Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Surface Modification of Thin Film Composite Forward Osmosis Membrane by Silver-Decorated Graphene-Oxide Nanosheets

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Materials and MethodS

Two series of functionalized membranes were prepared to investigate the synergetic effects of combining GO nanosheets with Ag NPs. Ag NPs were synthesized by chemically reducing silver nitrate with sodium borohydride. In this study, 10 mL of 5 mM sodium borohydride was added dropwise to 100 mL of 5 mM silver nitrate solution. During this process, the reaction medium was placed in an ice bath and stirred vigorously. The combined effect of low medium temperature and dropwise addition helped the formation of fine nanoparticles. The Ag NPs suspension was kept in a dialysis bag for two days. Next, the suspension was centrifuged for 30 min, washed three times, dried overnight in an oven, and then re-suspended in DI water. Similar to the conditions explained in the manuscript, the TFC membranes were also treated with cysteamine. This step was followed by dip-coating them in the Ag NPs suspension for 12 hr in a shaker at a speed of 100 rpm. The membranes were then washed three times by DI water. The GO functionalized TFC membranes were prepared by the dip-coating method, where 50 mg of GO nanosheets were added to 100 mL of DI water, followed by sonication for 30 min at 70% maximum power output.

To ensure durable covalent bonding of GO onto the TFC membrane, a previously published protocol was adapted from Perreault et al.[1]. Briefly, carboxylic groups of the polyamide were first converted to amine-reactive esters by direct contact of the membrane surface with 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS). An amide formation reaction with a reactive ester was used to bond ethylenediamine to the active membrane layer surface. The GO nanosheets were functionalized with EDC-NHS to free the amine groups of ED from the membrane surface. The steps are as follows: First, 4 mM EDC, 10 mM NHS and 0.5 M NaCl were dissolved in 10 mM MES buffer. The solution was adjusted to pH 5 with HCl and NaOH. The solution was then put in contact with the membrane surface for 1 h. Next, the membranes were washed and rinsed with DI water three times and then submerged in a solution of 10 mM ED, 0.15 mM NaCl in 10 mM HEPES buffer at pH 7.5. Finally, the membrane surface was washed with DI water to remove any unlinked ED.

Next, 100 mg of the GO nanosheets were exfoliated by dispersing them in 100 mL of 10 mM MES buffer at pH 6 and probe sonicating them for 15 min. This process also helped to prepare a stable suspension. Just before contacting the GO suspension (pH 7.5) with the ED functionalized

TFC FO membranes, 2 mM EDC and 5 mM NHS were added to the suspension. The GO functionalized membranes were washed, rinsed three times, and stored in DI water at 4°C until use.

Nanoparticles and Nanocomposites Characterization

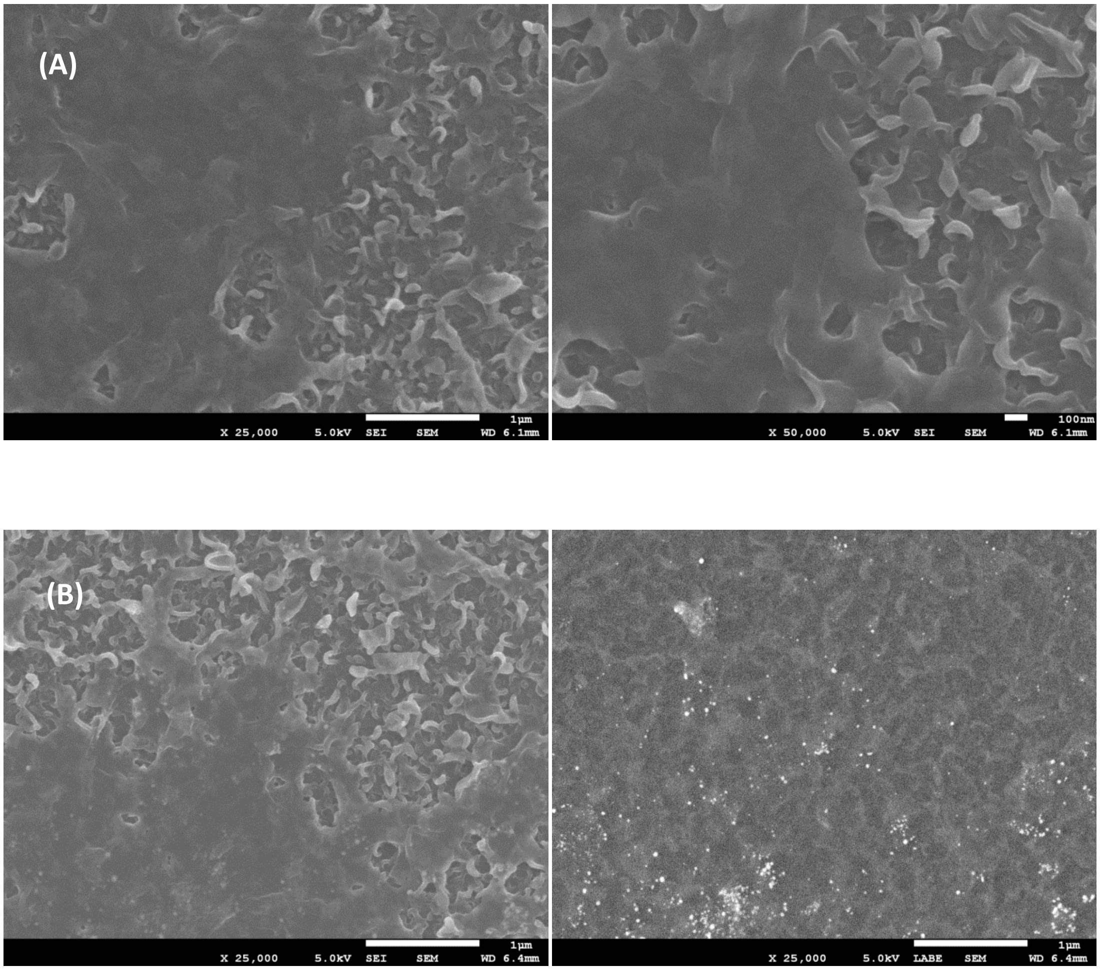

FIGURE S1. FE-SEM images and backscatter electron imaging for (A) GO functionalized TFC, and (B) GO/Ag nanocomposite functionalized TFC. Elements with higher atomic numbers backscatter electrons more strongly than elements with lower atomic numbers and, therefore, appear brighter on the image.

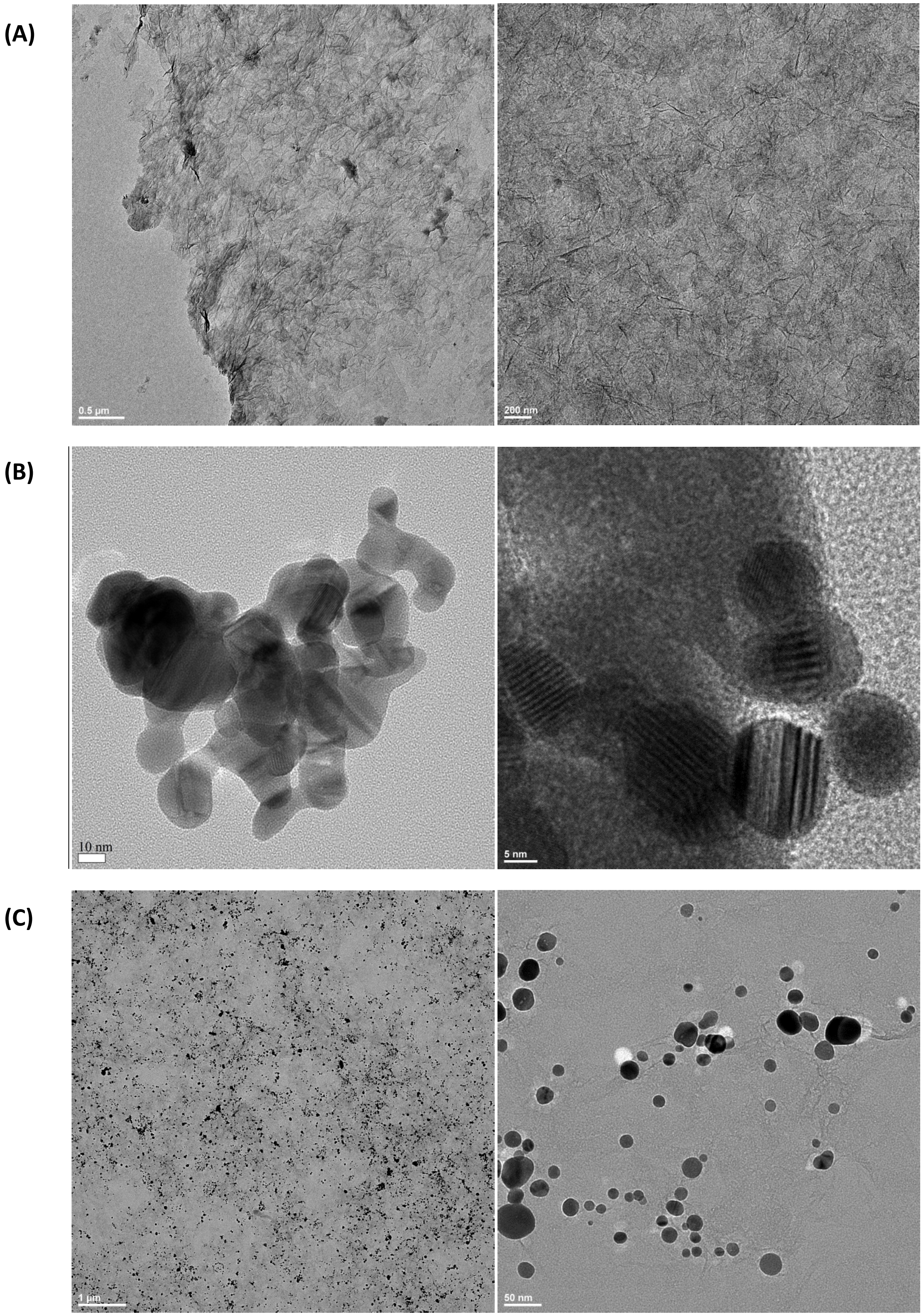

FIGURE S2. TEM images of (A) GO, (B) Ag NPs, (C) GO/Ag nanocomposite

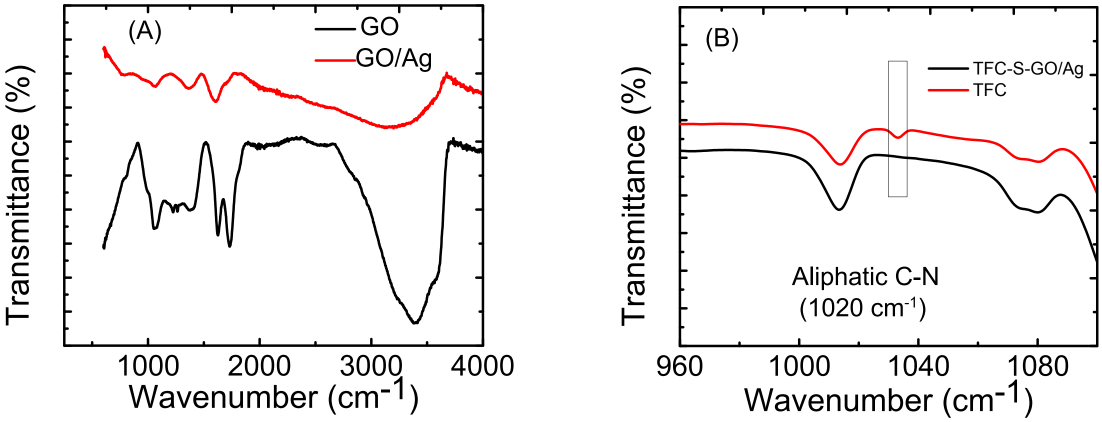

FIGURE S3. ATR-FTIR spectra of (A) GO nanosheets and GO/Ag nanocomposite, and (B) ControlTFC and GO/Ag nanocomposite functionalized TFC membranes.

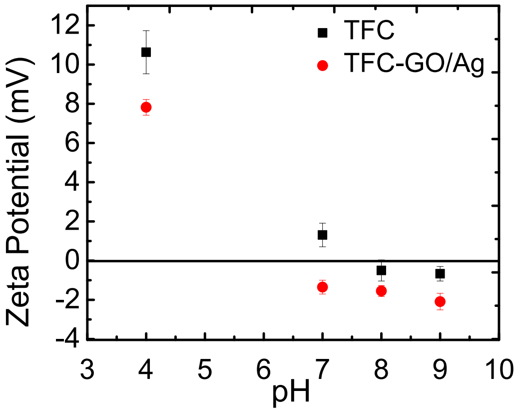

FIGURE S4. Zeta potential of the surface of the pristine and functionalized membranes as a function of solution pH. Measurements were taken at room temperature (23°C) in a solution of 1 mM KCl, by adjusting the pH with dropwise addition of HCl and NaOH.

Table S1. Surface roughness properties of the pristine and the GO/Ag functionalized TFC FO membranes

Sample	R_{max} (nm)	R_a (nm)	R_q (nm)	SAD (%)
TFC FO	486 ± 22	52.2 ± 0.5	65.5 ± 1.5	67.4 ± 2.1
TFC-GO/Ag	310 ± 33	25.2 ± 2.8	35.2 ± 4.24	13.2 ± 1.2

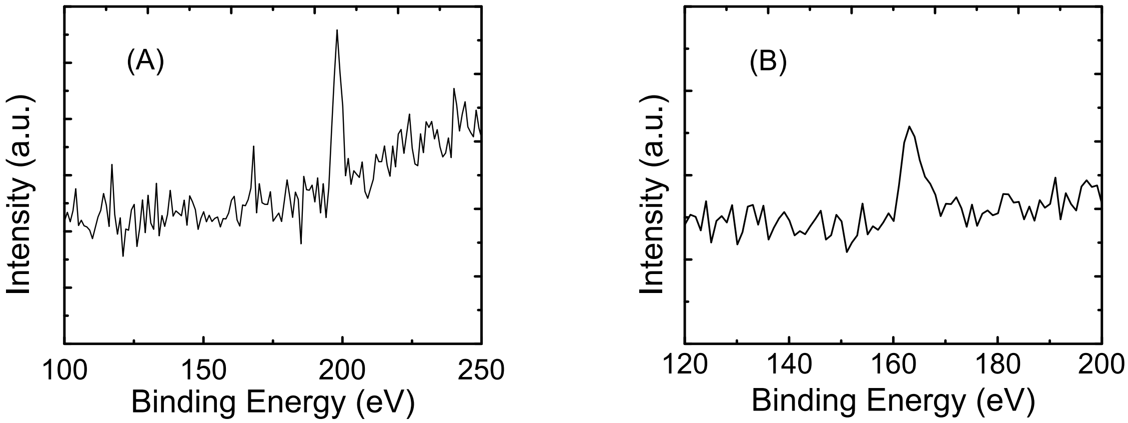

Figure S5. XPS results for (A) pristine membrane, and (B) cysteamine treated TFC FO membranes. The peaks at 198 eV for Cl2P and at 162 for Sulfor S2P are shown in (A) and (B), respectively.

Table S2. Elemental composition by XPS analysis of the membrane surface of pristine and functionalized membranes, before and after sonication.

Sample	C (%)		O (%)		N (%)		S (%)		Ag (%)		Cl (%)	S (%)
	Before	After	Before	After	Before	After	Before	After	Before	After		
TFC	71.95±0.44	-	21.19±1.59	-	6.86±1.34	-	-	-	-	-	1.5 ± 0.1	0
TFC-GO/Ag	71.8±1.07	69.8±2.25	18.56±0.81	20.28±.8	8.06±0.29	8.98±0.87	1.07±0.07	0.74±0.3	0.5±0.1	0.47±0.19	0	1.12 ± .03

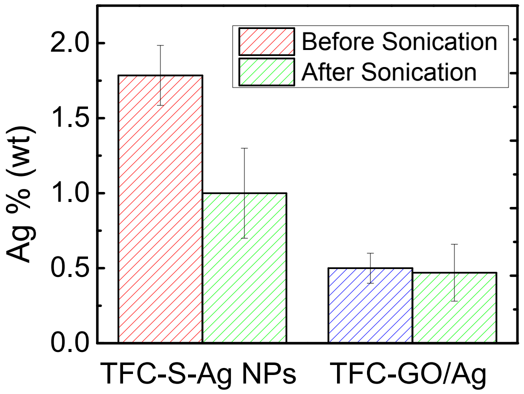

FIGURE S6. XPS results showing physical stability of silver NPs for Ag NPs decorated and GO/Ag functionalized membranes. 7 min bath sonication was applied to the membranes and silver % present on the surface was measured.

1. Perreault, F.; Tousley, M. E.; Elimelech, M., Thin-Film Composite Polyamide Membranes Functionalized with Biocidal Graphene Oxide Nanosheets. *Environmental Science & Technology Letters* **2014,** *1*, (1), 71-76.