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PHOTO-ACTIVATED NANOCATALYSTS FOR THE SELECTIVE MODIFICATION OF FREE CARBOHYDRATES

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PURPOSE OF THE ABSTRACT

Thanks to their renewability and abundance, the use of carbohydrates as biomass feedstock and their conversion into useful chemicals are becoming increasingly attractive to prepare products capable of replacing petroleum-based chemicals.[1] Sugars are polyfunctional and so, can lead to a wide variety of high-value products such as detergents, pharmaceuticals and cosmetics after chemical modifications (oxidation, reduction, isomerization, glycosylation...).[2] Among these transformations, oxidation is of particular interest since it leads to aldonic acids, which are biocompatible, biodegradable and are considered as important platform compounds.[3] However, the modification of these chiral polyhydroxylated substrates requires the means of protective groups to synthesize well-defined carbohydrate derivatives: ie. if one hydroxyl is supposed to react, the other functions, and more particularly the numerous hydroxyl groups, need to be masked. So, conventional glycochemistry is often characterized by multi-step protocols, requiring unsafe chemicals, and by poor atom efficiency. The development of new methodologies that allows modifying selectively free carbohydrates represents therefore a great challenge. Using reusable heterogeneous catalysts, mild conditions and eco-friendly activation mode would also help to respect green chemistry principles and participate to establish "all green" strategies.

In a context of sustainable chemistry, the use of solar energy to drive organic syntheses is a very excited approach whereas it has been lowly investigated so far. The anatase TiO2 is one of the best and most versatile photocatalyst. However, its major drawback stems from its large band-gap value of 3.20 eV which restricts the spectral absorption to UV light representing only 4% of the solar spectrum. Moreover, the highly oxidizing strength of holes located into the valence band (VB) (EVB= 2.8 V vs. ENH) is responsible of its poor selectivity because of the formation of free HO. and HO2. radicals. One approach to overcome the poor light harvesting is the surface modification by noble metals such as Au nanoparticles which affords (i) to create a broad absorption band at around 550 nm as a result from surface plasmon resonance effect (SPR) and (ii) prolonging the excited-state lifetime by improving the charge separation states. These photocatalytic properties open new perspectives for photo-assisted organic chemistry and for the selective transformation of biomass-derived compounds.[4]

We recently described an efficient and versatile methodology for the selective oxidation of sugars into corresponding sodium aldonates.[5] Hydrogen peroxide was used as a cheap and green oxidant, in the presence of only 0.003-0.006 mol % of gold in basic conditions. Three photocatalysts were studied, namely Au/Al2O3, Au/TiO2 and Au/CeO2, the latter being the most efficient (TOF > 750 000 h-1) and perfectly selective. Only 10 minutes of standard A.M. 1.5G light exposure affords total conversion of glucose into the corresponding sodium gluconate. This methodology is perfectly versatile to convert oligosaccharides from dp 2 to at least dp 8) into the corresponding aldonates in quantitative yield and high purity (>95%) without any purification step.

In this communication, we will describe the nanocatalysts and discuss the role of the different experimental parameters in the photolysis performances. For the first time, we will also discuss a possible mechanism to account for the high selectivity of this photocatalytic reaction on the basis of complementary set of technics such

as in situ electron paramagnetic resonance under illumination and time-resolved absorption and emission spectroscopies.

FIGURES

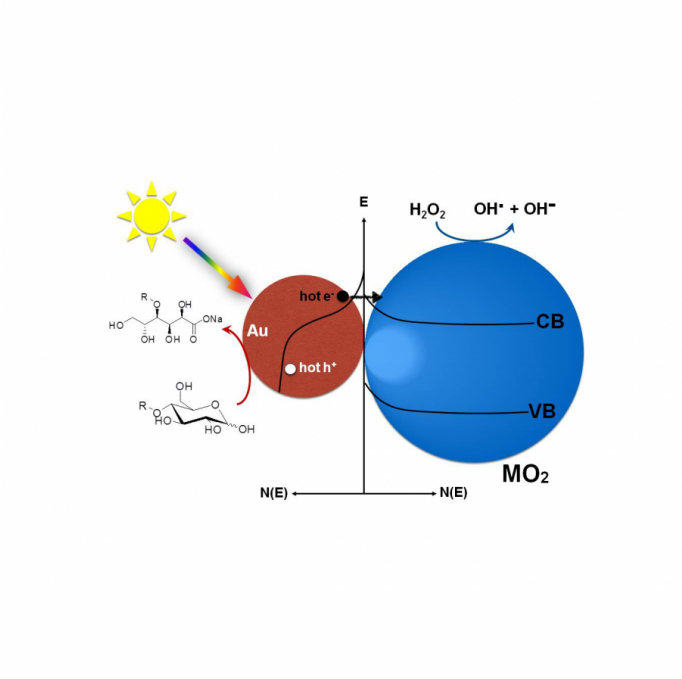

FIGURE 1

Figure 1:
D-glucose oxidation using gold supported catalysts under illumination

FIGURE 2

KEYWORDS

photocatalysis | gold-catalyzed oxidation | free carbohydrates

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