Photocatalytic deoxygenation of nitrogen oxide compounds

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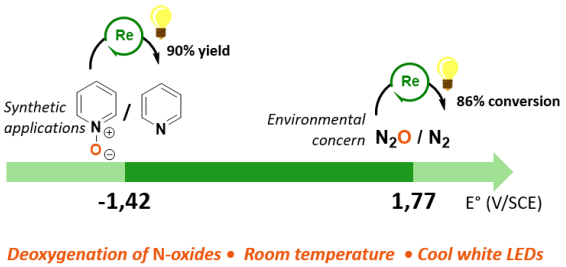
The accumulation of nitrogen oxides in the environment calls for new pathways to interconvert the various oxidation states of nitrogen, and especially their reduction. However, the large spectrum of reduction potentials covered by nitrogen oxides makes it difficult to find general systems capable of efficiently reducing various *N*-oxides.

Commonly known as 'laughing gas', nitrous oxide N_2O is an ozone-depleting substance 298 times more powerful a greenhouse gas than CO_2. It accumulates in the atmosphere due to its kinetic stability (120 years), thus contributing to 6% of anthropogenic greenhouse effect.[1,2] A solution would be the reduction of N_2O back to N_2, which would close the nitrogen cycle; however, few methods have been proposed due to the low reactivity of N_2O. Herein we describe a new pathway to reduce N_2O back to nitrogen at room temperature by means of photocatalysis. N_2O being isoelectronic with CO_2, inspiration came from previous work on the photoreduction of CO_2 to CO first disclosed by the group of Lehn.[3] Remarkably, $[Re(bpy)(CO)_3Cl]$ and its derivatives proved successful for the reduction of N_2O, up to 86% yield.

Encouraged by this success, we extended this methodology to the reduction of other N−O bonds, leading to a selective and synthetically applicable photocatalytic version of the deoxygenation of pyridine *N*-oxides. The mechanism of the N–O bond deoxygenation was studied on this substrate using laser flash photolysis and spectroelectrochemistry. These mechanistic insights enabled to optimize the system by shortening the reaction time from 34 h to 2 h. This unlocked the path to the deoxygenation of a broader scope of organic, *N*-oxide compounds.



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[2] M. Dameris, *Angew. Chem. Int. Ed. Engl.*, **2010**, *49*, 489-491.

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