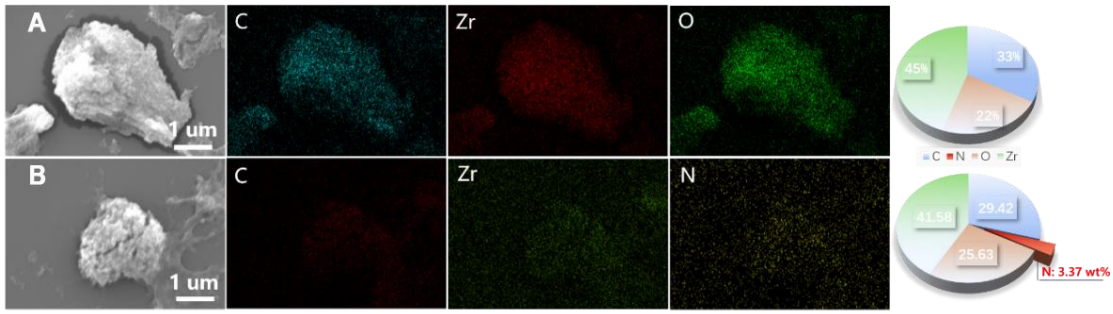
Supplementary Materials

Graphene oxide membranes using MOF@Chitosan core-shell nanoparticles as dual modulators for dye separation

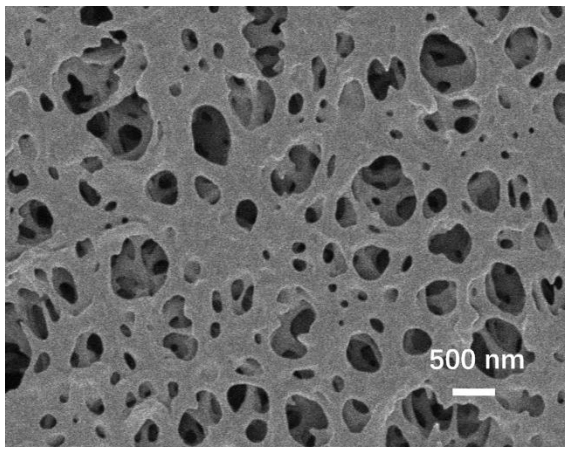
Xingying Wang[1,#], Yongmei Guo[2,#,*], Xiaolei Cui[1,#], Zhikun Wang[3], Zhihan Zhang[1], Lubomira Tosheva[4], Hailing Guo[1,*]

[1]College of Chemical and Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, Shandong, China.
[2]Fujian Key Laboratory of Novel Functional Textile Fibers and Materials, Minjiang University, Fuzhou 350108, Fujian, China.
[3]School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao 266580, Shandong, China.
[4]Department of Natural Sciences, Manchester Metropolitan University, Manchester M1 5GD, UK.
[#]Authors contributed equally.

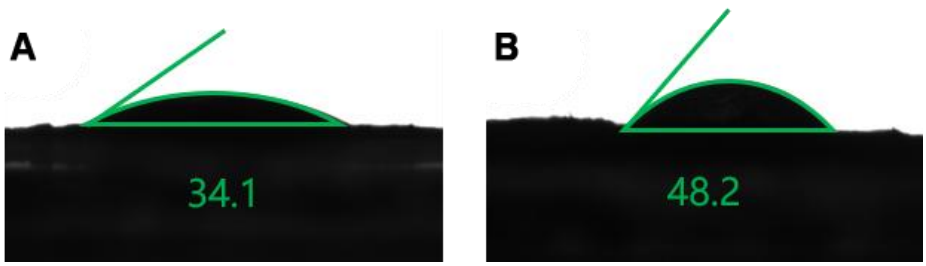
[*]**Correspondence to:** Prof. Yongmei Guo, Fujian Key Laboratory of Novel Functional Textile Fibers and Materials, Minjiang University, No. 200 Xiyuangong Road, Minhou County, Fuzhou 350108, Fujian, China. E-mail: yongmeiguo@mju.edu.cn; Prof. Hailing Guo, College of Chemical and Chemical Engineering, China University of Petroleum (East China), No.66 Changjiang West Road, Huangdao District, Qingdao 266580, Shandong, China. E-mail: guohl@upc.edu.cn



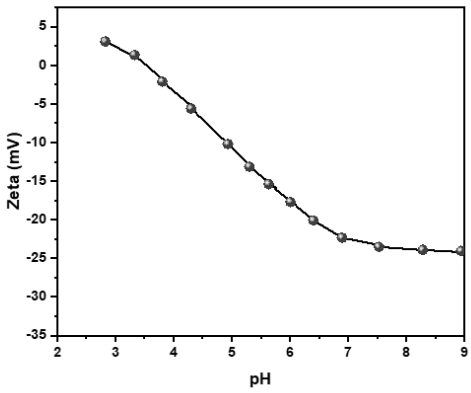
Supplementary Figure 1. SEM images with EDS mapping for (A) UiO-66-COOH and (B) MOF@CS core-shell nanoparticles.



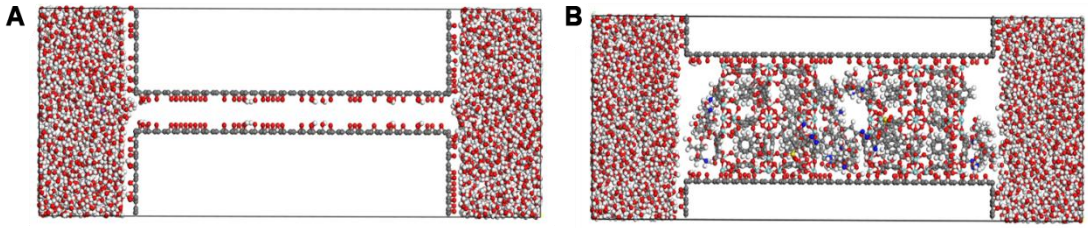
Supplementary Figure 2. SEM images of PES substrate.



Supplementary Figure 3. The water contact angles of (A) GO and (B) MOF@CS.



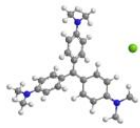
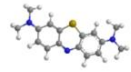
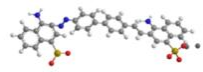
Supplementary Figure 4. Zeta potential data of M3.



Supplementary Figure 5. (A) GO nanochannel; (B) MOF@CS-GO nanochannel.

All-atom molecular dynamics (MD) simulations were performed to study the physical insights of the motion of water inside the membrane using the Materials Studio software. The initial models are given in Supplementary Figure 4. The GO sheets forming the nanochannel were constrained during MD simulations. All the Zr atoms forming the UiO-66 cluster were also constrained, while the connecters (1,2,4-benzenetricarboxylic acid) and grafted chitosan segments were allowed to move, during MD simulations. Periodic boundary conditions were applied to all three directions of the simulation boxes. The COMPASSII force field was used to describe all the inter- and intramolecular interactions. The summation methods for electrostatic and van der Waals interactions were Ewald (accuracy = 0.001 kcal/mol, buffer width = 0.5 Å) and Atom based (cutoff distance = 12.5 Å, cubic spline width = 1 Å, buffer width = 0.5 Å), respectively. Long range correction was applied to the calculation of van der Waals interactions. The simulation models were first optimized using the Smart algorithm (energy: 0.001 kcal/mol, force: 0.5 kcal/mol/Å). Then MD simulations were conducted on the optimized models. The NVT ensemble was applied, and the NHL thermostat (Q ration = 0.01, decay constant = 1.0 ps) was used to control the system temperature at 300 K. The total simulation time was 1 ns, while the last 500 ps was used for result analysis. The time step was set to 1 fs.

Supplementary Table 1. The detailed information of dyes

Dye	Crystal violet	Methylene blue	Congo Red
Chemical structure			
Molecular formula	$C_{25}H_{31}N_3$	$C_{16}H_{18}ClN_3S$	$C_{32}H_{22}N_6Na_2O_6S_2$
Charge	Positive	Positive	Negative
Size	13.1 × 13.1 Å	13.2 × 5.3 Å	25.6 × 7.3 Å
Molecular weight	373.85 $g{\cdot}mol^{-1}$	319.85 $g{\cdot}mol^{-1}$	696.68 $g{\cdot}mol^{-1}$

Supplementary Table 2. The performance comparison of M3 with other NF membranes prepared in literatures

Membrane	Dye	*Pressure* (*bar*)	Permeance ($Lm^{-2}h^{-1}$ bar^{-1})	Rejection (%)	Ref.
MWCNT@CS-PEBA/PES	CR[a]	2	5.3	95	[1]
Fe_3O_4/CS/PES	DR[b]	4	9	99	[2]
TiO_2/GO	DR	5	10.8	87.2	[3]
GO	MB[c]	1	11.5	96.29	[4]
GO	CR	8	11.34	79	[5]
PA/UiO-66	CV[d]	5	13	90	[6]
SiO_2/GO	MB	1	14.8	88.92	[7]
MOF@GO-CS	CR	3	14.62	99	[8]
GO/NH_2-Fe_3O_4	CR	5	15.6	94	[9]
UiO-66@GO/PES	MO[e]	-	15.7	88.6	[10]
GO/PES	DR	3	16	88.8	[11]
UiO-66-$(COOH)_2$/prGO	MB	1	20	92.55	[12]
GO/MXene	CR	0.5	25	90	[13]
Sm-MOF/GO	MB	-	26	91	[14]
GO	MB	3.4	27.6	66	[15]
MOF@CS-GO	CR	2	34.	95.6	This work

[a]Congo red; [b]Direct red; [c]Methylene blue; [d]Crystal violet; [e]Methyl orange.

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