Using radicalized NO\textsuperscript{?} derivatives supported on metal oxides
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NO\textsubscript{X} (X=1 or 2) emitted from stationery/mobile sources are conventionally deemed as notorious, anthropogenic precursors of ultrafine particulate matters (PM2.5) because NO\textsubscript{X} can undergo a series of SO\textsubscript{2}-assisted photochemical transformative stages to finally evolve PM2.5 functioning as an air pollutant. Recently, a research group in South Korea rectifies the general notion of NO\textsubscript{X} (vide supra) by proposing an interesting means to exploit NO\textsubscript{X} in creative fashion.

The Korea Institute of Science and Technology (KIST) has announced that a KIST research group with principal investigators of Dr. Jongsik Kim and Dr. Heon Phil Ha has collaborated with a research team led by Prof. Keunhong Jeong in the Korea Military Academy (KMA) to graft NO\textsubscript{3}\textsuperscript{-} species on a metal oxide via chemical fusion between NO\textsubscript{X} and O\textsubscript{2} under a low thermal energy (? 150 °C). The resulting supported NO\textsubscript{3}\textsuperscript{-} species can then be radicalized to generate NO\textsubscript{3}\cdot analogs that serve as degraders of refractory organic substances present in a wastewater.

Aqueous recalcitrant compounds including phenolics and bisphenol A are typically eliminated from water matrices via sedimentation with the use of coagulants or via degradation into H\textsubscript{2}O and CO\textsubscript{Y} (Y=1 or 2) with the injection of OH shuttles such as H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3}, etc. However, these methods require additional stages to recover coagulants or suffer from short lifespans and/or chemical instabilities innate to \textsuperscript{\cdot}OH, H\textsubscript{2}O\textsubscript{2}, and O\textsubscript{3}, thus severely limiting the sustainability of H\textsubscript{2}O purification processes currently being commercialized.

As a substitute of \textsuperscript{\cdot}OH, NO\textsubscript{3}\cdot can be particularly appealing due to its longer lifetime and/or greater oxidizing potential in comparison with \textsuperscript{\cdot}OH, \textsuperscript{\cdot}OOH, or O\textsubscript{2}\cdot, thereby being predicted to enhance the efficiency in degrading aqueous pollutants over the other radicals stated above. Nevertheless, NO\textsubscript{3}\cdot production is not trivial and has a bunch of constraints such as the need of highly energized electrons in the presence of a radioactive element or highly acidic environments.

Dr. Kim and co-workers make it viable under a wastewater including H\textsubscript{2}O\textsubscript{2} and NO\textsubscript{3}-functionalized manganese oxide that surface manganese species (Mn\textsuperscript{2+}/Mn\textsuperscript{3+}) initially activate H\textsubscript{2}O\textsubscript{2} for the formation of \textsuperscript{\cdot}OH, whereas \textsuperscript{\cdot}OH subsequently activates NO\textsubscript{3}- functionality for its transition into NO\textsubscript{3}\cdot (denoted as \textsuperscript{\cdot}OH ? NO\textsubscript{3}\cdot), all of which are evidenced by density functional calculation (DFT) techniques alongside a bunch of control experiments.
Schematic representation of (A) H2O2 scission cycle on surface Mn+ species (n=2 or 3) and radical transfer from surface-unbound OH radical to NO2 radical or NO3 radical species supported on ?-/?-/?-MnO2 surfaces (NO2 radical SUP or NO3 radical SUP), leading to the production of supported NO2 radical (NO2 radical SUP in B) utilized for degrading aqueous pollutants. Illustration of porous architectures for ?-MnO2(D). Credit: Korea Institute of Science and Technology(KIST)

The resulting NO3• species were demonstrated to escalate degradation efficiency of textile wastewater by five- or seven-fold compared to those provided by conventional radicals (’OH/’OOH/O2•−). Of significance, the catalyst (NO3•-functionalized manganese oxide) discovered herein is ~30 % cheaper than a traditional commercial catalyst (iron salt) and is mass-producible. Of additional significance, the catalyst is reusable ten times or more. This is in contrast to a traditional catalyst that only guarantees one-time utilization in decomposing aqueous pollutants via homogeneous H2O2 scission (’OH generation).

Dr. Kim remarks that “The ’OH ? NO3• technology has been patented and sold to a domestic company (SAMSUNG BLUETECH). Given a plenty of merits imparted by the catalyst modified with NO3• functionalities, we basically expect to install the catalyst in a wastewater treatment unit so soon.”

The research was published in JACS Au.

More information: Jongsik Kim et al, Deciphering Evolution Pathway of Supported NO3• Enabled via Radical Transfer from •OH to Surface NO3– Functionality for Oxidative Degradation of Aqueous Contaminants, JACS Au (2021). DOI: 10.1021/jacsau.1c00124

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