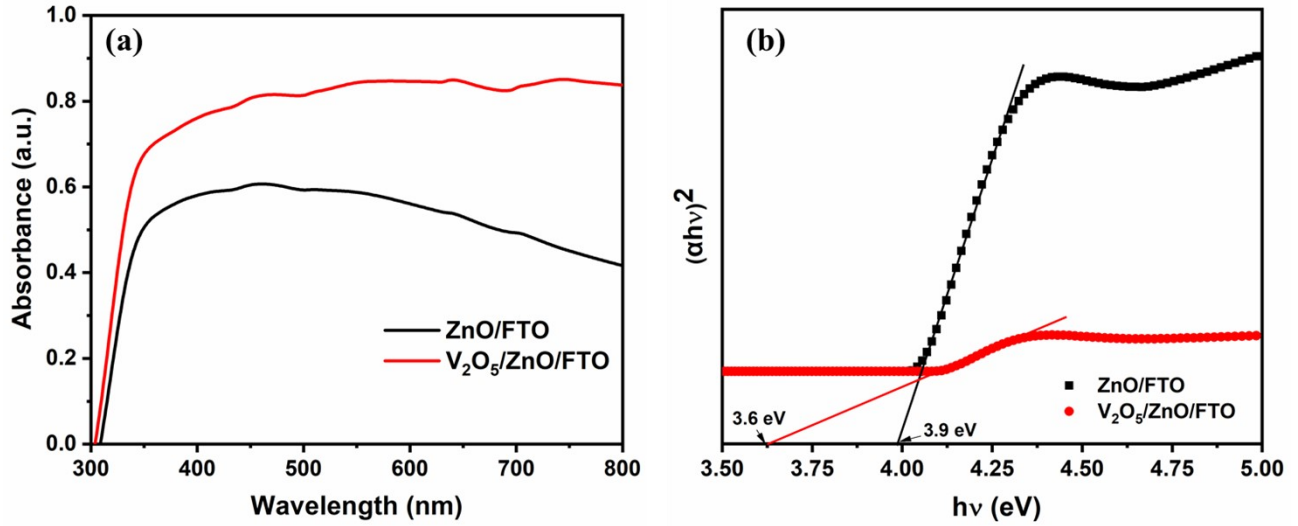


Fig. S3(a) UV-Visible spectra and (b) corresponding Tauc plots to calculate the band gap of ZnO/FTO and V₂O₅/ZnO/FTO heterostructure.

The UV-Visible spectroscopy of the synthesized heterostructure showed good optical absorbance in the UV (315-400 nm) and visible (400-780 nm) range of the electromagnetic spectrum (**Figure S3(a)**).¹ Interestingly, the heterostructured V₂O₅/ZnO showed a higher light absorption in the UV and visible range than ZnO, implying that the heterostructure is optically active and suitable for optoelectronic applications. The band gaps were evaluated by plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (Tauc plots, **Figure S3(b)**) according to Kubelka-Munk theory as:

$$\alpha h\nu = A(h\nu - E_g)^n, \quad (1)$$

where α is the absorption coefficient of the material, A is an energy-independent constant, $h\nu$ is photon energy in eV, E_g is the material's bandgap, and n is a constant that depends upon the type of optical transition ($n = 1/2$, for direct transition). The calculated band gap values from the Tauc plots are 3.9 eV and 3.6 eV for ZnO/FTO and V₂O₅/ZnO/FTO, respectively. The slight reduction

in the bandgap of the heterostructure is advantageous for the electron transfer from the valence band to the conduction band under light irradiation.

4 Raman spectroscopy analysis

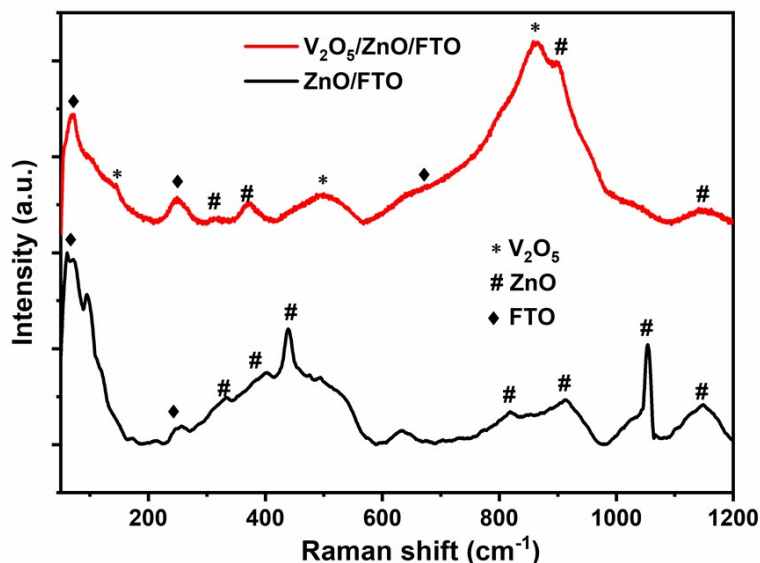


Fig. S4 Raman spectra of ZnO/FTO and V_2O_5 /ZnO/FTO heterostructure.

The Raman spectrum of the synthesized heterostructure is compared to that of ZnO in the 50-1200 cm^{-1} range (**Figure S4**). The peaks at 320, 371, and 437 cm^{-1} belong to the E_2 mode and the longitudinal mode vibrations of wurtzite ZnO nanorods.² Similarly, the peak at 1145 cm^{-1} corresponds to the multi-phonon vibration of ZnO.³ The ZnO's Raman peak at 1055 cm^{-1} corresponds to the rocking vibration of $-\text{CH}_3$ from zinc acetate, while peaks at 820 and 916 cm^{-1} correspond to the C-C stretching vibration of zinc acetate. The peak at 500 cm^{-1} is due to triply coordinated oxygen ($\text{V}_3\text{-O}$) stretching of the V_2O_5 structure.² The low-frequency peak at 145 cm^{-1} shows the layered structure of V_2O_5 , which is useful in ion intercalation during electrochemical charge storage. The appearance of a vibrational peak at 850 cm^{-1} confirms the composite formation

between the two metal oxides.⁴ The rest of the peaks correspond to the FTO substrate, some of which are slightly shifted due to the heterostructure formation.

5 Fourier transform infrared spectroscopy analysis

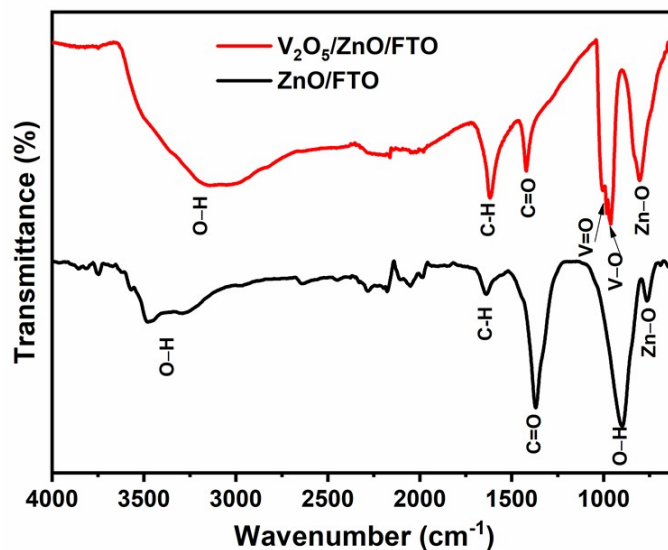


Fig. S5 FTIR spectra of ZnO/FTO and V_2O_5 /ZnO/FTO heterostructure.

The characteristic FTIR transmission spectra of ZnO and V_2O_5 /ZnO heterostructure are shown in **Figure S5**. The peak at 750 cm^{-1} corresponds to the Zn–O stretching mode that confirms the formation of ZnO,⁵ while the heterostructure's spectrum shows the 960 and 1000 cm^{-1} peaks that correspond to the symmetric stretching vibration of the V–O and V=O bond of vanadyl oxygen, respectively.^{6,7} The 1366 cm^{-1} peak corresponds to the C=O bond stretching vibration, and the 1622 cm^{-1} peak to the C–H vibration resulting from the partial transformation of zinc acetate ions ($\text{Zn}(\text{CH}_3\text{COO})_2$) into aldehyde during the synthesis.^{5,7} The O–H stretching vibration is observed as a broad peak ranging from 3200 to 3600 cm^{-1} .

6 Electrochemical analysis of $V_2O_5/ZnO/FTO$ heterostructure in a three-electrode system

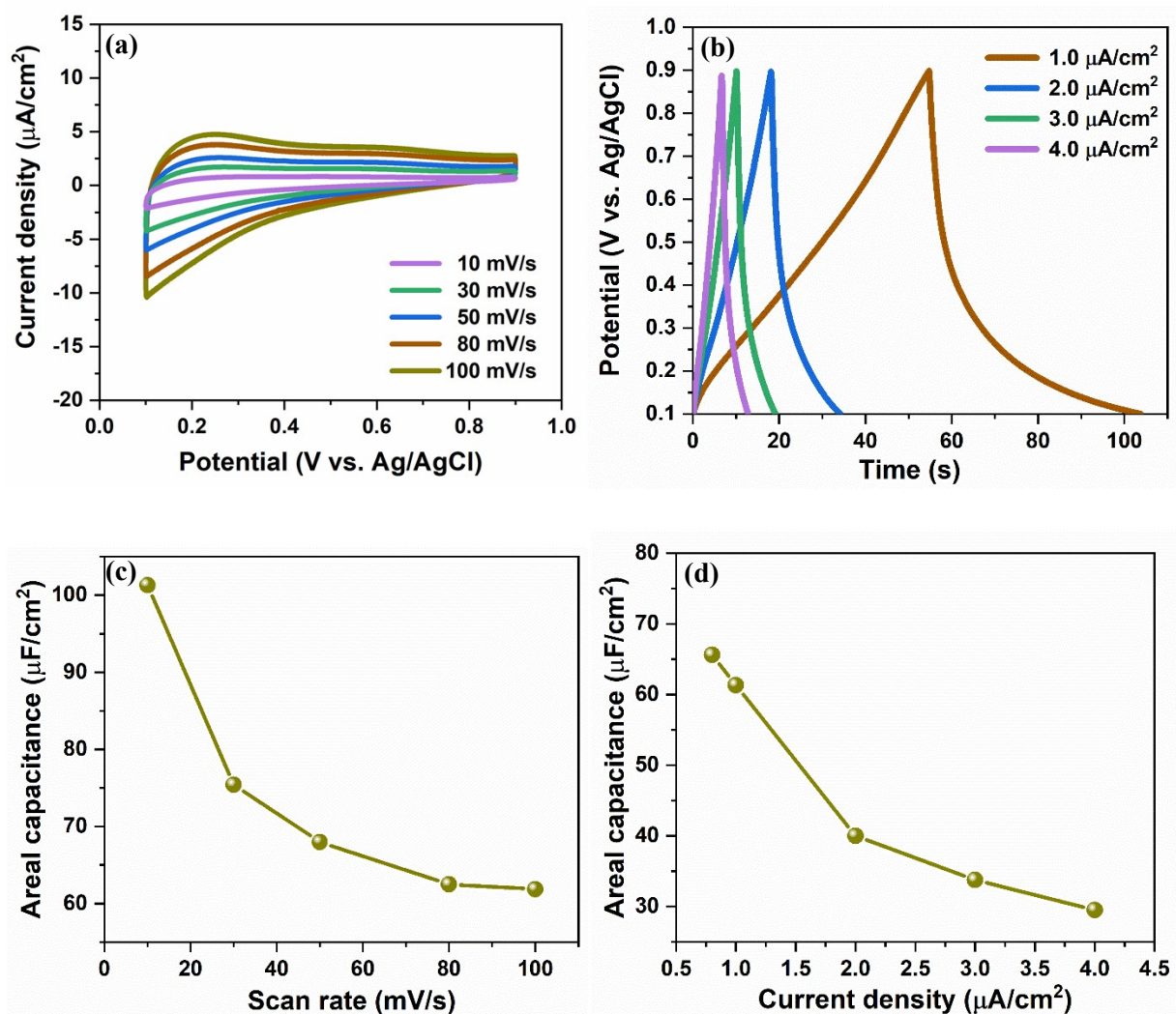


Fig. S6 (a) CV and (b) GCD curve of $V_2O_5/ZnO/FTO$ electrode measured in three-electrode system in the potential range of 0.1 to 0.9 V. (c) and (d) shows corresponding areal capacitance calculated from CV and GCD curve, respectively.

7 Coulombic efficiency of the $V_2O_5/ZnO/FTO$ heterostructure

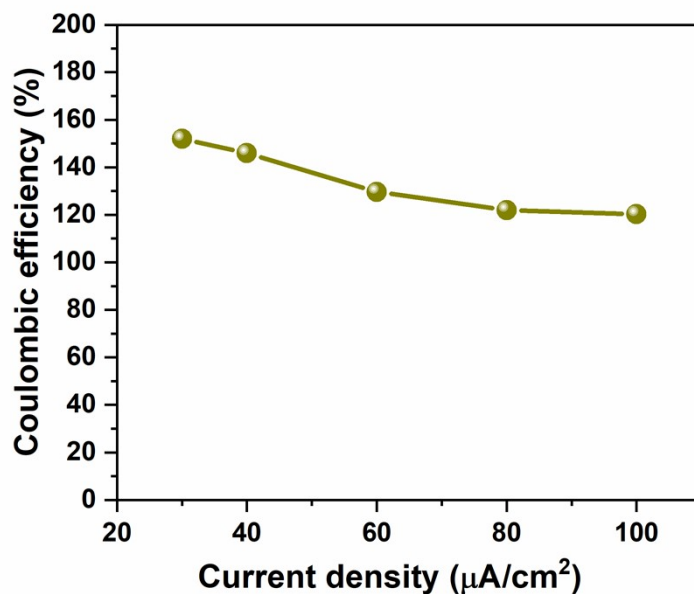


Fig. S7 Coulombic efficiency of $V_2O_5/ZnO/FTO$ heterostructure at different current densities.

8 Areal capacitance of device

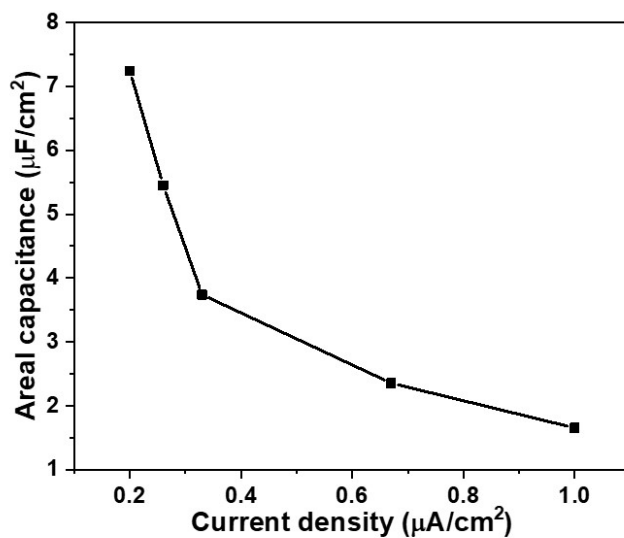


Fig. S8 Areal capacitance (C_A) of the device at various current densities calculated from GCD curve using the integration method.

9 Cyclic voltammetry comparison of the device under dark and UV-illuminated conditions

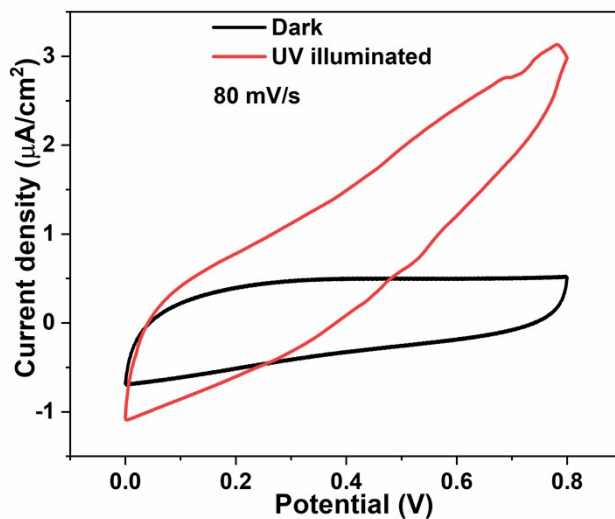


Fig. S9 CV curve of SSD at 80 mV/s scan rate under dark and UV illuminated conditions.

10 Capacitance retention

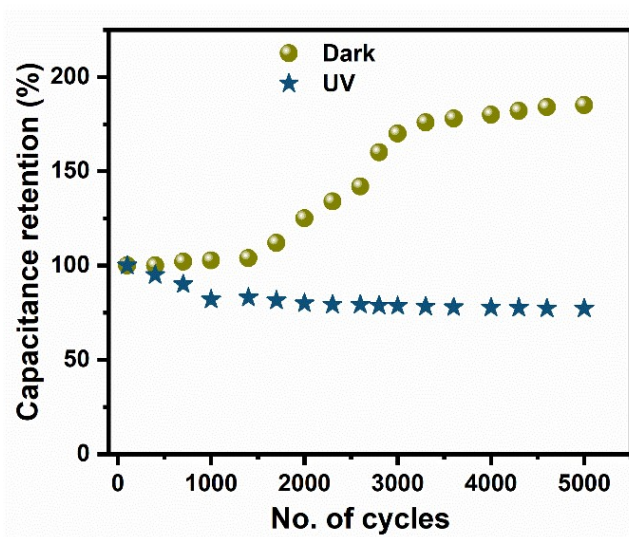


Fig. S10 Capacitance retention of the supercapacitor under dark and UV illuminated conditions.

11 Effect of electrochemical cycles on the morphology and structure of $V_2O_5/ZnO/FTO$ heterostructure

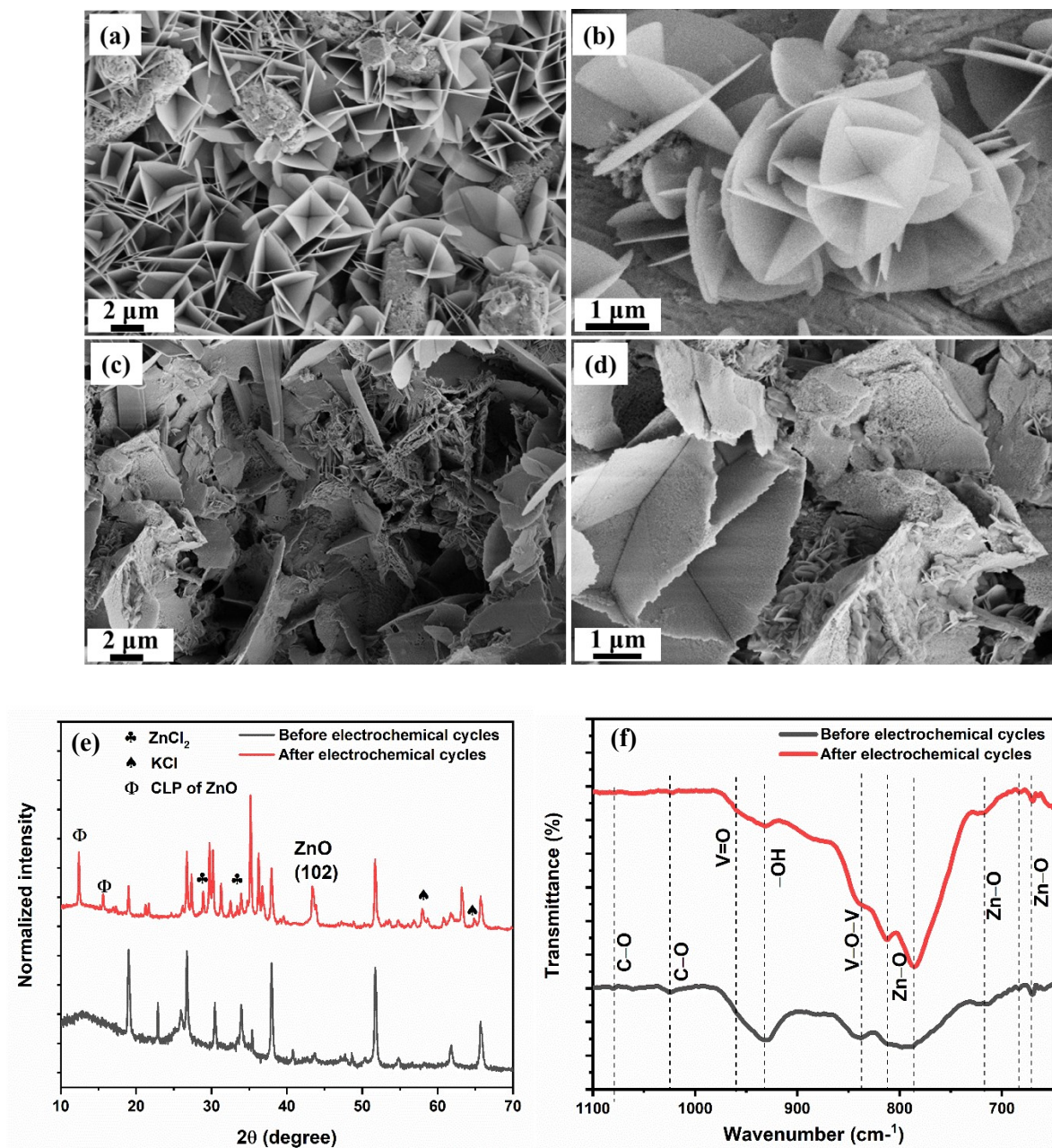


Fig. S11 (a) and (b) SEM images of $V_2O_5/ZnO/FTO$ heterostructure before electrochemical cycles. (c) and (d) SEM images of $V_2O_5/ZnO/FTO$ heterostructure after 3000 electrochemical cycles. (e) XRD and (f) FTIR analysis of $V_2O_5/ZnO/FTO$ heterostructure before and after charge-discharge cycles in 1M KCl electrolyte. (CLP: chloride lamellar phase)

12 Comparison with other studies

Table S1: Comparison of V₂O₅/ZnO/FTO-based supercapacitor with similar studies conducted in past

S. No.	Material	Electrolyte	Capacitance	Ref.
1	Graphene thin films	PVA/H ₃ PO ₄	12.4 $\mu\text{F}/\text{cm}^2$	14
2	Graphene	PVA/H ₂ SO ₄	5.33 $\mu\text{F}/\text{cm}^2$	15
3	MAPbI ₃ perovskite	PVA/KOH/Chlorobenzene	8.06 $\mu\text{F}/\text{cm}^2$	16
4	graphene-graphene quantum dots chelate	PVA/H ₃ PO ₄	9.09 $\mu\text{F}/\text{cm}^2$	17
5	Silicon nanowires	NEt ₄ BF ₄ /polycarbonate	6.6 $\mu\text{F}/\text{cm}^2$	18
6	ZnO nanowires over FTO glass	1M KCl	20 $\mu\text{F}/\text{cm}^2$	19
7	Multilayer graphene	6M KOH	4 $\mu\text{F}/\text{cm}^2$	20
8	V₂O₅/ZnO/FTO	PVA/KCl	~15 $\mu\text{F}/\text{cm}^2$	This work

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