Perspectives on the use of bismuth-based materials for sensing and removal of water pollutants

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Abstract

Bismuth based materials are among the most versatile species for the production of electroactive, adsorptive and photocatalytic materials. Their high tuneability has spread their use in many fields of application, proving for instance to be one of the most solid solutions for water monitoring and purification. Accordingly, we summarize the most recent and cutting edge achievements of bismuth-based materials in the field of water research.

Highlights

- Bismuth based materials could be used for the detection of both inorganic and organic species in aqueous medium.
- Bismuth based materials are effective adsorptive materials for the removal of heavy metals, radionuclides and organic pollutants.
- It is possible tuning the band gap of bismuth based materials to photoactivate them with visible light using several simple scalable routes.

Keywords: bismuth oxide, electrosensing, photocatalyst, adsorption, environmental remediation

1.Introduction

Water is an essential resource for all life on earth, and in 2010 the United Nations General Assembly formally recognized the access to clean drinking water and sanitation as a human right. However, rapid economic growth, intensification of agriculture and substantial population rise have caused a significant deprecation in water quality [1]. The limited capacity for renewal of groundwater and surface water resources, combined with lax regulatory frameworks on industrial and municipal waste effluents has further exacerbated the problem. Among all the freshwater contaminants, heavy metals and persistent organic pollutants are especially concerning, not only for the adverse effects they have on human health but also for their tendency to bio-accumulate [2]. Consequently, the quantitative detection and removal of critical pollutants is of paramount importance. Bismuth based materials (BBMs) have demonstrated to be extremely well suited for both sensing and water regeneration purposes, due to their wide-ranging properties[3]. Over the last decades BBMs have attracted the attention of academic and non-academic players because of their low cost of extraction, their peculiar photo and electrocatalytic properties and easily production [4]. Accordingly, we briefly discuss the most relevant and exciting works where BBMs were employed in the fabrication of affordable next generation electrochemical sensors for contaminant detection, and highly efficient adsorbent or photocatalytic systems.

2. BBMs production and properties

Nowadays, bismuth is mainly used in the form of halide, oxo-halide, nitrate and oxidederivative as summarized in figure 1.

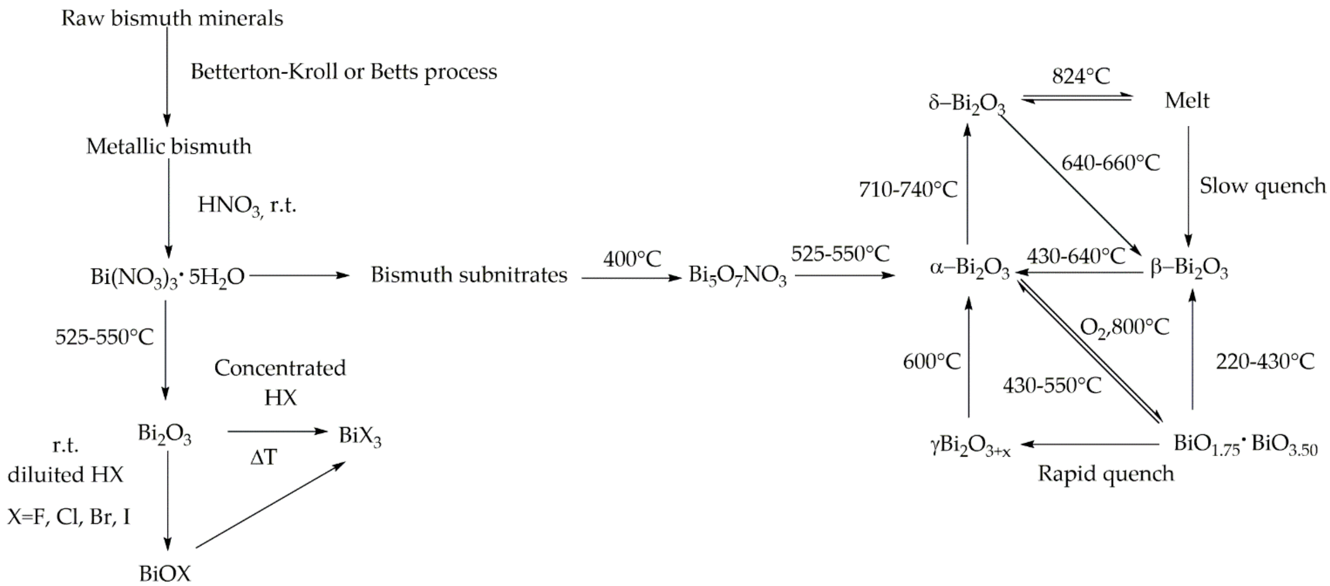

Figure 1: Main BBMs produced from thermal and thermochemical conversion of raw bismuth minerals.

The most common precursor of BBMs is $Bi(NO_3)_3$, produced through the oxidation of metallic bismuth by using HNO_3. $Bi(NO_3)_3$ is a very useful material that can be easily converted into several subnitrates with a wide range of stoichiometry up to $Bi_5O_7NO_3$. $Bi_5O_7NO_3$ represents the last thermally stable subnitrate prior the conversion of BBMs into pure oxides. Bismuth oxides are a heterogeneous family with up to 5 different well defined structures and several sub-oxides[5]. Bismuth oxides can be converted into BiX_3 (X = F, Cl, Br, I) using a HX in aqueous medium and then into BiOX through a partial hydrolysis of by adding the specific acid.

BBMs can also be prepared by combining bismuth oxides and bismuth nitrates with several other element, producing doped BBMs with well-known stoichiometry (*i.e.* $BiFeO_3$, $BiVO_4$, Bi_2WO_6) or through substitutional doping tune the band gap and induce desired magnetic properties in BBMs[6].

The great variety of BBMs allows to fine tune two main properties of interest for electrochemical sensing and pollutants removal: surface area and band gap. Said parameter can be easily be varied by tuning process parameters such as the heating rate, the highest temperature reached and the use of surfactant.

The surface area is generally reached only few dozens of m^2/g while the band gap could be tuned from 2.06 eV up to 3.50 eV[7].

3. BBMs for electrochemical sensing of pollutants

3.1 Heavy metal ions

Mercury based electrodes have been historically used for heavy metal ions detection, through stripping voltammetry analysis. However, given the well-known toxicity of mercury, significant effort has been put into finding alternative materials with comparable electroanalytical performances while being more environmentally friendly. Bismuth based electrodes have shown to be an attractive and economical solution for heavy metal analysis, and the most common deposition techniques are ex situ plating, in-situ plating or deposition of a bismuth precursor [8]. The addition of a Nafion (perfluorosulfonated cation-exchange polymer) membrane to a glassy carbon electrode can enhance the sensor's sensitivity, and this was found to be true both for mercury and bismuth film electrodes. In a recent work, Zhang et al. [9] exploited the high ionic conductivity of Nafion for the electrophoretic deposition of nano-bismuth and nano- bismuth oxide obtaining a stable and well adherent coating. Moreover, the combination of bismuth with nanoparticles, carbon nanotubes, or 2D nanomaterials such as graphene is currently the subject of intensive study and has demonstrated to be a fruitful approach. Novel advancements include the fabrication of a Bi/MXene nanocomposite [10], obtained by the deposition of bismuth nanoparticles on $Ti_3C_2T_x$ sheets for the detection of Pb^{2+} and Cd^{2+}, with detection limits of 10.8 nM and 12.4 nM respectively. Another exciting development is represented by the work of Jin *et al.* [11] where through a hydro/solvothermal synthesis a heterostructure of Bi_2O_3 nanosheets and tin sulfide (SnS) nanoparticles is reported. The synergistic interaction between Bi_2O_3 and SnS allowed for fast electron transfer kinetics and exceptional detection limits for Pb^{2+} and Cd^{2+}: 1.5nM and 1.4nM respectively.

2.2 Organic pollutants

Persistent organic pollutants are a set of toxic chemicals released in the environment as a result of human activity, mostly from agrochemical or industrial processes, oil spills and combustion of fuels. Conventional methods of detection include separation and spectrometric techniques such as liquid chromatography - mass spectrometry, atomic absorption spectrometry or inductively coupled plasma mass spectrometry. Nevertheless, these methods tend to be cumbersome and expensive, whereas electrochemical techniques allow for simple, low cost, and easy online detection of critical organic pollutants. In a common approach a carbonaceous electrode is thus functionalized with a inorganic or organic species to enhance its response. Noble metals, nanostructured carbon and their respective combinations have been widely employed, but they suffer from high costs, irreversible adsorption and are affected by the presence of metal impurities. In an effort to develop more sensitive and affordable electrochemical sensors, BBMs have been proposed as novel electrocatalysts usually with nanostructured carbon heterojunctions as shown in figure 2.

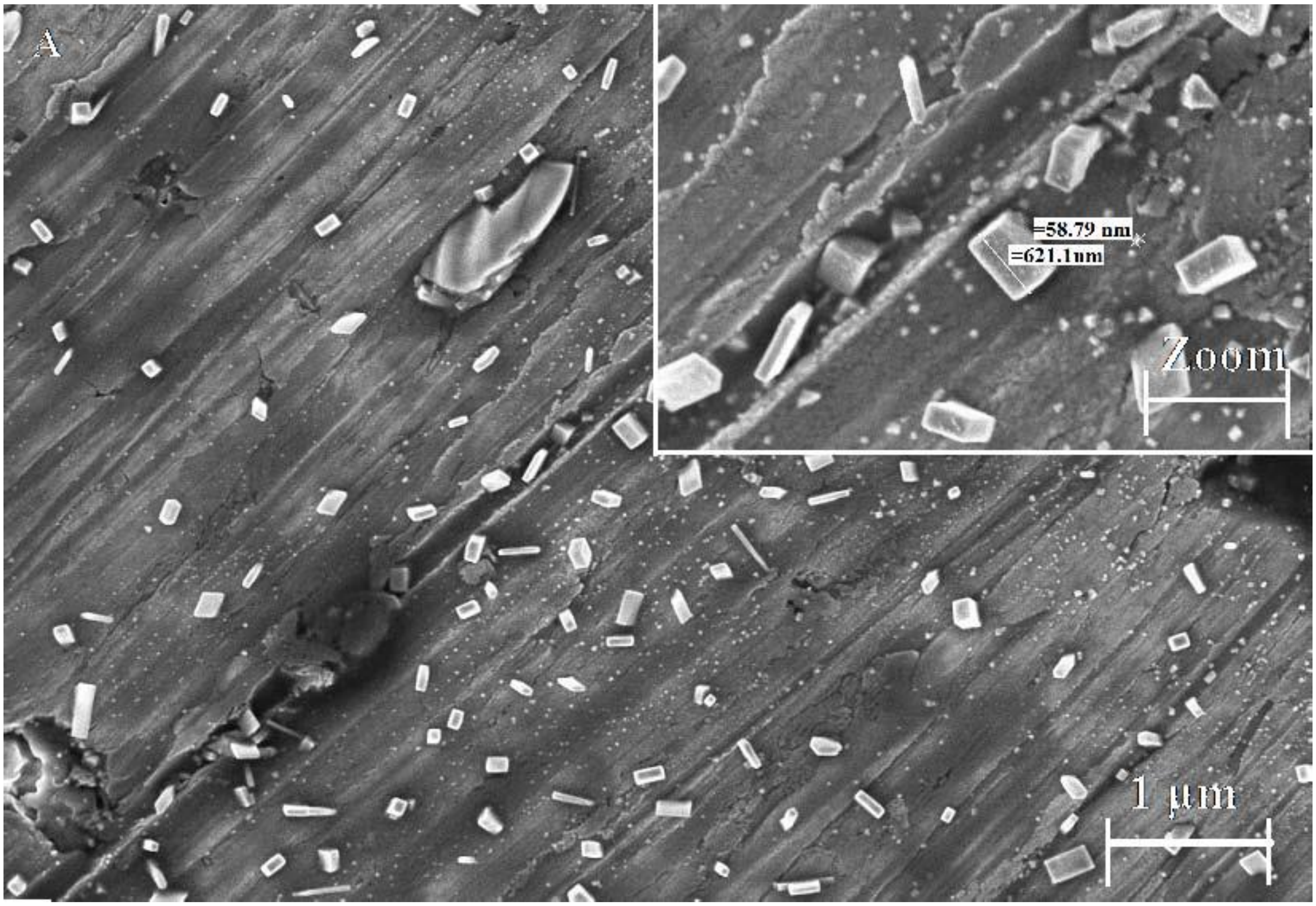

Figure 2: Modified screen printed carbon based electrode tailored with $BiONO_3$ as reported by [12]. Reprinted with all permission from IEEE.

The interaction between BBMs and organic materials is quite complex and there are few comprehensive studies. Franceschini et al.[13] evaluated the interaction between Bi_2O_3 and $Bi_5O_7NO_3$ with paracetamol by using computational approach highlighting the relevance of surface defect in the electron transfer rate efficiency.

For the detection of 2-nitroalinine, Krishnapandi *et al.* [14] obtained notable results with a Bi_2MoO_6 / carbon nanofiber (CNF) functionalized sensing platform, with a limit of detection of 43.7nM for a differential pulse voltammetry (DPV) measurement. Such a remarkable response was attributed to the peculiar catalytic activity of bismuth molybdate ($BiMoO_4$) and the well-known charge transfer properties of CNFs. Similarly, Gopi *et al.* [15] developed a glassy carbon electrode modified with molybdenum bismuth vanadate impregnated on graphene oxide ($GO - MoBiVO_4$) to detect via DPV 2, 4, 6 trichlorophenol in aqueous medium. The authors reported a synergistic interaction between $MoBiVO_4$ and GO, good stability, selectivity against common interference compounds and a wide linear range (from 0.199 to 17.8μM). The use of BBMs for the detection of organic pollutants has also found interesting application in the field of photoelectrochemical sensing, supported by a great body of evidence detailing the photocatalytic properties of BBMs [16]. Recently, Yan *et al.* [17] reported an efficient hydrothermal synthetic route for the synthesis of bismuth phosphate ($BiPO_4$) nanocrystals and nanosheets of bismuth oxy chloride (BiOCl) facilitate the separation of photogenerated charge carriers enhancing the detection of 4-chlorophenol.

Especially since the development of nanostructured bismuth oxide tailored on screen printed electrodes BBMs reached a commercial breakthrough [18].

3. Bismuth based materials for environmental remediation

3.1 Adsorptive designed materials

Adsorption is the most common route for water purification and BBMs have proved to be extremely versatile in the removal of the major contaminants from drinking water [19]. BBMs have demonstrated notable efficiencies in the removal of different harmful inorganics in a wide range of concentrations. Among them, anions such As(III) and As(V) are a real plague in south-east Asia and in central America. Bi_2O_3 has shown remarkable performances in the capture of arsenic anions due to its defective crystal structure reaching an efficiency of up to 33.1 μmol/m^2 and 31.6 μmol/m^2 for As(III) and As(V) respectively [20]. Defectiveness of BBMs was key to the successful removal of arsenic as proved by the use of bismuth hydroxides for the concurrent removal of arsenic fluoride and nitrates from drinking water

[21] and or BBMs doping with cations such as magnesium, calcium or iron[22]. Iron doped BBMs could also be an interesting solution for the immobilization of arsenic in paddy solid after the combination with bioderived carbon source though ferrolisys route[23]. The addition of iron boosts the performance of BBMs, as reported by Murtaza *et al.*[24]. The authors decorated metallic bismuth microparticles with nanoscale zerovalent iron particles achieving a removal of Cd(II) from a concentration of up to 10 mg/L down to 0.4 mg/L retaining the same efficiency for 6 cycles.

Similarly, the coupling of metallic bismuth atoms with nitrogen based carbon nanodots increased of up to 40 % the ability of the adsorption of Cu(II) [25] and the modification of BBMs with metal organic frameworks let to the realization of a selective adsorber for phosphates[26].

Maksoud et al. [27] reported a noteworthy application of bismuth tungstate (Bi_2WO_6) for the removal of radionuclides ^{134}Cs and $^{152+154}Eu(III)$) with an efficiency of up to 46 mg/g and 112 mg/g at 24 °C respectively. The authors reached a very effective water purification efficiency, removing up to 92 % of radionuclides and outperforming any other adsorption material and reaching the same performances of activated alumina, the best in the field. Han et al.[28] also proved the viability of Bismuth Iodate ($Bi(IO_3)_3$) tailored graphene oxide for the removal of radioactive iodine with an efficiency higher than 99 %. Such an exceptional result was mainly due to the formation of stable bismuth iodide (BiI_3) with a similar process as the one described by Reda et al.[29] for iodine.

Furthermore, the adsorption of hazardous inorganic species could be easily coupled with the removal of organic species [30, 31]. As reported by Najdanović et al. [32], bismuth nitrate clusters could reach high dye removal efficiencies, up to 1049 mg/g. Similarly, emerging pollutants such as doxorubicin could be adsorbed and degraded by using bismuth ferrite ($BiFeO_3$) with an efficiency of up to 93% [33]. Considering the moderate surface area of BBMs, adsorptive procedures are generally neglected and BBMs are more commonly used as photocatalysts for organic pollutants’ degradation. Furthermore, the regeneration and the cost of a BBMs adsorption process is far to be competitive with respect to cheaper materials currently available (e.g.activated carbon).

3.2 Catalytic designed materials

BBMs possibly represent the most tuneable resource for the production of photocatalysts in the visible light region [16] with a mechanism of action sketched in figure 4.

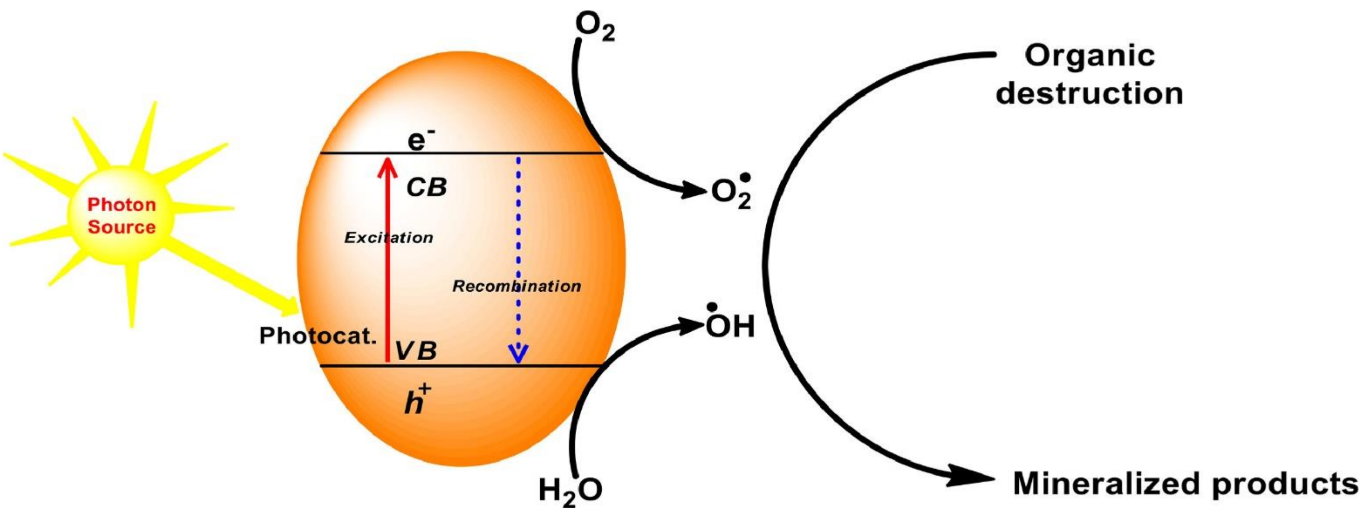

Figure 4: Action mechanism of photocatalyst during organic materials degradation. Reprint from [16] with all permission from Elsevier.

As reported by Gadhi et al.[34], it is not easy to discriminate between the partial degradation and fully mineralization of organic species. This task represents the main challenge to be fully solved before a real breakthrough of on-field applications of BBMs can be realized. The radical degradative pathway of each pollutant is unique and should be carefully considered, while avoiding the formation of new organic species that could be more harmfully than the starting one.

Contrary to a simple adsorption process, photocatalytic degradation activity should be carefully evaluated balancing both adsorption and degradative effects, as reported by Hernández-Gordillo *et al*.[35]. This is not a trivial task and can be accomplished only by combining kinetic and structural studies. A simpler approach is generally used in the scientific literature, where the contribution of adsorption is neglected. This operative route overestimates the actual photocatalytic activity of BBMs but for highly performing materials is still acceptable. Among BBMs, bismuth oxides are the most studied due to their facile thermal synthesis [36]and their band gap ranging from 2.3 up to 2.7 eV. Furthermore, bismuth oxide could be combined with clay filters in large batch reactors reaching a mineralization efficiency up to 70 % [37] for organic materials or could be used to tailor biochar for the removal of steroids from drinking water [38]. The natural photocatalytic activity of bismuth oxide could also be enhanced by creating heterostructures with bismuth subnitrates so as to be active even in the visible-light spectrum [39] due to an improved charge carriers separation at the heterojunction interphase with an enhanced formation of reactive oxygen species. Bismuth oxide/bismuth subnitrate heterostructures have been tested both for organic molecules degradation [40] and pathogen removal [41] under visible light proving a remarkable efficiency.

Other interesting heterostructures are produced by combining Bi_2O_3 with BiOX (X=Cl, Br, I). Tang *et al*.[42] tested the effectiveness of BiOBr/β-Bi_2O_3 against pure BiOBr and β-Bi_2O_3 reporting a fifty times higher photocatalytic activity of the heterostructure.

BiOX could also be used as pure materials even if the fast recombination rate of photogenerated charge carriers limits their practical use [43]. BiOCl has attracted a lot of interest due to its layered structure with a high surface area but it has a band gap of around 3.2–3.4 eV that requires the use of UV light. Nevertheless, several materials ranging from ternary oxyhalides to BiOI have been developed to overcame the stability issues. The addition of iodine ions to BiOCl structure leads to beneficial effects such as an increased stability and a reduction of band gap in the visible light region. Zhang et al.[44] developed a microwave synthetic route to directly incorporated I^- into BiOCl producing a photocatalyst abled to degrade hydroxyl derivatives of paraben under solar light. Similar results could be achieved by incorporating BiOX (X=Cl, Br) into carbonaceous[45] or polymeric [46] membranes.

Oxalides heterostructures with other bismuth based species such as bismuth selenide were very effective for recalcitrant pollutants degradation under visible LED irradiation [47].

The addition of other metallic species into BBMs structures represent an alternative approach to improve the photocatalytic activity as proved by the combination of BiOI with CdS for water de-oiling [48].

The production of BBMs included in complex clusters such as Bi_2WO_6, $BiVO_4$ or $Bi_2Sn_2O_7$ is also useful for reducing the band gap down to 2.4-2.9 eV. This approach was reported as very effective for the removal of several emerging pollutants such as drug traces in drinking water [49]. Also, BBMs are a good solution to tune the photocatalytic properties of traditional materials such as Titania [50].

4. Conclusions

BBMs properties represent a unique combination of versatility and effectiveness. The scientific literature is rich of researches that claim water purification efficiencies up to 99% but this is true only under idealized conditions for a few substrates. Nevertheless, BBMs could be used to treat polluted waters where several contaminants occurred simultaneously on a regular basis. The possible use as both adsorption and degradative materials is another unneglectable advantage of BBMs over other materials such as the more diffuse resin filters are more appealing for real application. Furthermore, BBMs could also provide a very effective tool for monitoring both inorganic and organic species even in low concentrations. Many challenges must still be overcome before suggesting BBMs as alternatives to traditional materials used in environmental remediation, but the research is moving fast in this direction as briefly summarized in table 1.

Table 1: Advantages and disadvantages related to the use of BBMs in sensing and environmental remediation.

BBMs uses	**Materials**	**Advantages**	**Disadvantages**
Detection of inorganic species	▪ Bismuth oxides	▪ High tuneability of oxygen vacancies and electron transfer rate. ▪ Easy synthesis through thermochemical routes. ▪ Good detection limits and linear range	▪ Requires pH adjustment. ▪ Poisoning ▪ Surface modifications
Detection of organic species	▪ Bismuth oxides ▪ Bismuth subnitrates ▪ Bismuth Molibdate ▪ Bismuth oxahalide	▪ High tuneability of oxygen vacancies and electron transfer rate ▪ High control on surface modifications. ▪ Good detection limits and linear range.	▪ Lack of selectivity compared with enzymatic based sytems
Adsorption of pollutants	▪ Bismuth oxides ▪ Bismuth ferrites ▪ Bismuth wolframate	▪ Good adsorptive performances. ▪ Poor leaching.	▪ High cost ▪ Regeneration
Photodegradation of pollutants	▪ Bismuth oxides ▪ Bismuth subnitrates ▪ Bismuth molibdate ▪ Bismuth oxahalide	▪ High structural and morphological tuneability. ▪ Tuneable band gap.	▪ Poisoning ▪ Need to be tested under on-field large scale conditions

	▪ Bismuth ferrites	▪ High efficiency in recalcitrant pollutants treatment ▪ Good regerability

We firmly believe that BBMs will represent one of the game changing materials for water treatment and monitoring that will allow to regenerate and preserve the water resources of mankind.

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