Lifetime Improvement of UV Phosphors through Protective Particle Coatings via a Photochemically Induced Precipitation Method

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1. Phosphor converted Xe-excimer lamps in application

Wastewater e.g. from textile factories, chemical industry, or medical facilities are often contaminated with biologically incompatible substances, leaving an effective physical-chemical pre-clarification essential. Alongside separation-disposal techniques, so called advanced oxidation processes (AOP) facilitate an effective pre- or even complete clarification of contaminated wastewater. Numerous AOPs rely on the exposure with UV radiation, which has furthermore found its way into numerous applications for air and liquid disinfection. [1] Recent advancement of established techniques is given by the exchange of commonly used Hg low- or high-pressure lamps by Xe-excimer lamps. Such lamps efficiently produce VUV radiation peaking at around 172 nm enabling the use of conversion phosphors. [2]

Main Advantages:

- **Instant-On Lamp,** no warm up phase
- **Hg-free lamp** technique, ecologically beneficial, anticipation for possible upcoming prohibition of Hg-containing lamps
- **Energy efficient** emission of primary 172 nm emission (28-40 % [3]) by excimer discharge, lack of reabsorption caused by the activator
- **Optimization of emission characteristics,** e.g. for disinfection efficiency by selection of suitable phosphor

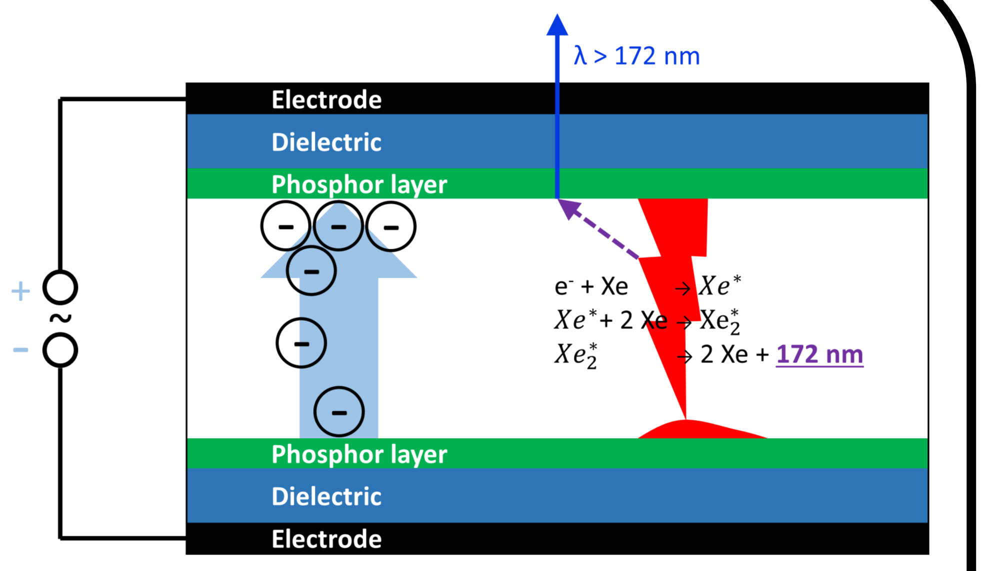

Fig. 1 Schematic illustration of a working Xe-excimer DBD-lamp

2. Lamp Phosphors: constrains, choice and aging

Main problems:

- **Reductive power** of hot e⁻
- **Solarisation** by high energy radiation (172 nm and lower)
- **Reactive Xe-plasma** may cause reactions on particle surface
- **Surface defects** due to ion impacts

Phosphor requirements:

- **High band gap** host matrix
- **Inert host matrix,** protection of dopant
- **Excitation band at 172 nm**
- **VUV and/or UVC emission bands,** suitable for application
- **High isoelectric point** (IEP)

Suitable UV phosphors: YPO_4:Bi, YPO_4:Pr or YPO_4:Nd.[4]
However, these phosphors do not resist the harsh conditions of the Xe plasma and the Xe-excimer discharge leading to rather fast aging. Figure 2 shows spectroscopy of YPO_4:Bi recovered from a used lamp.

Problem: Rapid degradation of phosphor caused by activator reduction und host material solarisation and surface bombardment results in short overall lamp lifetime
<u>Approach: A protective coating with an inert high bandgap, high IEP material !</u>

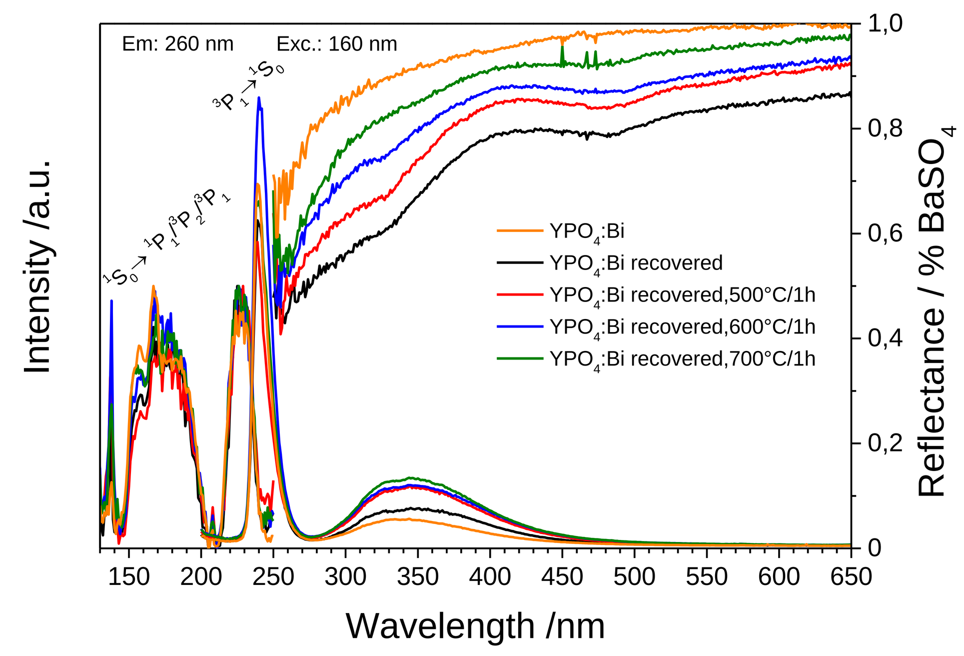

Fig. 2 Excitation (left), emission (middle) and reflectance spectra (right) of YPO_4:Bi from a prepared lamp body, recovered from a used Xe-Exc.-DBD lamp and recovered and tempered at different temperatures.

2.1 Conventional Particle Coating Procedure via precipitation driven by Urea hydrolysis

Coating procedure / deposition reaction

$$YPO_4:Bi_{(s)} + Al_2(SO_4)_3 \times 18\,H_2O_{(aq.)} \xrightarrow[\text{2. Calcination}]{\text{1. }\Delta T;\ H_2O,\ \text{Urea, Malonic Acid, } NH_4Cl} Al_2O_3@YPO_4:Bi$$

YPO_4:Bi particles are dispensed in a homogeneous solution of reactants and additive. The precipitation of $Al(OH)_3$ is thermally controlled by Urea hydrolysis.

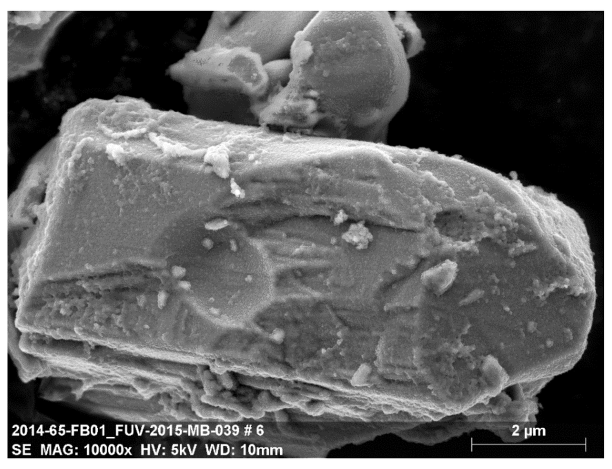

Fig. 3 SEM image of Al_2O_3 coated YPO_4:Bi particle

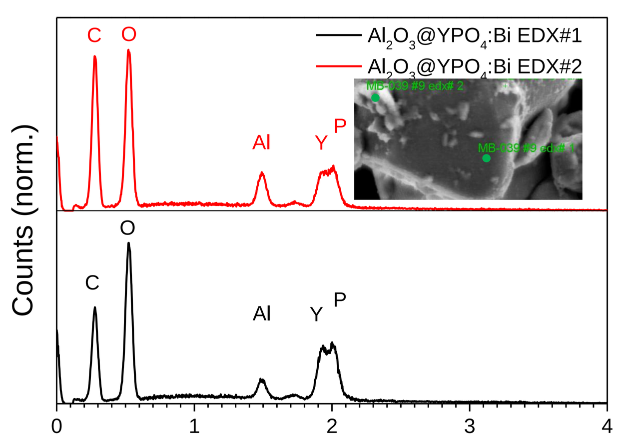

Fig. 4 EDX spot measurement of Al_2O_3 coated YPO_4:Bi particle

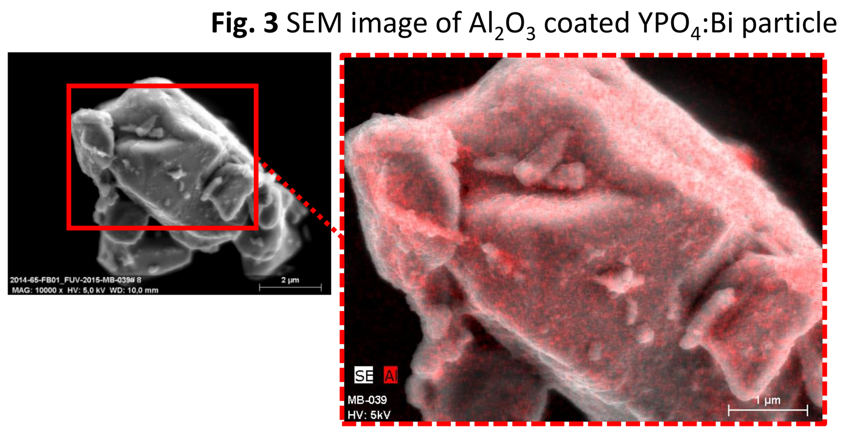

Fig. 5 EDX Mapping for Aluminium (red) coated onto YPO_4:Bi overlapped with SEM image of respective particle

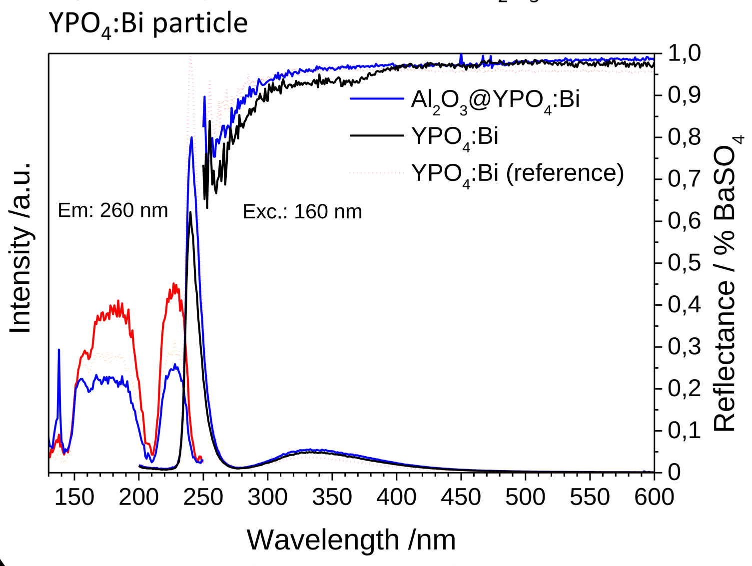

Fig. 6 Excitation (left), emission (middle) and reflectance Spectra (right) of neat and Al_2O_3 coated YPO_4:Bi

- **Dense coating** revealed by SEM & EDX
- **Simple „One-pot synthesis"**
- **Fine coating** as Malonic acid stabilizes Al_3^+ in solution
- **Improvement** of Phosphor emission characteristics through coating procedure by basic „washing at elevated temperature suggested

2.2 Novel Particle Coating Procedure via photochemically induced precipitation

Coating procedure / deposition reaction

$$2\,N_3^-{}_{(aq)} + h\nu_{UV} \longrightarrow 3\,N_{2(g)} + 2\,e^-$$
$$2\,H_2O + 2\,e^- \longrightarrow 2\,H_{2(g)} + 2\,OH^-$$
$$Al^{3+}{}_{(aq)} + 3\,OH^- \xrightarrow[\text{Calcination}]{+\,YPO_4:Bi_{(s)}} Al_2O_3@YPO_4:Bi$$

A UV-reactor system running a Hg-amalgam lamp peaking at 254 nm is used to irradiate a homogenous solution of NaN_3 and $Al_2(SO_4)_3$ x 18 H_2O

- Precipitation of $Al(OH)_3$ via UV induced degradation of N_3^-
- **Dense and fine coating** after calcining revealed by SEM & EDX
- **No additives** used needed through coating procedure
- **Closed reactor system** at room temperature
- **Controlled** by exposure, shallow slope of pH curve

Fig. 7 SEM image of Al_2O_3 coated YPO_4:Bi particle

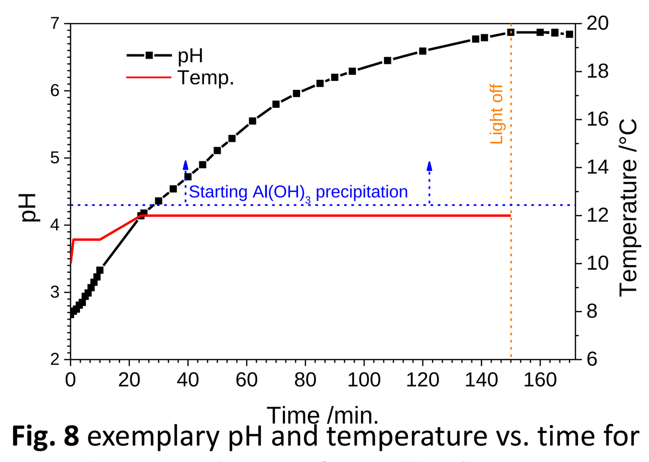

Fig. 8 exemplary pH and temperature vs. time for a coating procedure performed in the UV-reactor system

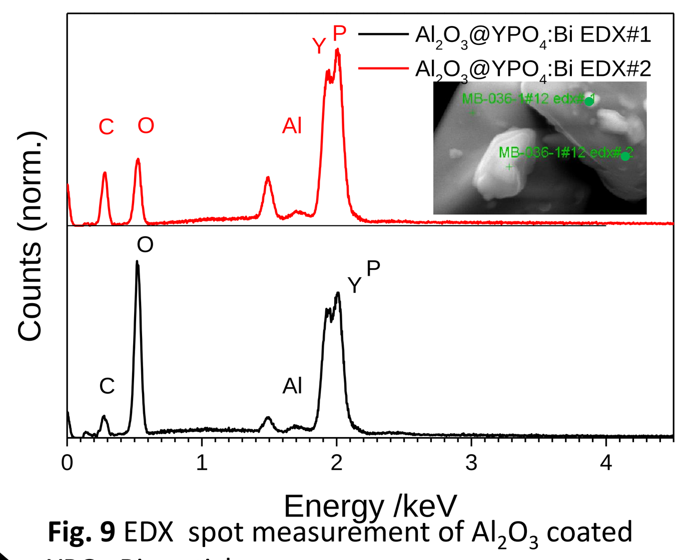

Fig. 9 EDX spot measurement of Al_2O_3 coated YPO_4:Bi particle

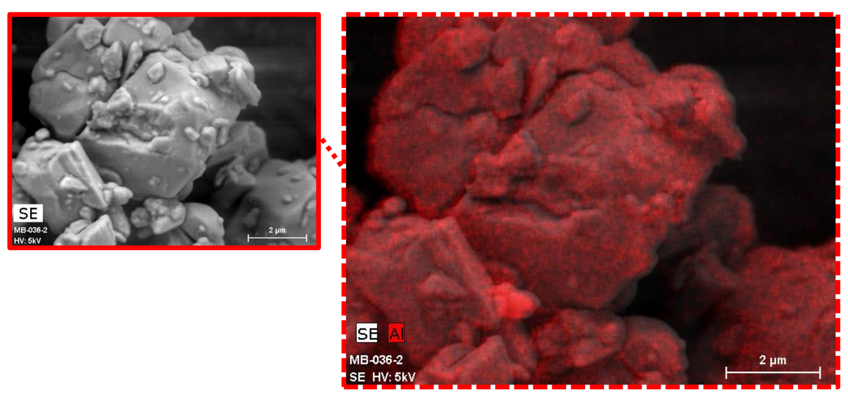

Fig. 10 EDX Mapping for Aluminium (red) coated onto YPO_4:Bi overlapped with SEM image of respective particle

3. Manipulation of Particle Surface Charge by Coating

- Neat YPO_4:Bi reveals an acidic IEP at pH 3.14, that the surface charge is strongly negative.
- Al_2O_3 has an IEP measured at pH 8.06
- Coating of YPO_4:Bi with Al_2O_3 (IEP at pH 8.06) leads to a upshifting of the IEP
- The more dense the coating, the higher the upshift
- Manipulation of particle overall surface charge enabled
- Higher IEP reflects less pronounced negative or even positive surface charge, as desired for a phosphor used under plasma conditions

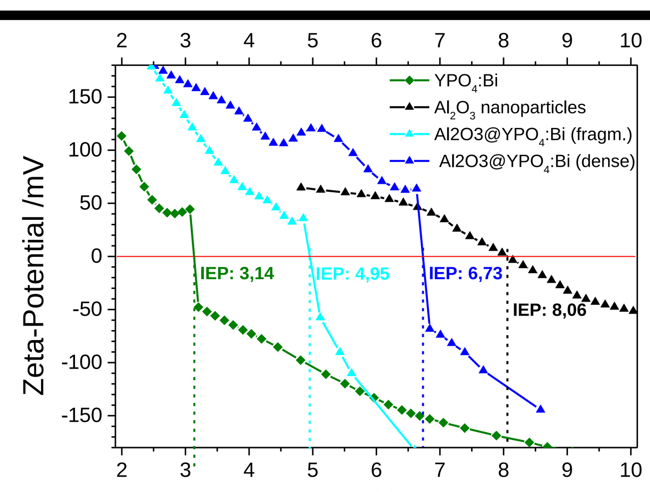

Fig. 12 Zeta potential vs pH measured by ESA method for neat YPO4:Bi, Al_2O_3 coated YPO4:Bi and pure Al_2O_3

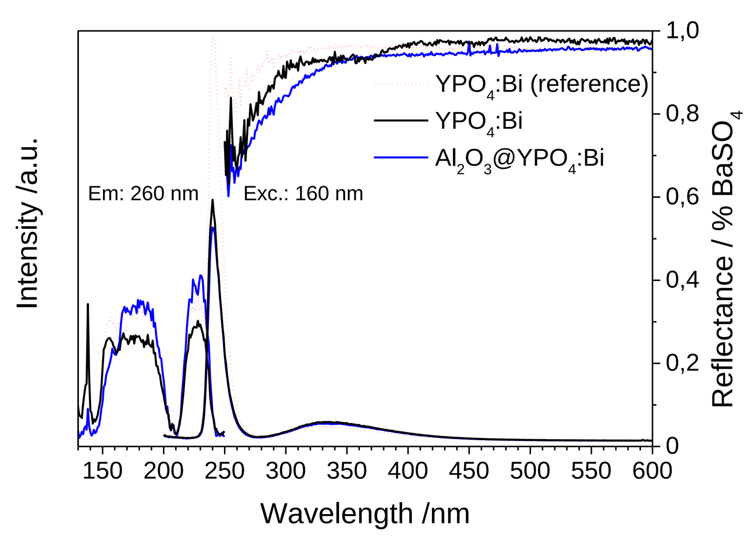

Fig. 11 Excitation (left), emission (middle) and reflectance Spectra (right) of neat and Al_2O_3 coated YPO_4:Bi

Acknowledgement:
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