Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

CO_2 and Temperature Dual Stimuli-Responsive "Smart" Mxene Phases

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Experimental

Materials

All chemicals were analytical grade or of the highest purity available. Vanadium powders (99.5% purity, 200 mesh) were obtained from Liuyang Yaguang Co. Ltd, Aluminium powders (99.9% purity, 300 mesh) were bought from Targets Research Center of General Research Institute for Nonferrous Metals. Flake Graphite (99.5% purity, 200 mesh) was obtained from Qingdao OER graphite Co. Ltd. Methanol, alcohol and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. 2-dimethylaminoethyl methacrylate (DMAEMA) was purchased from the Energy Chemical Company.

Preparation of V_2AlC [1]

The V_2AlC phase was synthesized using commercially available powders. Vanadium, Aluminium and flake graphite were mixed at molar ratios of 2:1.2:0.9 by planetary ball mill for 12h. The milling medium was alcohol. The powder mixture after dried at 50℃ in oven for 24h was then cold pressed in a graphite mold. The green pellet was further calcined in a Pulse-Electric-Current-Sintering device (HP D 25/3, FCT Group) at 1500℃ for 30min in Ar atmosphere. The initial heating rate from 450℃ to 1300℃ was 50℃/min and the following heating rate from 1300℃ to 1500℃ was 20℃/min. The initial cooling rate from 1500℃ to 1300℃ was 50℃/min and the second cooling rate from 1300℃ to 450℃ was 100℃/min. Then the pellet was cooled with furnace cooling. The pressure applied on the green body was 30MPa at latter part of holding stage for 10min. **Fig. S1** showed the details of sintering curve.

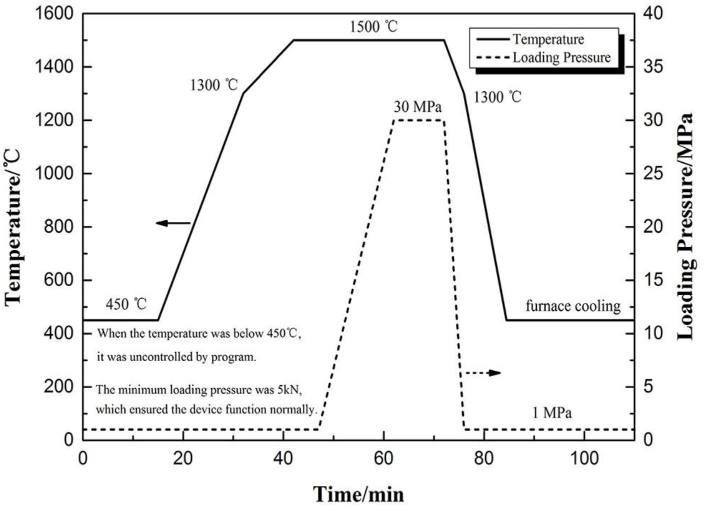


Fig. S1 The sintering curve of 2V-1.2Al-0.9C by pulse electric current sintering.

Preparation of V_2C [1]

The as-synthesized product bulk was pulverized (whose particle size should be below 300 mesh) to prepare V_2C MXene. The details of the process were as follows: First, the V_2AlC particles were immersed in HF solution (40 wt. %) for 7d and the solution should be stirred slightly every 12h. Then the nano-slices were successively cleaned by deionized water and alcohol and dried at RT for 48h.

SIPGP [2]

20 mg of V_2C, 2 mL of monomer (DMAEMA) were added into a tube. The tube was placed under a UV lamp and irradiated for 40 min at room temperature. A 250 W high-pressure mercury lamp from Jiguang Co. (Shanghai, China) was used for SIPGP. Its wavelength ranged from 200 to 400 nm. The distance between the reaction mixture and the light source was 10 cm. The reaction mixture was stirred with a magnetic stirrer under dry nitrogen at room temperature during the irradiation. The reaction mixture was centrifuged at 8000 rpm for 10 min in methanol, which led to sedimentation of the polymer-grafted V_2C. The supernatant, which contained unreacted monomer was discarded. The particulate sediment was redispersed in methanol and centrifuged two more times. To remove the ungrafted polymer, the precipitate was dispersed in acetone and centrifuged repeatedly. The black polymer-grafted V_2C was collected and dried in vacuum at 40 ^{o}C for 24 h before characterization.

Characterizations.

The synthetic bulk and immersed powders were characterized by X-ray diffractometer (XRD, Bruker AXS D8 Advance, Germany) with Cu K_α radiation and their spectra were collected at a step scans of

0.02° 2θ and a step time of 0.2 sec. Small Angle X-ray diffractometer (SAXD) of powders were also tested by X-ray diffractometer (XRD, Bruker AXS D8 Advance, Germany) with Cu K_α radiation, while their spectra were collected at a step scans of 0.01° 2θ and a step time of 0.2 sec. The microstructure and chemical component were observed by Field Emission Scanning Electron Microscope (SEM, S4800, Hitachi, Japan) equipped with Energy Dispersive Spectrometer (EDS). Confocal Micro-Raman Spectrometer (Renishaw inVia Reflex, UK) with 532nm laser line was applied to record the Raman spectra of V_2AlC, V_2C and V_2C@PDMAEMA. Fourier transform infrared (FTIR) Spectroscopy (Nicolet 6700, Thermoscientific, USA): The spectra were measured with a spectrometer. Absorbance spectra were collected using a spectral resolution of 4 cm^{-1} at room temperature over a frequency range of 4000-500 cm^{-1}. The background spectra were recorded on corresponding KBr. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO-TGA/DSC I instrument with a heating rate of 10 °C min^{-1} in flowing N_2 and a sample of 3-5 mg. UV-vis absorption spectra of the samples were recorded using a Lambda 950 spectrophotometer (Perkin-Elmer). Measurements of the solutions were taken in 3mL quartz cuvettes. X-ray Photoelectron spectrum (XPS) (AXIS ULTRA DLD, Kratos Analytical Ltd., Manchester, UK) measurements were carried out at pressures between 10^{-9} and 10^{-8} mbar. All peaks are referenced to the signature of the C 1s peak for carbon at 284.8 eV, the XPS system was equipped with a monochromatic Al Kα source. The transmittance of the dispersion was measured by Lambda 950 spectrophotometer (Perkin-Elmer). The wavelength of 610 nm in the visible region was selected to determine the transmittance to exclude the influence of aromatic rings in the polymer skeleton. The conductivity of V_2C@PDMAEMA aqueous suspension and the pure water was measured with a DDSJ-308F conductometer (Shanghai INESA Instrument) at 25 °C, and the average values were calculated from three runs of a certain measurement.

Figures

As shown in **Fig. S2,** the presence of -OH groups after HF treatment was firstly confirmed in V_2C. In the spectrum of neat PDMAEMA, an intense increase of the absorption peak appears at 1728 cm^{-1} corresponding to the stretching vibration of ester carbonyl group in the PDMAEMA. By comparing the FT-IR spectra of pure V_2C and pure PDMAEMA, in the spectrum of V_2C@PDMAEMA, the presence of asymmetric and symmetric stretching vibrations of $-CH_2$ on V_2C indicates the grafting of aminopropyl groups on the surface of V_2C. The characteristic bands located at 1620-1650 cm^{-1} were assigned to the bending vibrations of aliphatic amine (N-H) groups.

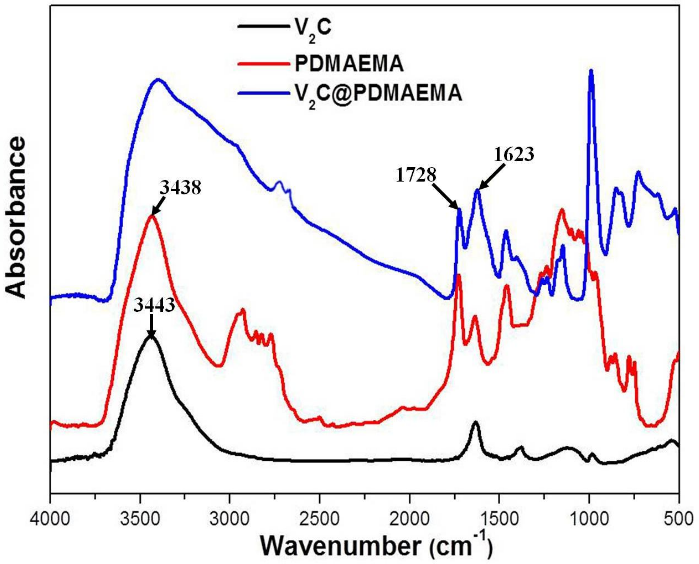


Fig. S2 FT-IR spectra of (black) V_2C, (red) PDMAEMA and (blue) V_2C@PDMAEMA.

Raman spectra of V_2AlC before and after HF treatment and V_2C@PDMAEMA are shown in **Fig. S3**. Peaks Ⅰ, Ⅱ, Ⅲ and Ⅳ vanished after treatment. Peaks Ⅰ to Ⅳ can be assigned to Al-V vibrations, while peak Ⅴ involves only V-C vibrations in V_2C. This fact confirms the loss of Al from the structure.[3] After grafting with PDMAEMA, the above bands belonging to V_2C powder were greatly decreased or even disappeared, possibly due to the high grafted amount of PDMAEMA in V_2C@PDMAEMA nanocomposites.

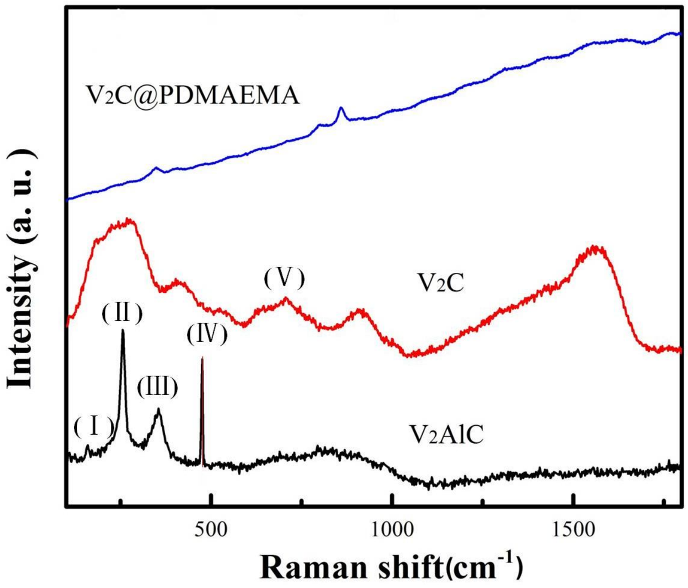


Fig. S3 Raman spectra of V_2AlC, V_2C and V_2C@PDMAEMA.

As shown in **Fig. S4**, a weight loss of 15% for the V_2C was assigned to the physically adsorbed water on the V_2C surface. For the resultant V_2C@PDMAEMA with the grafted PDMAEMA brushes, the weight loss was 30% with two distinct weight loss stages between 200 and 600 °C. The first weight loss until 200

°C was also due to the evaporation of the physically adsorbed water or solvent, and the second major weight loss from 200 to 600 °C was due to the decomposition of the polymer component in the shell layer of the corresponding nanocomposites. The V_2C@PDMAEMA nanocomposite showed 73% weight loss, indicating the weight percentage of PDMAEMA was about 58%.

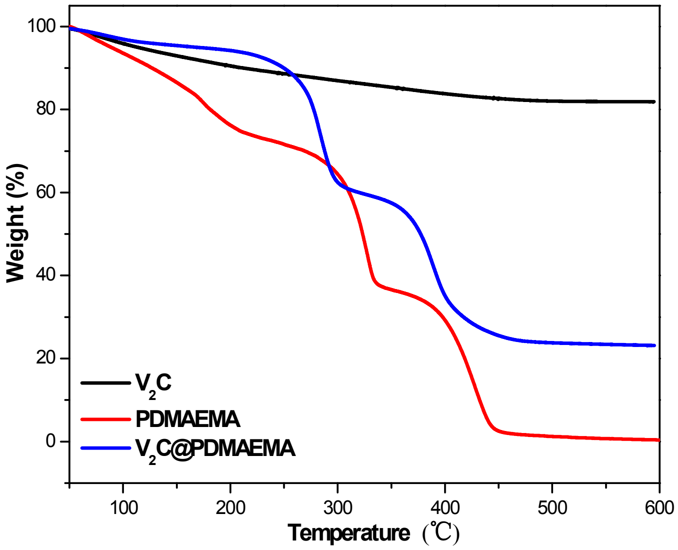


Fig. S4 TGA spectra of (black) V_2C, (red) PDMAEMA and (blue) V_2C@PDMAEMA.

We tested the distance between MXene layers of V_2C@PDMAEMA by SAXD. The patterns (**Fig. S5**) show that no diffraction peaks from 0.5° to 5°, whose identity distance is from 17.6nm to 1.8nm which calculated from Braggs' equation ($2d\sin\theta = \lambda$). Compared with the statistical result of SEM (about 100nm-200nm), it is obviously beyond the limit of this spectrum. Besides, the high background makes it difficult to test the layer distance exceeding 100nm. Moreover, the distance between MXene layers is unordered. It is difficult to form intense peak in SAXD.

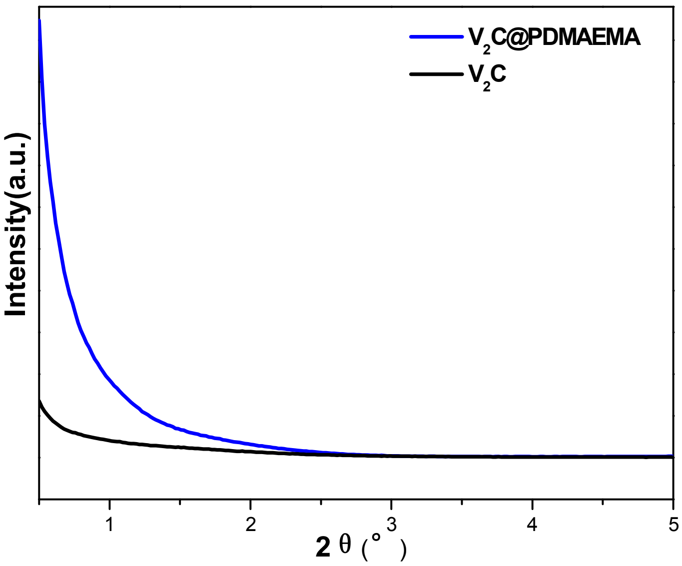


Fig.S5 Small angle diffraction of (a) V_2C and (b) V_2C@PDMAEMA from 0.5° to 5°.

Fig.S6 presented the X-ray photoelectron survey spectra (XPS) of V_2C, PDMAEMA and hybrid system of V_2C@PDMAEMA. A new peak of N1s was found after the V_2C being grafting with PDMAEMA to form hybrid V_2C@PDMAEMA.

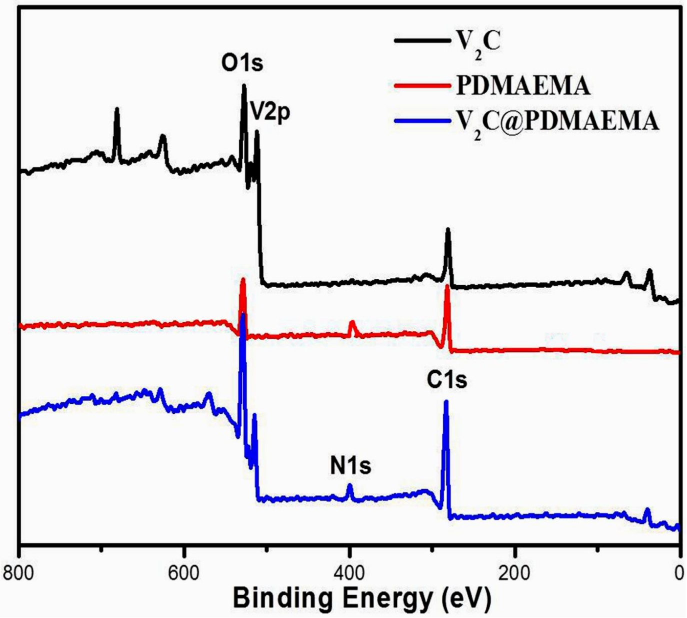


Fig. S6 XPS spectra of V_2C, PDMAEMA and hybrid system of V_2C@PDMAEMA.

The valence state of V_2C layers and V_2C@PDMAEMA hybrid materials are determined by X-ray photoelectron spectra (XPS). As presented in **Fig. S7**, both nitrogen and vanadium signals can be observed, suggesting that N species have been successfully incorporated into V_2C phases.

A high-resolution spectrum of the V2p region (**Fig. S7 (A)**) revealed the presence of photoemission which could be best fit with components corresponding to: i) unreacted MAX phase V_2AlC (V2p, 513.1

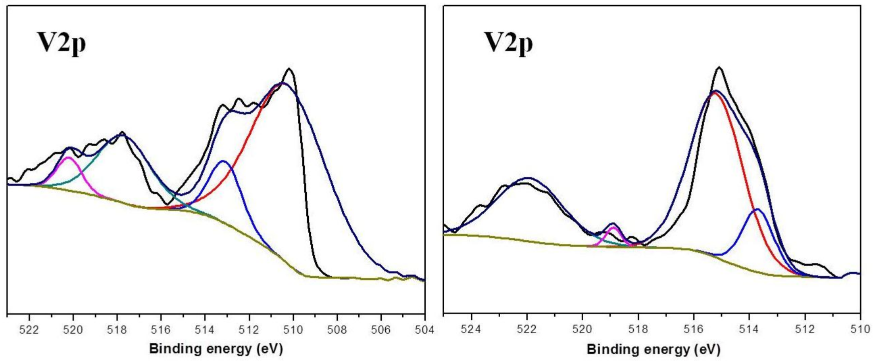
eV, V2p3/2, 520.2 eV) and, ii) oxidized vanadium (V2p, 517.7 eV).[4-5]

A high-resolution spectrum in the C 1s region (**Fig. S7 (B)**) was best fit by four components with the first two corresponding to adventitious contamination (C 1s, 286.4 eV, and, C 1s, 284.8 eV), a high-binding energy peak similar to a peak attributed to adsorbed alcohol (C 1s, 288.8 eV), [5] and a low-binding energy peak (C 1s, 282.4 eV) that corresponds to C in V_2C.[6] The C1s spectra of V_2C@PDMAEMA nanocomposites indicated the presence of three main types of carbon bonds, i.e., C–C and C–H (284.8 eV), C–O (286.4 eV) and C=O (288.3eV),

A high-resolution spectrum in the O 1s region (**Fig. S7 (C)**) could be fit by broad peaks at 526.0, 528.0 and 531.8 eV. The components centered at 526.0 eV and 528.0 eV are consistent with mixed vanadium oxide (VOx) and surface oxide groups,[4] while the peak centered at 531.8 eV is again consistent with intercalated water.[4,7] From the XPS data, the V_2C@PDMAEMA displayed high intense O1s peak due to the increased oxygen groups present in the PDMAEMA.

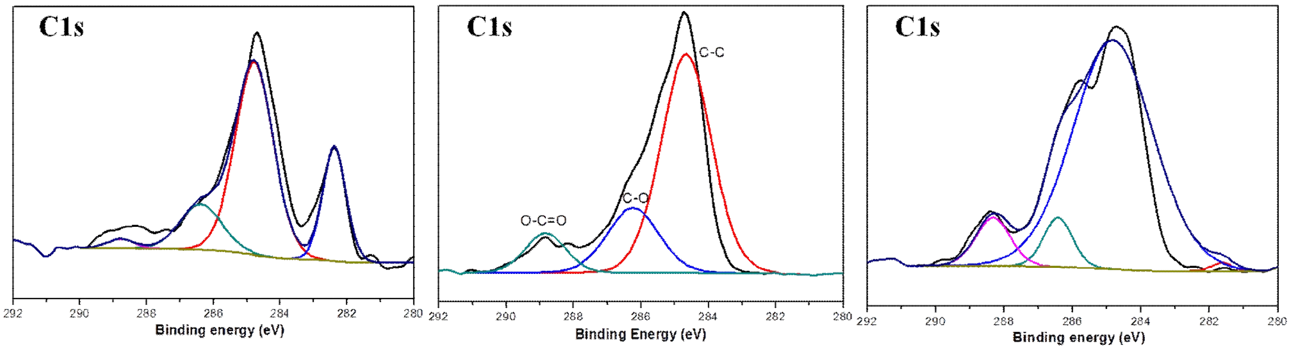
The high-resolution XPS N 1s spectrum of V_2C@PDMAEMA (**Fig. S7 (D)**) can be split into two sub-levels at 397.5 and 399.9 eV that can be assigned to the N-C and N-methyl bonds of the grafted PDMAEMA chains, respectively.

(A)



V_2C **V_2C@PDMAEMA**

(B)



V_2C **PDMAEMA** **V_2C@PDMAEMA**

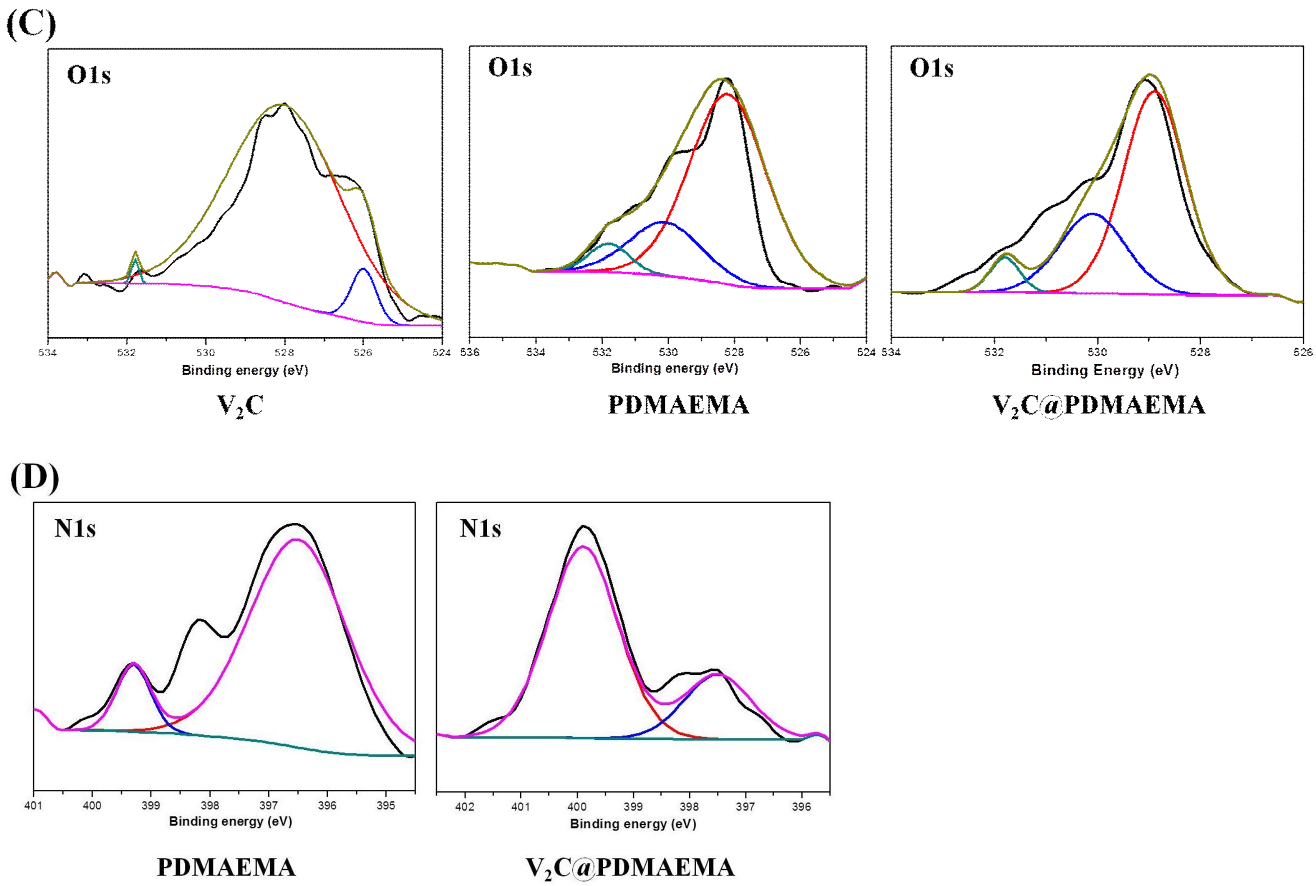


Fig. S7 High-resolution XPS spectra of V_2C, PDMAEMA and V_2C@PDMAEMA in the (A) V 2p region, (B) C 1s region, (C) O 1s region and (D) N 1s region.

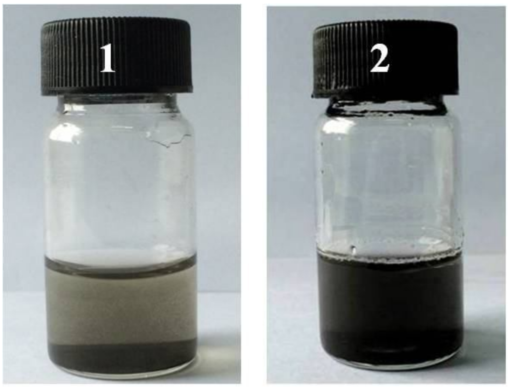


Fig. S8 Appearances of V_2C (1) and V_2C@PDMAEMA (2) in water after one week and the concentration of V_2C and V_2C@PDMAEMA are both 3 mg mL^{-1} .

References

1 M. Naguib, J. Halim, J. Lu, K. M. Cook, L. Hultman, Y. Gogotsi, M. W. Barsoum, *J. Am. Chem. Soc.* 2013, **135**, 15966-15969.

2 J. Chen, P. Xiao, J. C. Gu, D. Han, J. W. Zhang, A. H. Sun, W. Q. Wang, T. Chen, *Chem. Commun.* 2014, **50**, 1212-1214.

3 J. E. Spanier, S. Gupta, M. Amer, M. W. Barsoum, *Phys. Rev. B* 2005, **71**, 012103.

4 J. G. Choi, *Appl. Surf. Sci.* 1999, **148**, 64-72.

5 P. Frantz, S. V. Didziulis, L. C. Fernandez-Torres, R. L. Guenard, S. S. Perry, *J. Phys. Chem. B* 2002, **106**, 6456-6464.

6 M. W. Barsoum, A. Crossley, S. Myhra, *J. Phys. Chem. Solids* 2002, **63**, 2063-2068.

7 Y. Taki, O. Takai, *Thin Solid Films* 1998, **316**, 45-50.