RESEARCH OUTCOMES OF RECENT INTERACTION BETWEEN JINR DUBNA AND UNIVERSITY OF THE WESTERN CAPE

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Projects

- Elemental composition of fly ash:
  a comparative study using nuclear and related analytical techniques
- Photocatalytic membrane reactor based on nanostructured semiconductors and track etched membranes for water treatment processes;
- Track-etched of high performance polymers for gas separation and purification

ELEMENTAL COMPOSITION OF FLY ASH: A COMPARATIVE STUDY USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

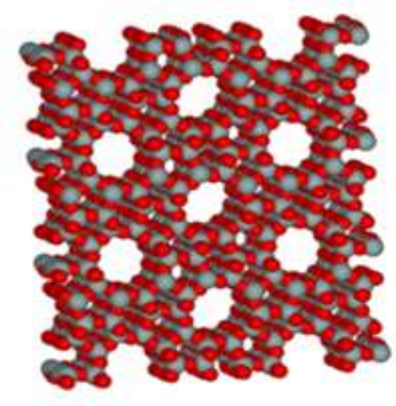
INTRODUCTION

- Worldwide huge amounts of coal fly ash are generated in order to meet up with energy demands and about 70 % of fly ash is disposed as waste



- CFA disposal is of great concern globally due to the environmental issues arising from the disposal methods that are currently employed


- One way of combating the problems caused by the enormous volume of fly ash is by optimizing the uses of fly ash so that it could become a valuable raw material



- To effectively valorise and manage CFA an accurate method of determining the chemical composition of CFA is fundamental in the qualitative and quantitative analysis of the elements of value and toxicity in fly ash

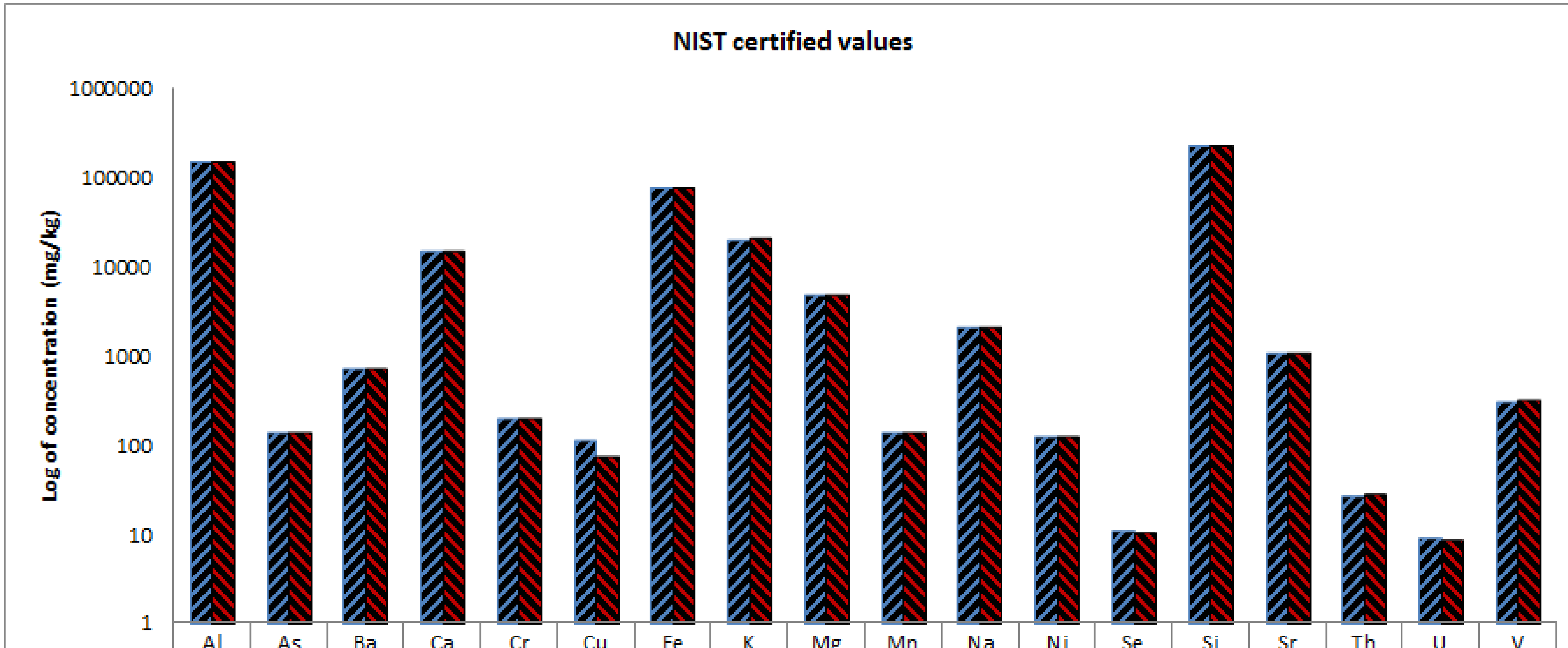
Objective

- To ascertain the analytical technique that is best suited for determining the different categories of elements that are contained in CFA

- Instrumental epithermal neutron activation analysis (ENAA), XRF, ICP-OES and LA ICP-MS were compared to determine the elemental composition of CFA

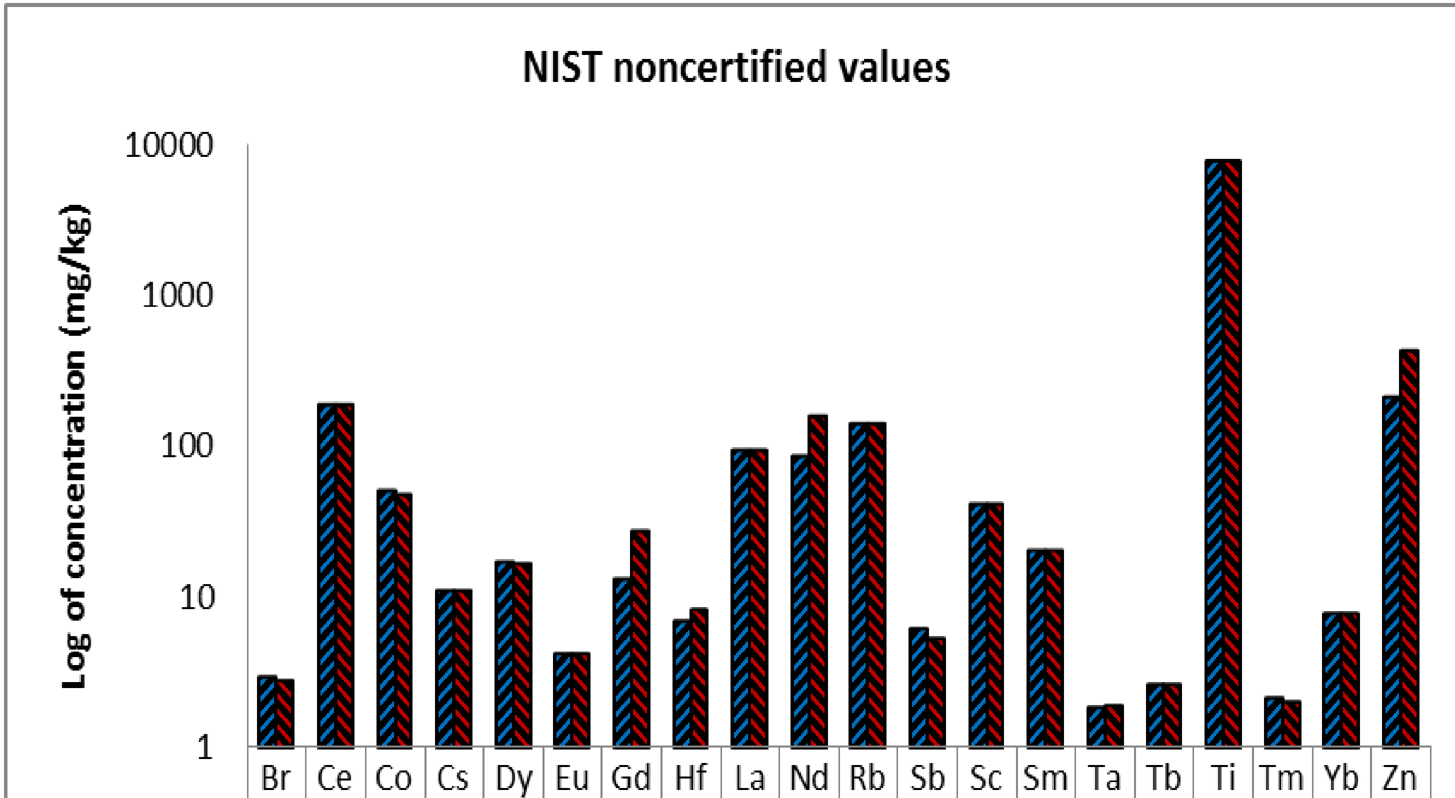
Results & Discussion

To assure the quality of ENAA the NIST Certified Reference Material 1633b was used. The concentrations of the elements in the NIST SRM 1633b determined by ENAA in Dubna (Analysed value) were compared to the known concentrations of the NIST SRM 1633b (certified value)



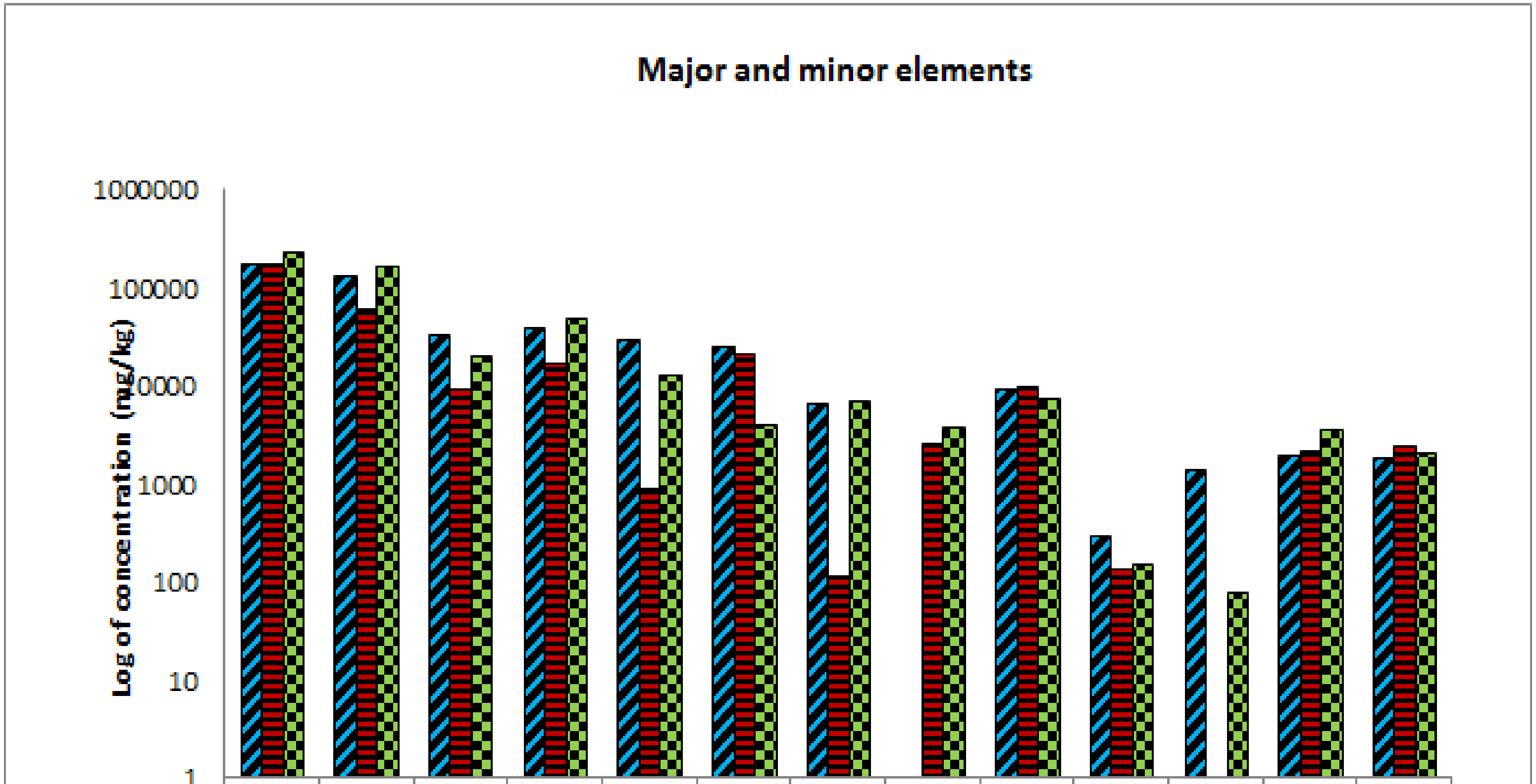
	Al	As	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Se	Si	Sr	Th	U	V
NIST	150500	136.2	709	15100	198.2	112.8	77800	19500	4820	131.8	2010	120.6	10.26	230200	1041	25.7	8.79	295.7
Analysed	151000	133	708	15100	198	71.9	77700	20400	4810	132	2090	121	9.83	230000	1040	27.4	8.49	312

- **There was a strong agreement between the results obtained by ENAA of the NIST SRM 1633b and the certified values of this standard. Except Cu**



	Br	Ce	Co	Cs	Dy	Eu	Gd	Hf	La	Nd	Rb	Sb	Sc	Sm	Ta	Tb	Ti	Tm	Yb	Zn
NIST	2.9	190	50	11	17	4.1	13	6.8	94	85	140	6	41	20	1.8	2.6	791	2.1	7.6	210
Analysed	2.7	190	48	11	16	4.1	27	8	92	157	140	5.3	41	20	1.8	2.6	792	2	7.6	436

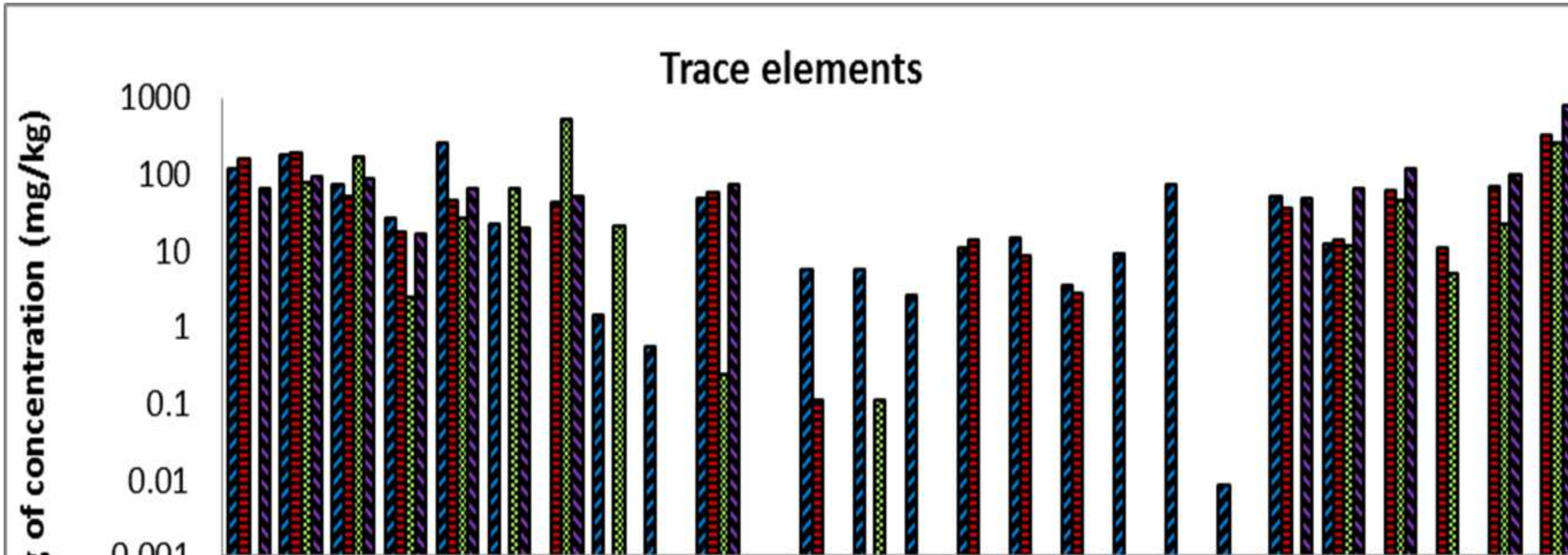
- **the noncertified values of some elements in the NIST SRM 1633b were compared to the amounts determined by ENAA. Except for Gd, Nd and Zn, there was also a good agreement between the two values**



	Si	Al	Fe	Ca	Mg	Na	K	P	Ti	Mn	S	Sr	Ba
ENAA	176000	129500	33100	38233	29233	25376	6640	0	9383	290	1420	1900	1823
ICP-OES	176760	62040	9201.6	17212	896.19	21033	116.4	2539.1	9558.2	132.41	0	2137	2372.1
XRF	225683	163495	19661	47983	12807	4101	6985	3873	7553	155	77.58	3495.6	2079.3

0 = Not determined

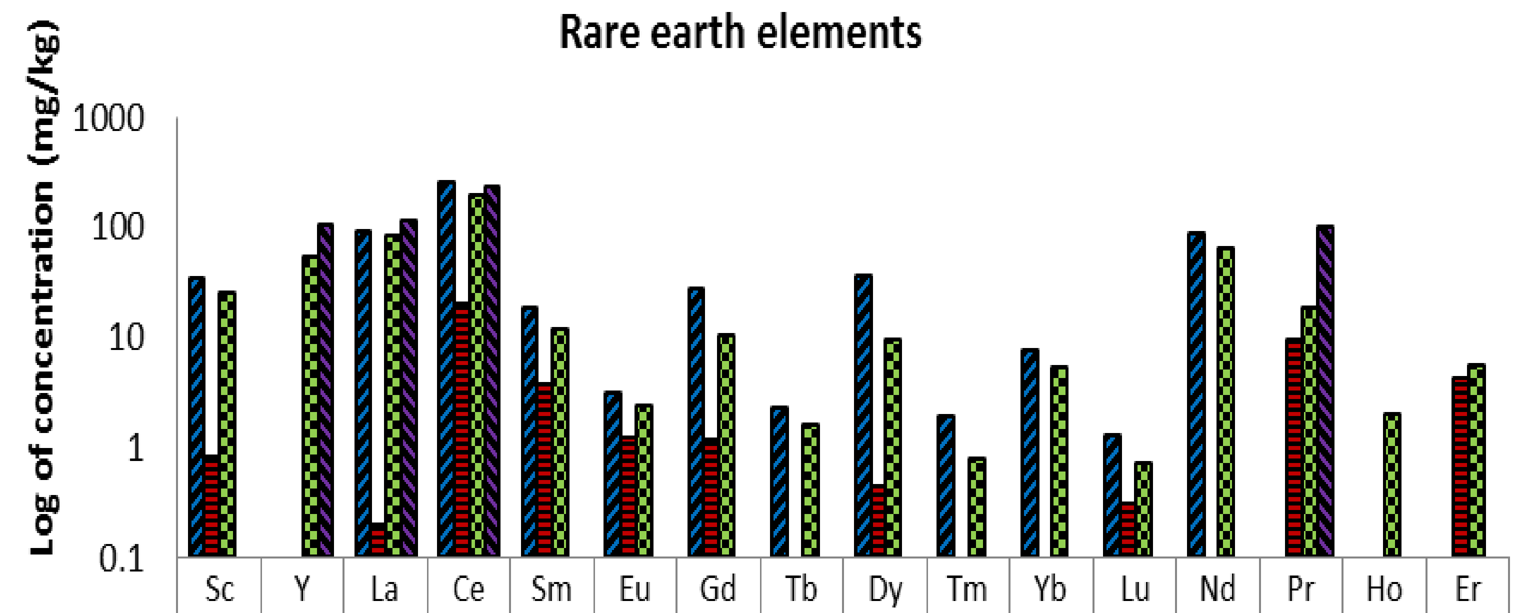
Concentrations of major and minor elements in Matla CFA determined by ENAA, ICP-OES, and XRF [number of determinations = 3]



	V	Cr	Ni	Co	Zn	As	Nb	Se	Br	Rb	Ag	Cd	Cd	Sb	Cs	Hf	Ta	W	Cl	Au	Th	U	Cu	Mo	Pb	Zr
ENAA	120	177	72	26	250	22	0	1.4	0.6	47	0	5.6	5.6	2.5	11	15	3.5	9	73	0	50	12	0	0	0	0
LA ICP-MS	154	183	50	17	45	0	43	0	0	55	0	0.1	0	0	14	8.6	2.7	0	0	0	35	13	62	10	69	314
ICP-OES	0	76	170	2.4	27	64	520	20	0	0.2	0	0	0.1	0	0	0	0	0	0	0	0	11	44	4.8	22	259
XRF	65	89	89	16	65	20	52	0	0	72	0	0	0	0	0	0	0	0	0	0	47	63	117	0	100	788

0 = Not determined

Concentrations of trace elements in Matla CFA determined by ENAA, ICP-OES, LA ICP-MS and XRF [number of determinations = 3]



	Sc	Y	La	Ce	Sm	Eu	Gd	Tb	Dy	Tm	Yb	Lu	Nd	Pr	Ho	Er
ENAA	33.8	0	92.23	247.3	18	3.11	27.57	2.26	35.23	1.89	7.64	1.26	88.4	0	0	0
ICP-OES	0.83	0	0.196	20.31	3.72	1.238	1.163	0	0.44	0	0	0.3	0	9.53	0	4.3
LA-ICP-MS	24.94	52.3	81.66	189.8	11.93	2.35	10.4	1.6	9.5	0.77	5.27	0.72	63.5	18.35	1.97	5.38
XRF	0	103.7	111.5	226	0	0	0	0	0	0	0	0	0	100.3	0	0

0 = Not determined

Concentrations of REEs in Matla CFA determined by ENAA, LA ICP-MS, ICP- OES, and XRF [number of determinations = 3]

Conclusion

- For the first time a total of 54 elements, among them 16 rare earths, were determined in the Matla CFA using ENAA, ICP-OES, LA ICP-MS, and XRF techniques.

- The concentration of the major elements in the CFA determined by ENAA and XRF is very similar apart from Na and correlates well with that of the certified SRM NIST 1633b.

- Determination of trace and REEs content obtained by the ENAA and LA ICP-MS techniques is more reliable than their determination by the XRF or ICP-OES techniques.

- CFA can be considered as a potential source for extraction of REEs for industrial use.

- The hazardous impact of heavy metals such as Cd, Pb, As, Sr, U, Th, in particular, observed in the studied CFA should be monitored in the reuse of fly ash in agriculture and construction materials

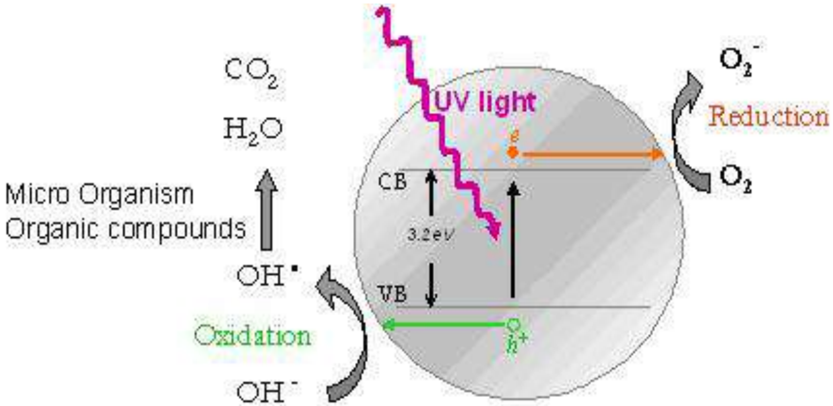
PHOTOCATALYTIC MEMBRANE REACTOR BASED ON NANOSTRUCTURED SEMICONDUCTORS AND TRACK ETCHED MEMBRANES FOR WATER TREATMENT PROCESSES

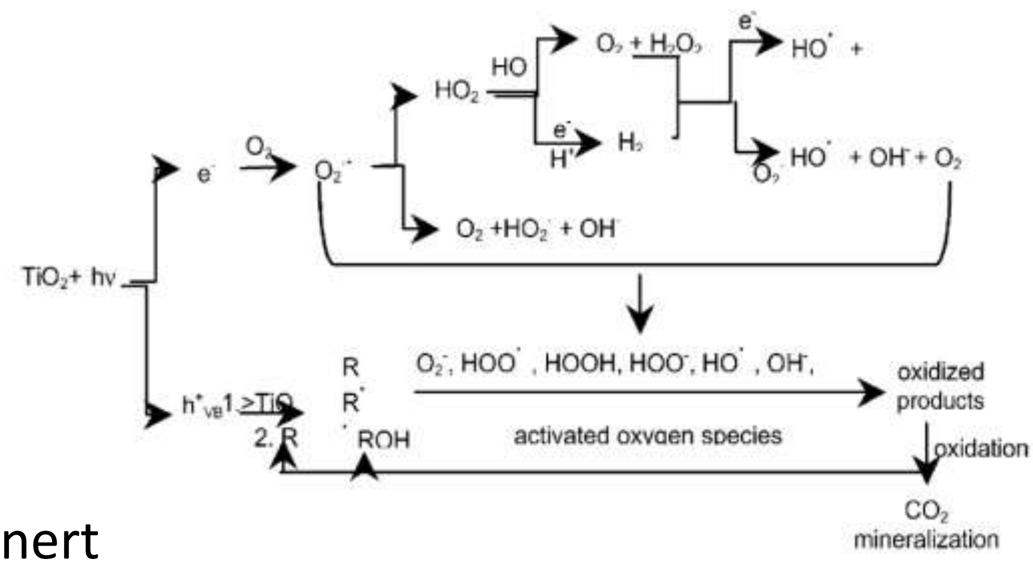
INTRODUCTION

Development of a Hybrid, Multifunctional Track-Etched Membrane using Photocatalytic Semiconductors for Advanced Oxidation Water Treatment Processes:

- A “Low- fouling” TM, with “self-cleaning” surface;
- TM with “superhydrophilic” surface for permeability enhancement;
- TM that is Anti-microbial;
- Ability for further modification by water soluble silanes.

Photocatalysis is a part of AOP's

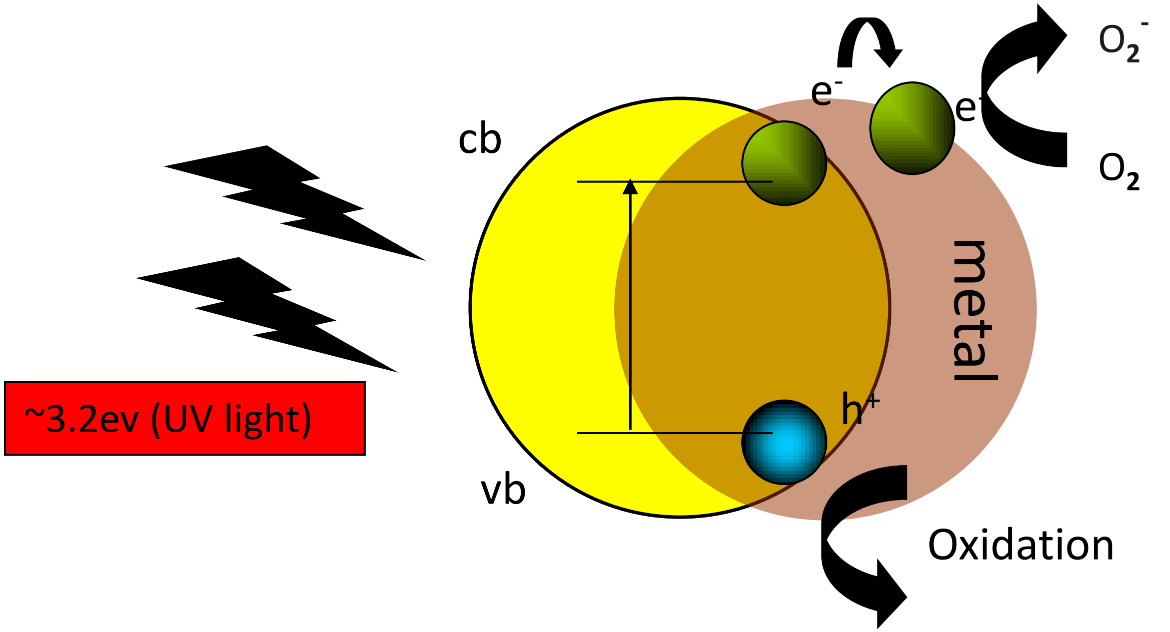




Why TiO_2?

- Cheap
- Non-toxic material
- Chemically and biologically inert
- Photocatalytically stable
- Wide-band gap semiconductor
- Photodegeneration of organic compounds by hydroxyl radicals

Role of metal in noble metal-titania nanocomposites

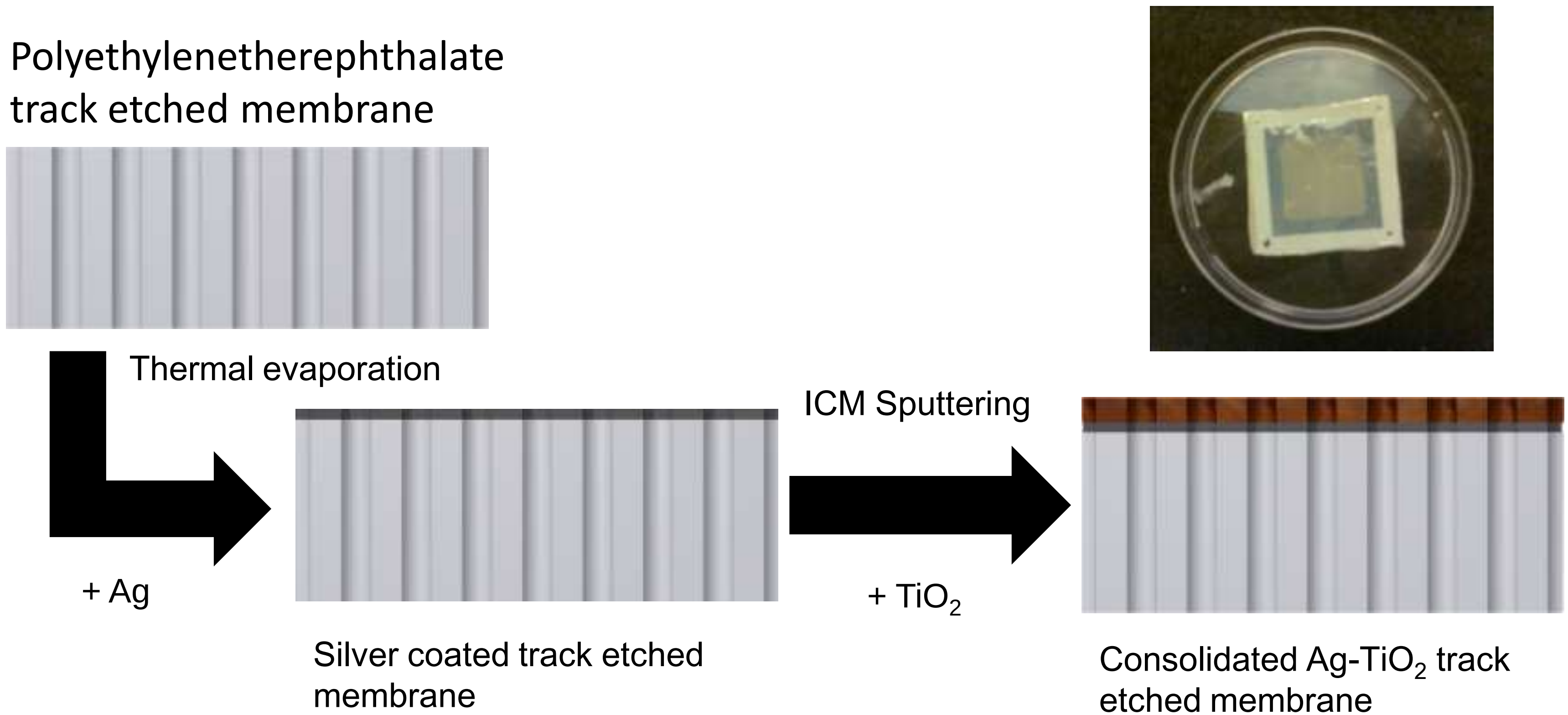


Metal nanoparticles act as an electron sink, promoting interfacial charge transfer and reducing the charge recombination rate. Plasmonic metals such as gold and silver have even higher band gap improving characteristics.

Why Silver is a good option for water treatment?

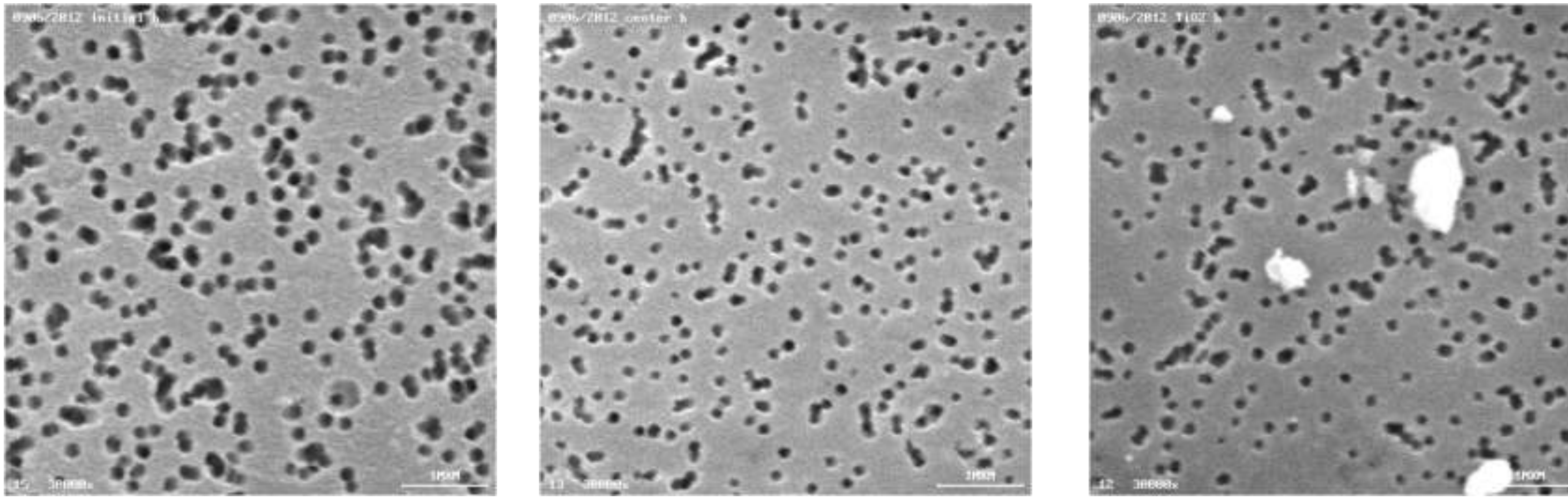
- Enhances antibacterial activity;
- Increases electron-hole pair generation;
- Promotes interfacial charge transfer and reduces charge recombination
- Cheaper than gold.

Results & Discussion



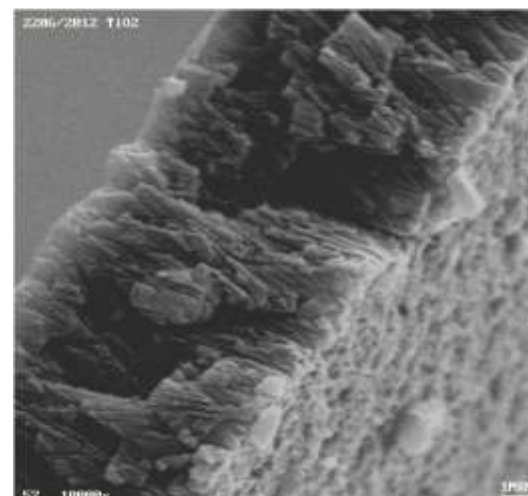
Ag-TiO_2 surface modified track etched membrane using thermal evaporation in conjunction with inverted cylindrical magnetron sputtering.

SEM surface analysis



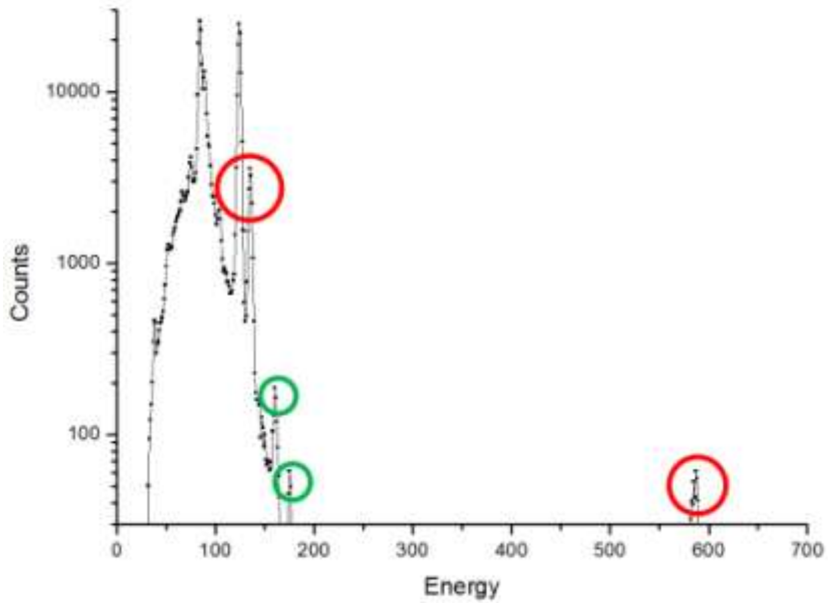
PET TM (left), coated by silver thermal evaporation (centre), coated by silver thermal evaporation and TiO_2 sputter(right).

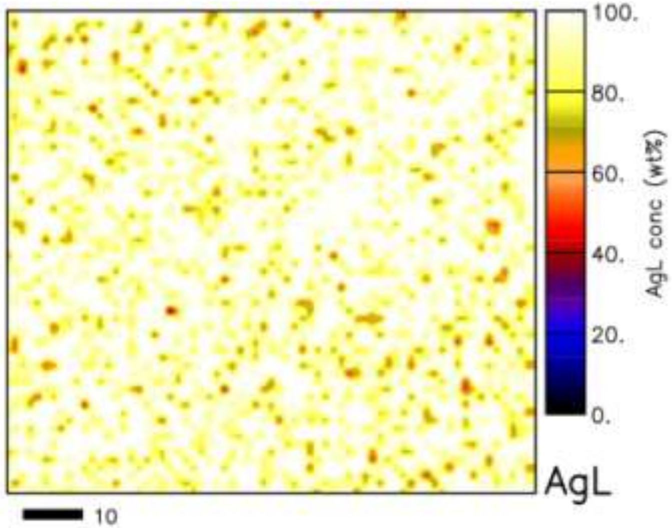
As deposited layer thickness increased, the pore size slightly decreased, remarkably without a loss in permeability

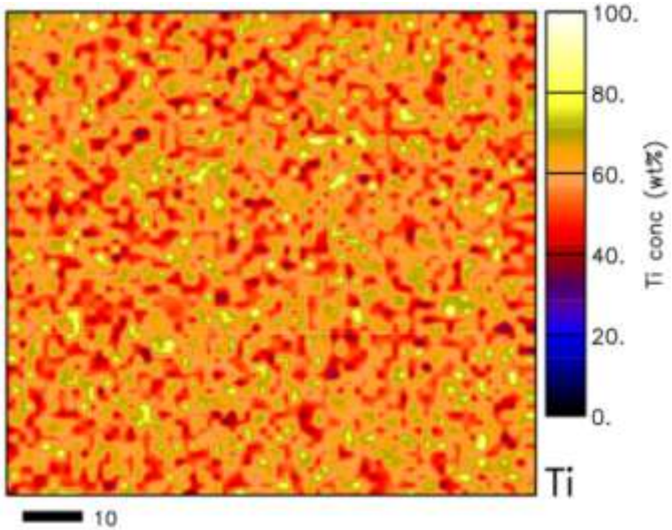


Cross-section of modified membrane.

PIXE elemental zoning of composite membrane



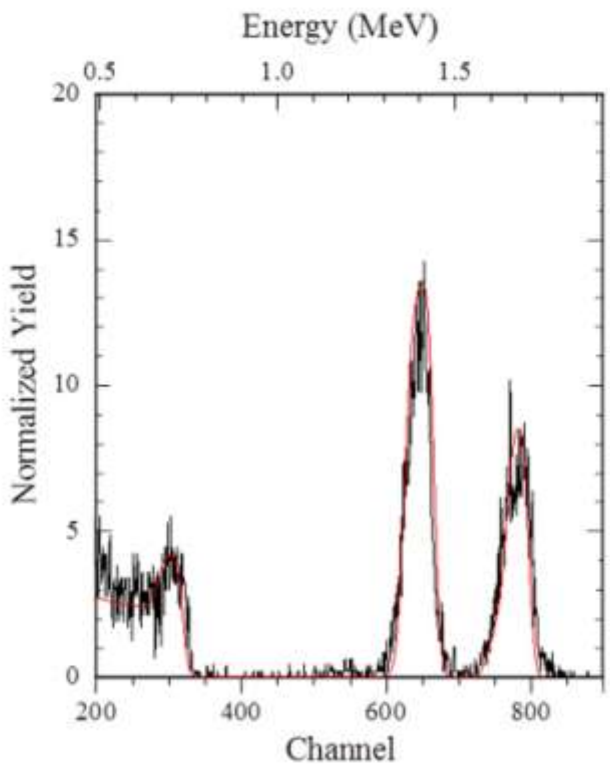




The double peaks are due to k-alpha and k-beta x-rays

PIXE elemental map for the Ag and Ti in Ag-TiO_2

RBS layer thickness and composition analysis



interfacial layers : TiO_2, Ag-TiO_2 and Ag-PET. No Ag was found on its own, this is most likely due to the very small amount present

The fringing along the bottom of the Ti and Ag peaks indicates a certain amount of elemental dispersal

Ag-TiO_2-TM with interfacial layers due to magnetron sputtering.

Analysis of UV-VIS transmission spectra for band gap calculation

Tauc-plot and Beer's law

Band Gap Calculations:

$$(ahv)^2 = A(hv - Eg)$$

$$a = \frac{1}{d} Ln\left(\frac{1}{T}\right)$$

$$A(hv - Eg) = \left(\left(\frac{1}{d} Ln\left(\frac{1}{T}\right)\right) hv\right)^2$$

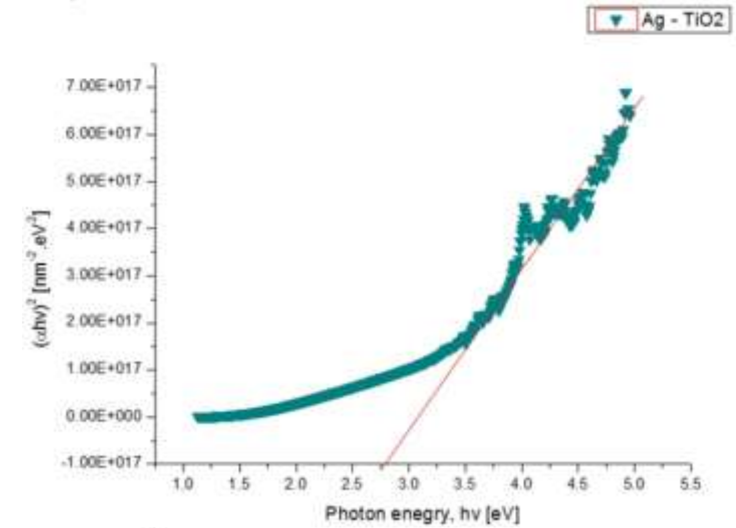
brookite

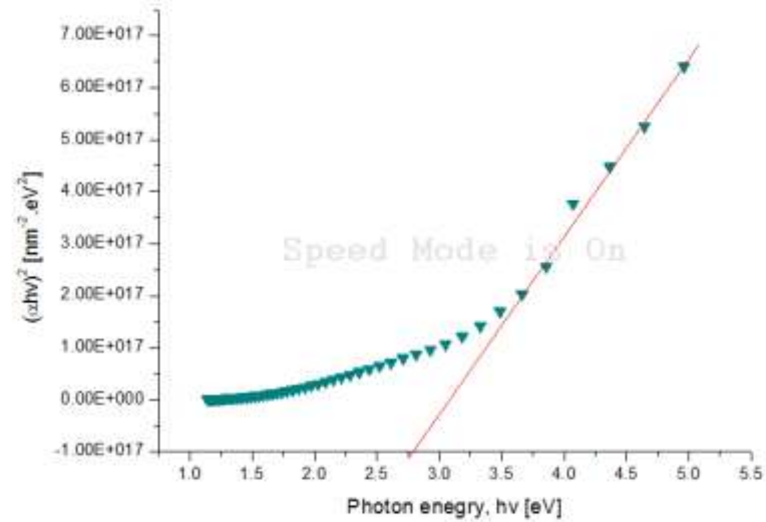
From straight line formula:

$$y = mx + c$$

$$hv = 2.76\ eV$$

Therefor $\lambda = \pm 450\ nm$



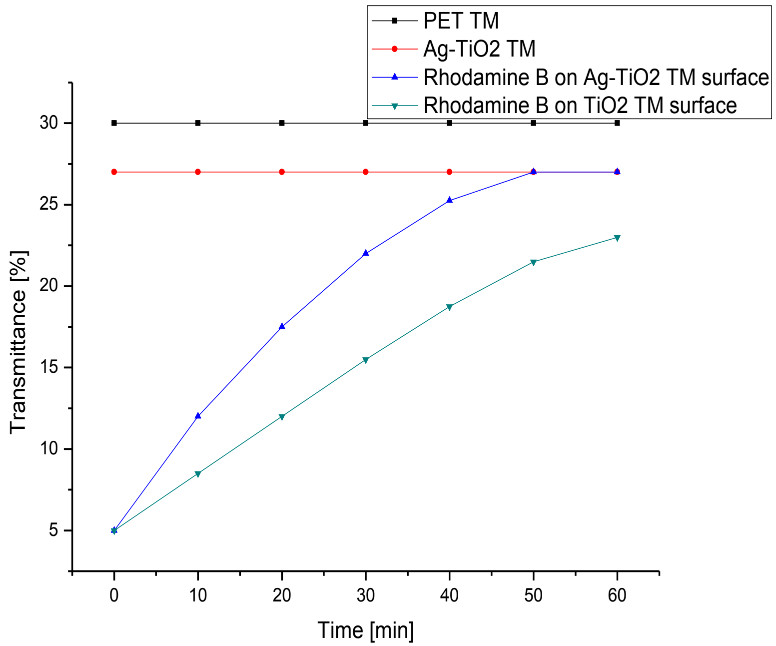


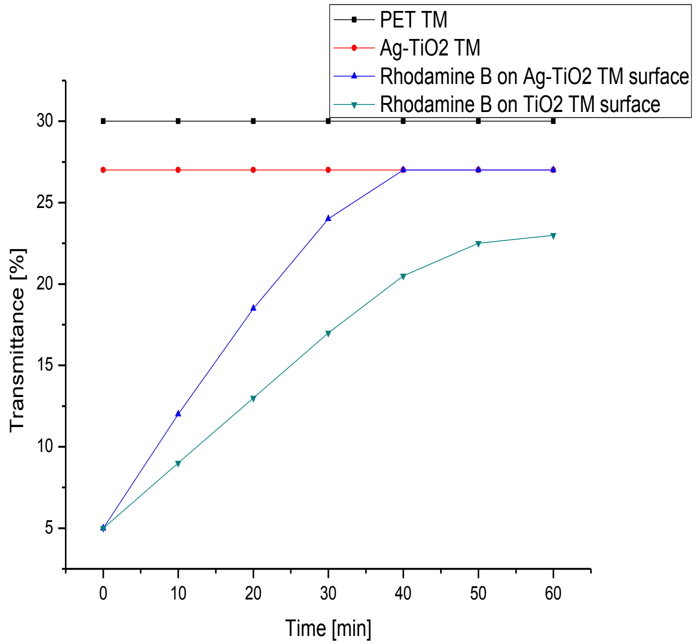
Two filtration cells designed for testing modified TM self-cleaning properties

Cross-flow reactor for testing

Dead-end reactor for testing

Self-cleaning properties of Ag-TiO_2 TM





99% of Rhodamine 6G on the Ag-TiO_2 TM surface was degraded after 40 min of UV irradiation at 355 nm. Dye degradation of 100 ppm Rhodamine 6G was measured at 550nm.

Conclusions

- Modified TiO_2 and Ag-TiO_2-PET TM were successfully prepared;
- By the addition of Ag and proper cooling the resulting band gap was reduced from 3.05 eV to 2.76 eV for photocatalytic layers of brookite-TiO_2;
- Interfacial layers formed during sputtering have a significant effect on deposition and layer formation.
- The self-cleaning properties:
  - TiO_2-TMs showed 80% regeneration after 40 min and
  - Ag-TiO_2 showed 99% regeneration after 40 min by dye-transmittance study;
- Permeability of modified Ag-TiO_2 showed an average of 15% increase;

TRACK-ETCHED OF HIGH PERFORMANCE POLYMERS FOR GAS SEPARATION AND PURIFICATION

INTRODUCTION

- **Key objectives of study:**

- **To develop and adopt robust conditions for track etched polymer surface functionalization**

- **To investigate and understand the effects of these conditions on polymer physico-chemical properties**

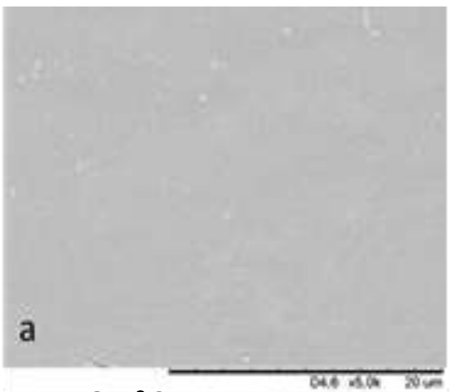
- **To investigate gas permeability and selectivity capacity of track-etched polymers**

EXPERIMENTAL

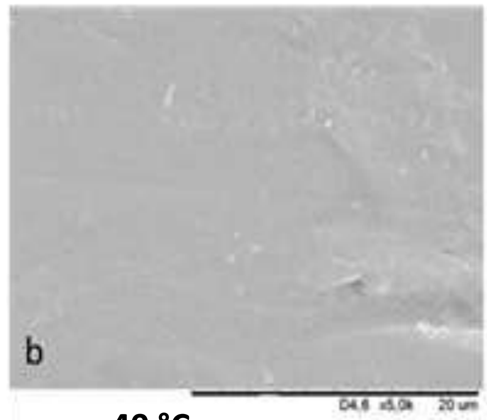
- PET and PMP polymer membranes tracketched
- Xe^{+26} used at energy 1.2 -1.5MeV/nucleon and 10^9 cm^2 fluence
- With and without Al foil absorber
- Track etched for 3-6min in 6M NaOH at 85 deg C
- Coated with Pd plating bath
- Permeability determined by gas carrier and vacuum pumping

Results & Discussion

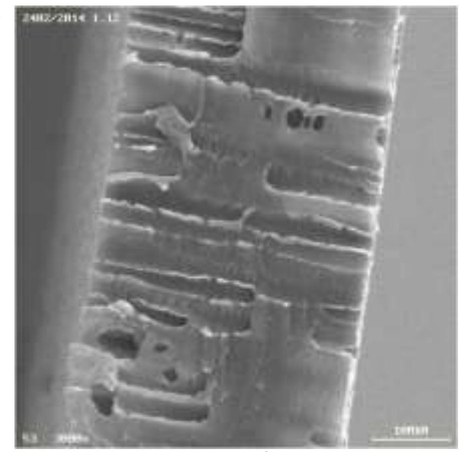
SEM micrograph of track-etched polymethylpentene (PMP) film with enhanced pore geometry under different temperature /time conditions



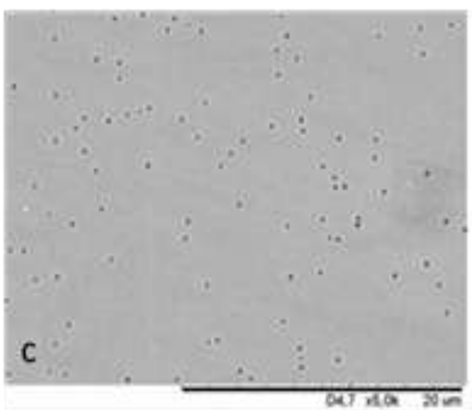
25 °C



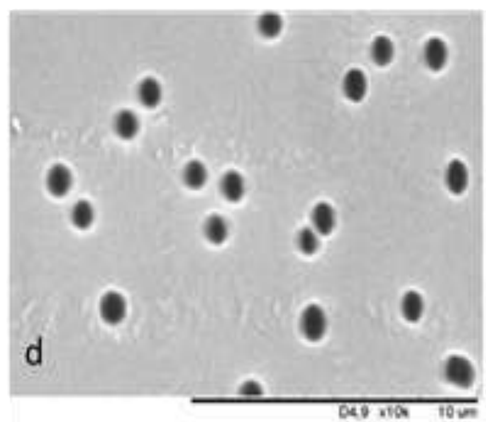
40 °C



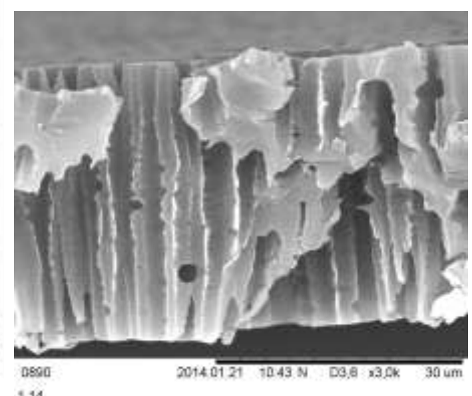
60 mins



60 °C

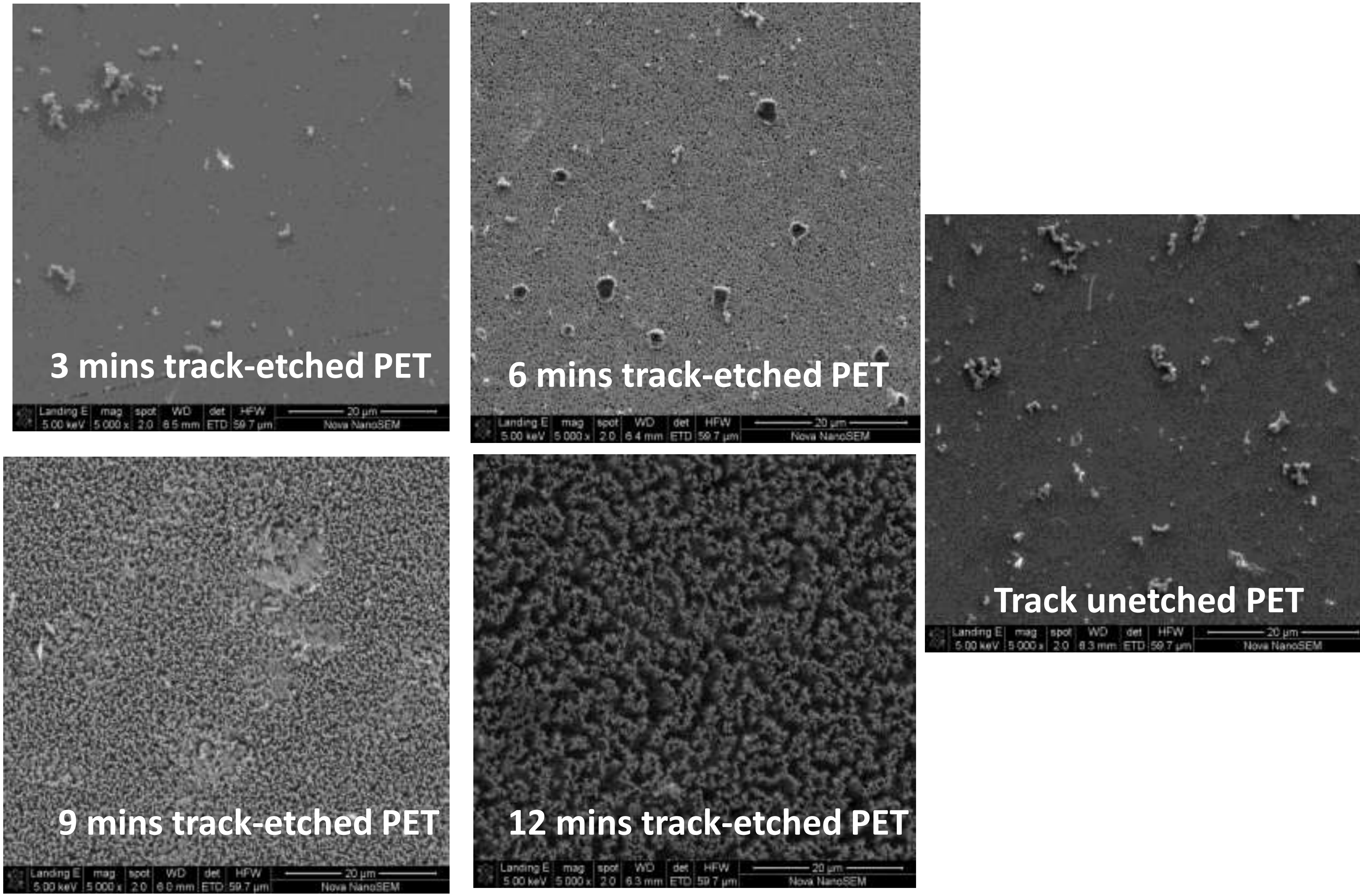


80 °C



90 mins

SEM micrograph of track-etched PET plated with 0.08M palladium



Gas permeability of irradiated PETF films

Sample	P, cm cm^3/cm^2 s cm Hg		
	He	CO_2	CH_4
PETF	1,0E-10	1,2E-11	1,3E-12
PETF 1 (Xe^{+26},E-1,5 MeV/W)	1,1E-10	1,4E-11	1,4E-12
PETF 2 (Xe^{+26},E-1,5 MeV/W, Al-foil)	1,1E-10	1,6E-11	1,5E-12

Gas permeability of track-etched PET plated with 0.08 M palladium

Sample		α	
	He/CO_2	He/CH_4	CO_2/CH_4
PETF	8,7	80	9,2
PETF 1 (Xe^{+126},E-1,5 MeV/W)	8,1	79	10
PETF 2 (Xe^{+126},E-1,5 MeV/W, Al-foil,	6,7	73	10

Conclusions

- Robust methodology was developed for the track-etch condition for PET and PMP polymers
- Preliminary kinetic of track-etching conditions (i.e. temperature and time) have been studied
- Track-etched polymers showed improved gas permeability and selectivity properties
- Conditions for controlled gas transport properties: 3-6 min etching time retained permeability and selectivity; longer etching time decreased selectivity
- Metal deposition via (electroless plating and magnetron sputtering) are in progress for hydrogen permeability and selectivity studies

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