Electronic Supplementary Information

Layered double hydroxide/boron nitride nanocomposite membranes for efficient separation and photodegradation of water-soluble dyes

^{b.} School of Chemistry, Trinity College Dublin, Dublin 2, Ireland, D02 PN40

Table of contents:

Section S.1: Zeta potential measurements

- Section S.2: Optimisation studies of composition of LDH/BNOx nanocomposite membranes
- Section S.3: Supplementary SEM and TEM images
- Section S.4: Water flux of LDH/BNOx nanocomposite membranes
- Section S.5: Adsorption of dyes by LDH/BNOx nanocomposite membranes

Section S.6: Photodegradation of dyes by LDH/BNOx nanocomposite membranes

Table of figures:

Figure S.1: Zeta potential measurement of exfoliated BNOx in water.

Figure S.2: Zeta potential measurement of CuAl-CO₃ nanosheets in water.

Figure S.3: Zeta potential of LDH/BNOx nanocomposite in water.

Figure S.4: UV-Vis spectra of the retention of 20 mL of Evans Blue by the LDH/BNOx nanocomposite membranes with various compositions.

Figure S.5: Pure CuAl-CO₃ LDH membrane and (b) 30:70 LDH/BNOx membrane, showing mechanical failure.

Figure S.6: pXRD pattern of 50:50 LDH/BNOx nanocomposite membranes. Brown colour change is shown in inset.

^{*a.*} Áine Coogan ^a, Natalia García Doménech ^{a,b}, Donagh Mc Ginley ^a, Tigran Simonian ^{a,c,e,f}, Aran Rafferty ^d, Quentin Fedix ^f, Amy Donlan ^a, Valeria Nicolosi ^{a,c,d,e} and Yurii K. Gun'ko* ^{a,b,c}

^{c.} BiOrbic, Bioeconomy Research Centre, University College Dublin, Belfield, Dublin 4, Ireland, D04 V1E8

^{d.} AMBER Research Centre, Naughton Institute, Trinity College Dublin, Dublin 2, Ireland, DO2 PN40

^{e.} CRANN Research Centre, Naughton Institute, Trinity College Dublin, Dublin 2, Ireland, D02 PN40 ^f, Centre for Dectoral Training in the Advanced Characterization of Materials, AMRER Research Centre, Trinity College Dublin, Dublin 2, Ireland, D02 PN40

^{f.} Centre for Doctoral Training in the Advanced Characterisation of Materials, AMBER Research Centre, Trinity College Dublin, Dublin 2, Ireland, D02 PN40

^{a.} Département Chimie Science des Matériaux, Institut Universitaire de Technologie Clermont-Auvergne, 8 rue Jean-Baptiste Fabre - 43006, Le Puy-en-Velay, France

Figure S.7: Additional top-view (a,b,c) and cross-section (d,e,f) images of LDH/BNOx nanocomposite membranes.

Figure S.8: Distribution of LDH/BNOx membrane thickness across membrane samples, as evaluated from SEM images.

Figure S.9: Distribution of LDH/BNOx flakes within membranes, as evaluated from SEM images.

Figure S.10: TEM images of exfoliated BNOx nanosheets.

Figure S.11: Particle size distribution of exfoliated BNOx nanosheets, measured from TEM images.

Figure S.12: UV-Vis absorbance spectra showing absorbance of (a) Evans Blue, (b) Methyl Orange, (c) Methylene Blue and (d) Rhodamine B by LDH/BNOx nanocomposite membranes.

Figure S.13: PFO kinetic modelling of 2nd and 3rd runs of photodegradation of (a) EB, (b) MO, (c) MB and (d) RhB by LDH/BNOx nanocomposite membranes.

Figure S.14: Photodegradation control experiment of dyes using $10\mu L H_2O_2$ (30% w/w), a 5W COB LED, and no photocatalytic membrane.

Figure S.15: Significant bubbling observed during the photocatalytic degradation of RhB by LDH/BNOx nanocomposite membranes.

Figure S.16: DR UV-Vis spectrum of CuAl-CO₃ LDHs.

Figure S.17: Removal of RhB from solution by LDH/BNOx membrane under dark conditions (black), visible light in the absence of H_2O_2 (purple), and light in the presence of H_2O_2 (fuschia).

Table of tables:

Table S.1: Retention values of LDH/BNOx nanocomposite membranes with various compositions.

Table S.2: Water flux studies of hydrophilic PVDF membrane support

Table S.3: Water flux studies of LDH/BNOx nanocomposite membranes on PVDF support

Table S.4: PFO analysis of 2nd and 3rd runs of photodegradation experiments.

Section S.1: Zeta potential measurements







Figure S.2: Zeta potential measurement of CuAl-CO $_3$ nanosheets in water.



Figure S.3: Zeta potential measurement of LDH/BNOx nanocomposite in water.

Section S.2: Optimisation studies of composition of LDH/BNOx nanocomposite membranes

Membranes were prepared from a variety of compositions of LDHs. Their retentions were tested for Evans Blue and it was observed that high retentions were observed for all samples, as shown in Table S1. The UV-Vis spectra of the feed and filtrates are shown in Figure S.4.

LDH/BNOx composition by mass	Average retention (%)	No. of samples
20:80	99	3
30:70	100	1
40:60	100	1
50:50	100	2

Table S.1: Retention values of LDH/BNOx nanocomposite membranes with various compositions.



Figure S.4: UV-Vis spectra of the retention of 20 mL of Evans Blue by the LDH/BNOx nanocomposite membranes with various compositions.

However, for LDH loading above 20%, two problems were encountered. The first was that the mechanical stability of the membranes suffered, due to significant shrinking of LDHs after drying, as a large amount of water can be incorporated into their interlayer. This resulted in mechanical failure of membranes prepared with a CuAl-CO₃ LDH mass loading of 30% or above, as shown in Figure S.5.



Figure S.5: (a) Pure CuAl-CO₃ LDH membrane and (b) 30:70 LDH/BNOx membrane, showing mechanical failure.

The second issue encountered was the formation of unwanted side products. At 50% mass loading of LDH, the formation of copper (II) oxide was observed by a colour change from light blue to brown, and was confirmed by pXRD, as shown in Figure S.6. Therefore, it was decided to proceed with the 20:80 LDH/BNOx membranes, as they did not impact the mechanical stability of existing LDH side products, and were reliable and reproducible, not resulting in the formation of side products.



Figure S 6: pXRD pattern of 50:50 LDH/BNOx nanocomposite membranes. Brown colour change is shown in inset.



Figure S.7: Additional top-view and (a,b,c) and cross-sectional (d,e,f) SEM images of LDH/BNOx membranes.



Figure S.8: Distribution of LDH/BNOx membrane thickness across membrane samples, as evaluated from SEM images.

Section S.3: Supplementary SEM and TEM images



Figure S.9: Distribution of LDH/BNOx flake sizes within membranes, as evaluated from SEM images.









Figure S. 10: TEM images of exfoliated BNOx nanosheets.



Figure S. 11: Particle size distribution of exfoliated BNOx nanosheets, measured from TEM images.

Section S.4: Water flux of LDH/BNOx nanocomposite membranes

7156

7684

	1 st run	2 nd run	3 rd run
Time (s)	10.36	10.48	9.76

7239

Table S.2: Water flux studies of hydrophilic PVDF support

Flux (L m⁻² h⁻¹)

Table S.3: Water flux studies	of LDH/BNOx nanocomposite	e membranes on PVDF support
-------------------------------	---------------------------	-----------------------------

	1 st run	2 nd run	3 rd run
Time (s)	44.87	47.20	46.40
Flux (L m ⁻² h ⁻¹)	1672	1589	1616





Figure S.12: UV-Vis absorbance spectra showing absorbance of (a) Evans Blue, (b) Methyl Orange, (c) Methylene Blue and (d) Rhodamine B by LDH/BNOx nanocomposite membranes.

membranes

Section S.6: Photodegradation of dyes by LDH/BNOx nanocomposite membranes



Figure S.13: PFO kinetic modelling of 2nd and 3rd runs of photodegradation of (a) EB, (b) MO, (c) MB and (d) RhB by LDH/BNOx nanocomposite membranes.

	2 nd run		3 rd run	
Dyes	k ₁ (min ⁻¹)	R ₁ ²	k ₁ (min ⁻¹)	R ₁ ²
EB	0.0063	0.9962	0.0095	0.9963
MO	0.0094	0.9991	0.0115	0.9984
MB	0.0187	0.9934	0.0145	0.9991
RhB	0.0148	0.9968	0.0143	0.9990

Table S.4: PFO analysis of 2nd and 3rd runs of photodegradation experiments



Figure S.14: Photodegradation control experiment of dyes using $10\mu L H_2O_2$ (30% w/w), a 5W COB LED, and no photocatalytic membrane.



Figure S.15: Significant bubbling observed during the photocatalytic degradation of RhB by LDH/BNOx nanocomposite membranes.



Figure S. 16: DR UV-Vis spectrum of CuAl-CO₃ LDHs.



Figure S. 17: Removal of RhB from solution by LDH/BNOx membrane under dark conditions (black), visible light in the absence of H_2O_2 (purple), and light in the presence of H_2O_2 (fuschia).