# Tailor-Made Anodic Aluminum Oxide Photonic Crystals for Photocatalytic Applications

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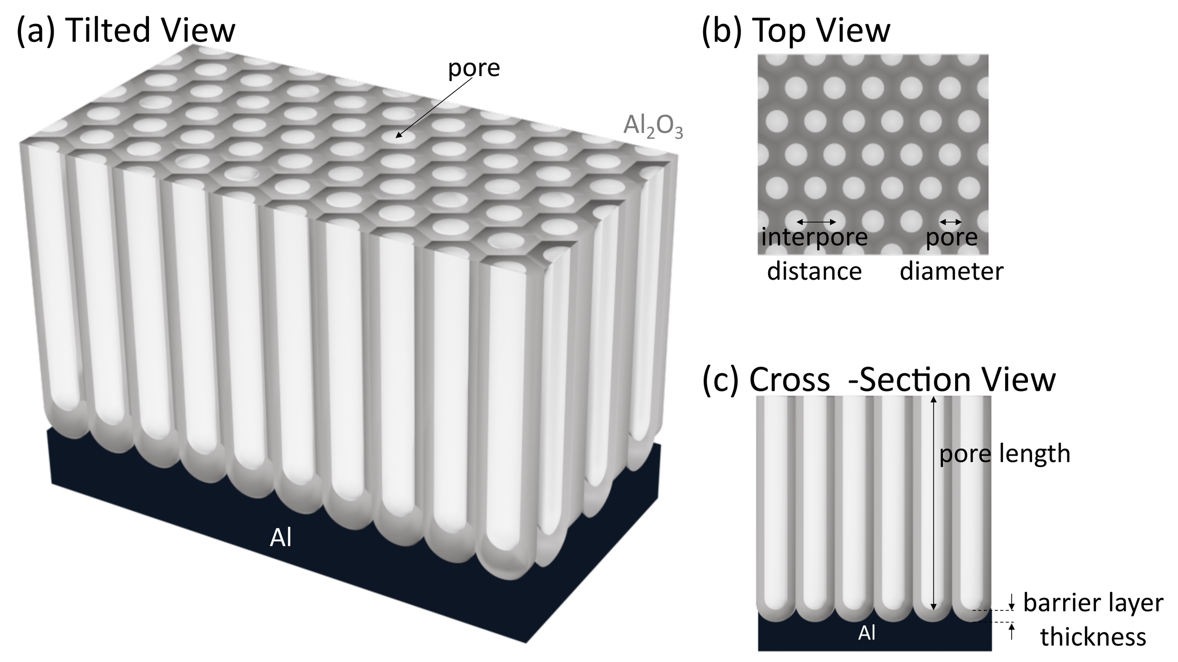
## Motivation

Anodic aluminum oxide membranes feature self-organized, highly ordered cylindrical pores with distinct geometrical characteristics. Modifying the electrochemical anodization parameters and applying pulse-like anodization profiles tailors the pore diameter along the growth direction. Such periodically modulated structures can act as photonic crystals.[1-3] These structures exhibit photonic stopbands in which light propagation is forbidden. Incoming photons of wavelengths near the stopband edges are slowed down within the tailored structure due to the so-called slow photon effect. This phenomenon results in an increased interaction probability of the photons with the structure material, hence, making photonic crystals very attractive for photocatalytic applications.[4]

Functionalization of the structure surface with photocatalytically active materials or tuning of the stopband position by adapting the pore morphology could further enhance the photocatalytic performance of anodic aluminum oxide photonic crystals.

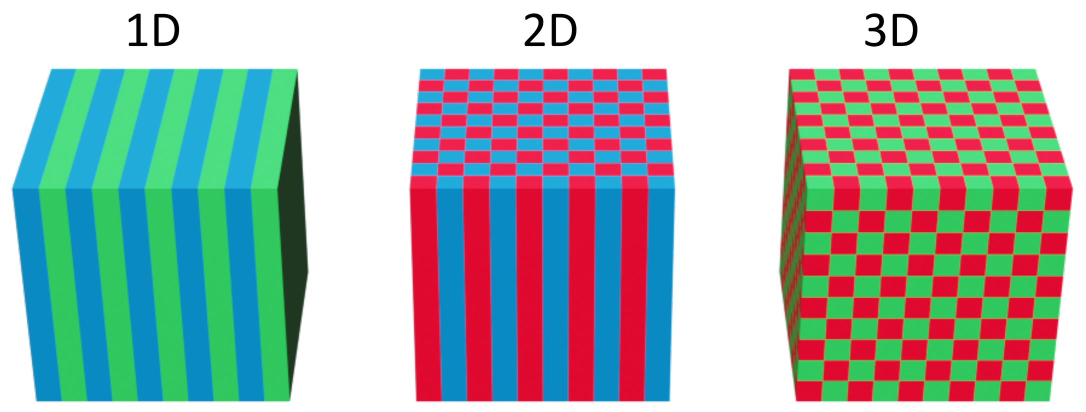
## Anodic Aluminum Oxide



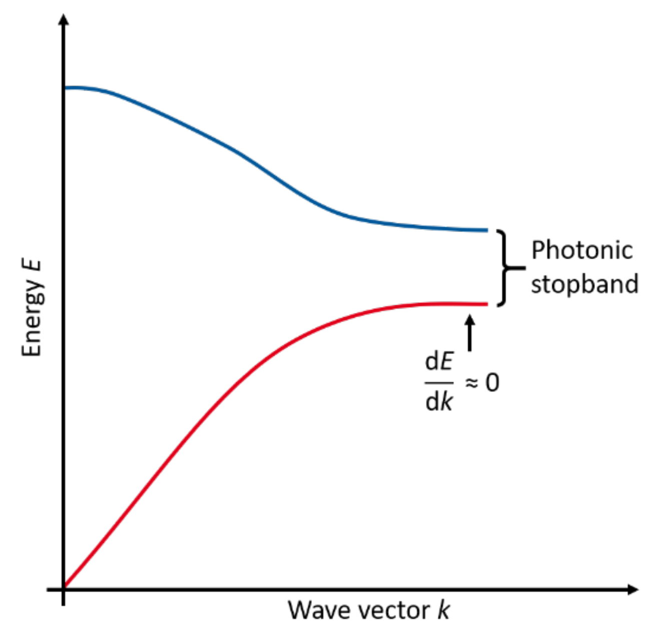

Pore dimensions of anodic aluminum oxide (AAO) are widely tunable by alteration of the anodization process.

## Slow Photon Effect in Photonic Crystals

Photonic Crystals (PCs) consist of periodic arrangements of materials with different dielectric permittivity.



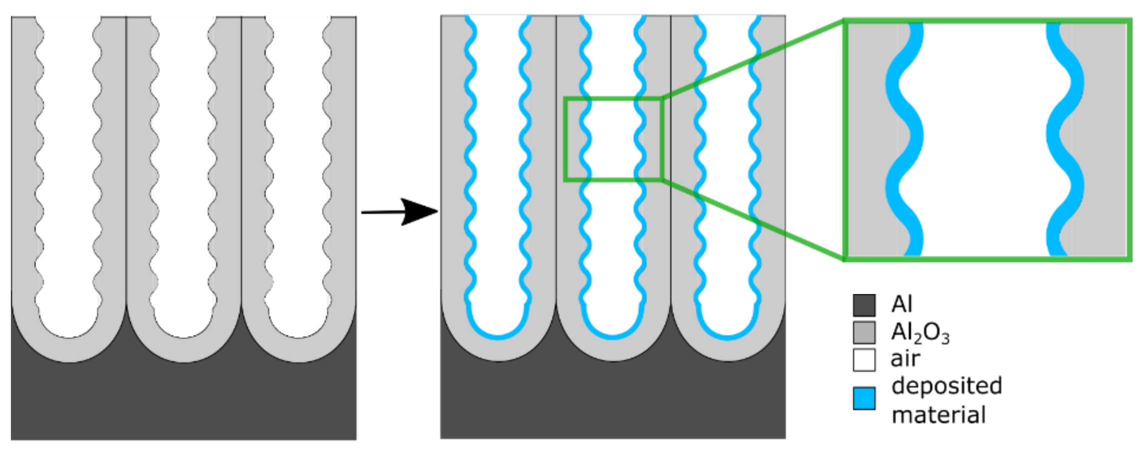

Periodic dielectric constant modulations result in formation of a photonic stopband (PSB) in which light propagation within the PC is forbidden.




Vanishing group velocity of photons near the PSB edges is called slow photon effect.

## Atomic Layer Deposition

Atomic layer deposition (ALD) is based on sequential, self-limiting gas-solid surface reactions.

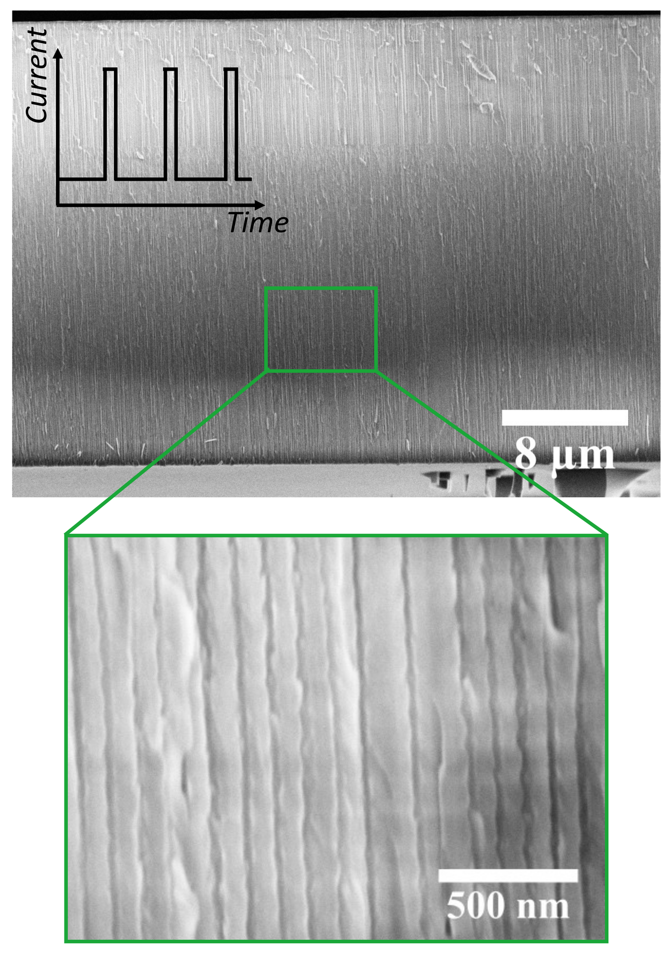


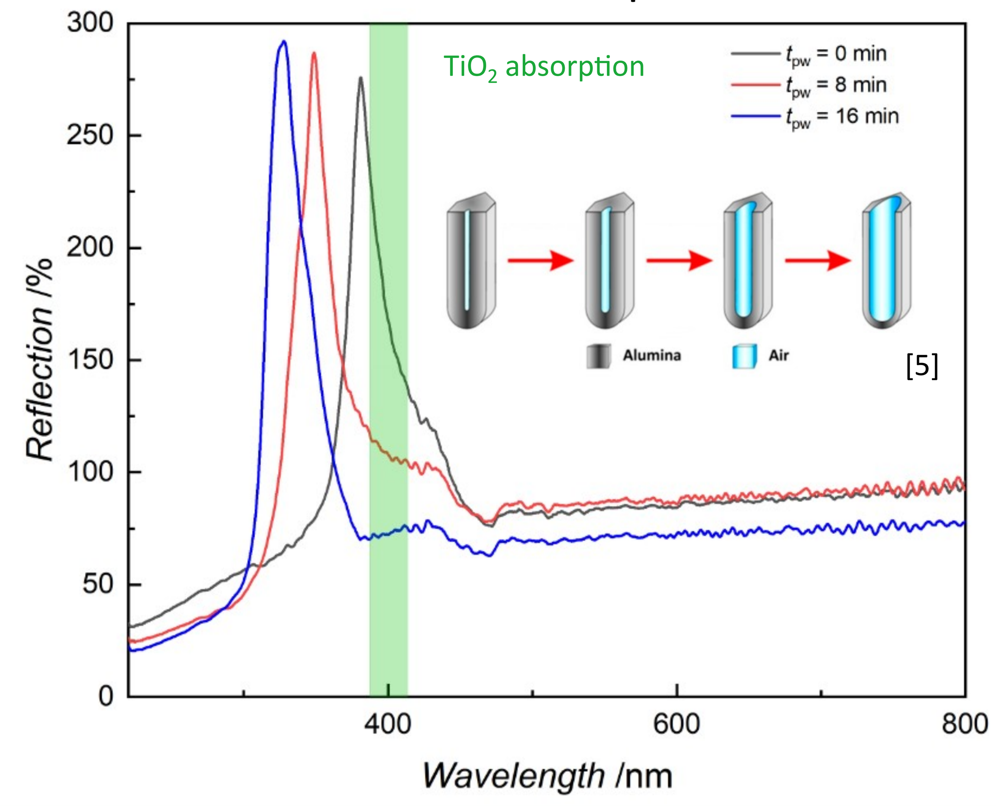

Highly conformal coatings even on complex structured substrates are obtained.

## Tailor-Made Anodic Aluminum Oxide Photonic Crystals

Application of rectangular shaped current pulse profiles during anodization

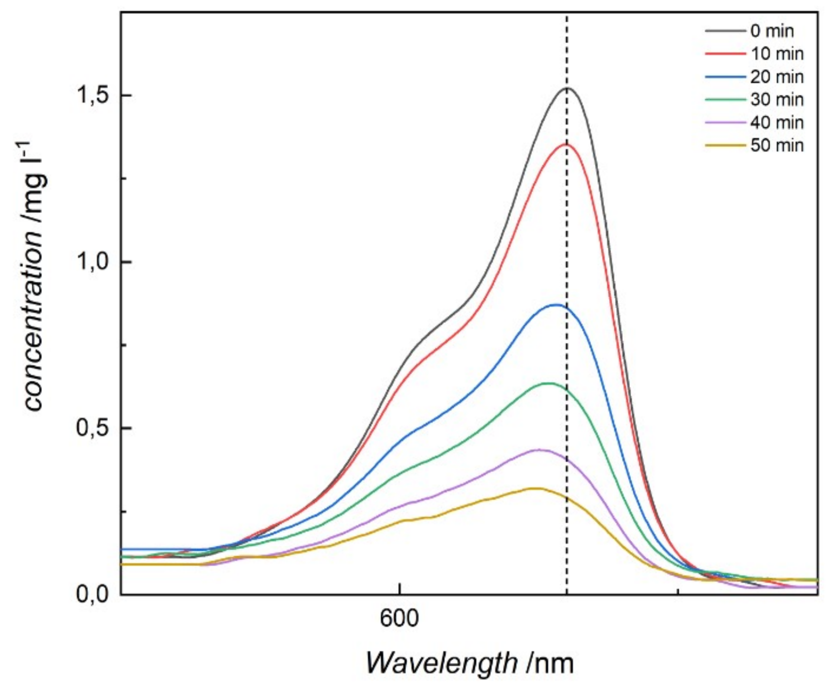
- ⇨ periodic modulation of pore diameter
- ⇨ modulated AAO membranes exhibit PSB
- ⇨ wet-chemical pore widening (pw) tunes the modulated effective refractive index → PSB position shift




## Photocatalytic Performance of AAO-PC

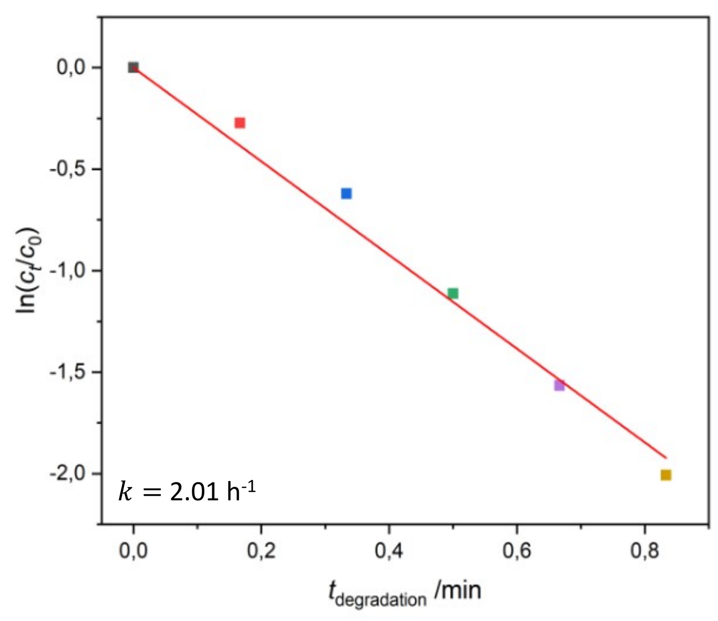
⇨ Photocatalytic degradation of methylene blue to assess photocatalytic efficiency




→ reaction follows Langmuir-Hinshelwood mechanism

$$\ln\left(\frac{c_t}{c_0}\right) = -k \cdot t_{\text{degradation}}$$

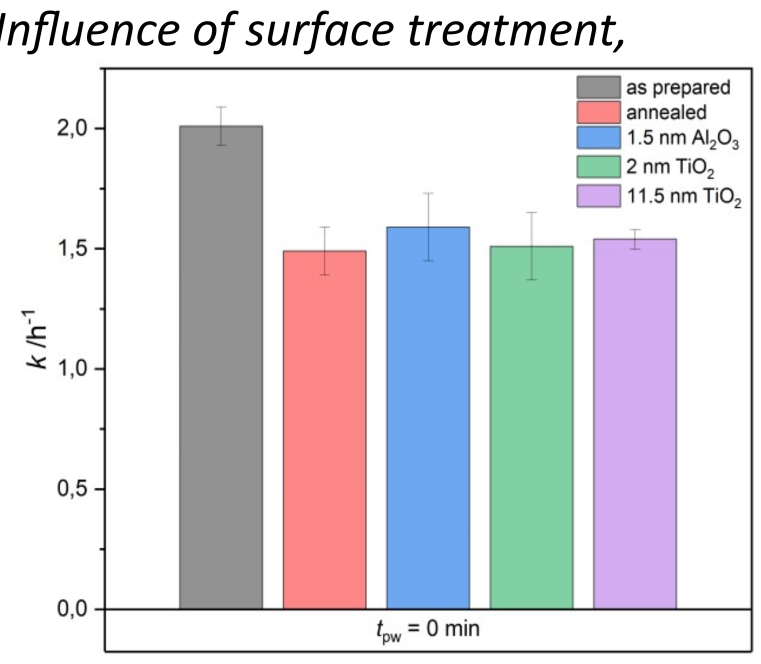
$c_t$: concentration at $t_{\text{degradation}}$
$c_0$: concentration at $t_{\text{degradation}} = 0$ min
$k$: apparent photocatalytic rate



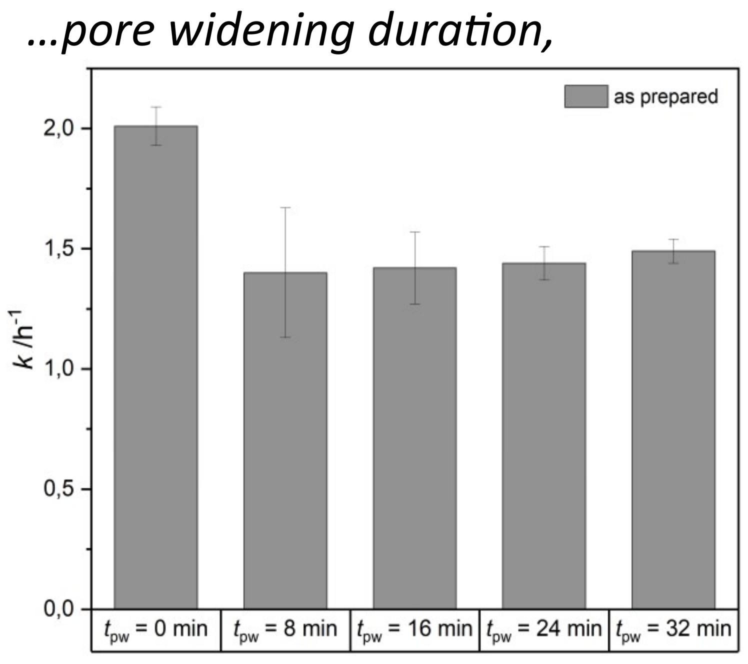

Photocatalytic activity enhancement by overlapping PSB red edge with $TiO_2$ absorption to use increased interaction probability of slow photons with PC material.

⇨ Study of AAO-PCs as prepared, annealed, pore widened, and coated with $Al_2O_3$ or $TiO_2$ thin films by ALD

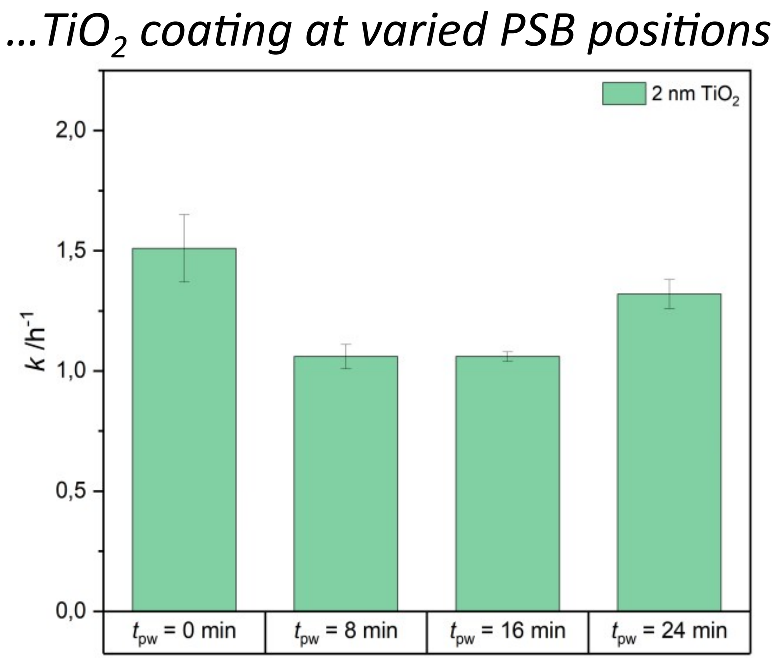
*Influence of surface treatment,*




*...pore widening duration,*




*...$TiO_2$ coating at varied PSB positions*




→ as prepared AAO-PCs contain unsaturated surface groups → high photocatalytic activity

- removal of surface groups by annealing or surface saturation by material deposition onto structures
- modification of unsaturated surface groups also possible by pore widening
- 0-16 min: decreased activity also present with $TiO_2$
- 24 min: PSB edge starts to overlap with $TiO_2$ absorption
  → photocatalytic activity increase

## References

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## Summary and Outlook

Photonic crystals can be easily produced by anodization of aluminum. The surface of as prepared AAO is dominated by unsaturated groups that are formed during the production. Contribution of these groups to the photocatalytic activity can be reduced by modifying the AAO surface. A beginning alignment of the PSB edge with the $TiO_2$ absorption by pore widening results in an increased photocatalytic activity.

Optimizing and combining the different preparation strategies to further enhance the photocatalytic efficiency and to tune the wavelength selectivity of AAO-PCs could expand their usage as tailor-made photocatalysts in the future.