

# Generating, probing and utilising photo-induced surface oxygen vacancies for trace molecular detection.

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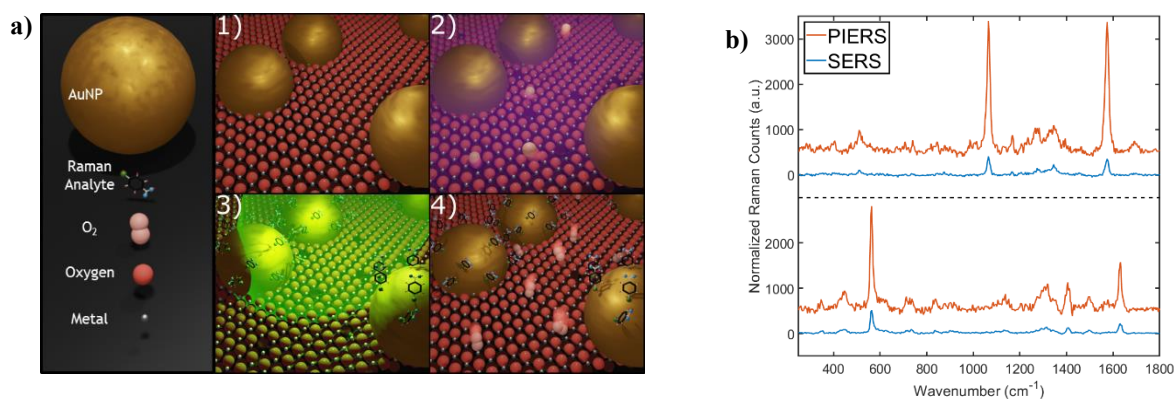
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Metal oxide semiconductors (MOS) are extensively used for a wide range of industrial applications [1–3], where defects states in MOS can strongly affect their overall performance, even at very low concentrations [4,5]. The functionality of MOS has been reported to be significantly altered through the addition of defects, whereby the materials can become more/less chemically active or the electronic properties are altered. Surface defects, in particular, are often one of the most reactive sites on the surface, greatly influencing MOS photocatalytic activity. Under UV irradiation conditions, interactions with photo-induced charge carriers can generate temporary oxygen vacancies,  $V_O$ , defect states on the surface of MOS [6], affecting the material properties during the defects' lifetime.

We have recently shown that surface  $V_O$  on photocatalytic MOS can be probed indirectly through the use of Raman spectroscopy, termed PIERS (photo-induced enhanced Raman spectroscopy) [7–10]. The presence of  $V_O$  alters the surface charge distribution and therefore can be probed through vibronic coupling charge transfer resonances to Raman active molecules on the surface, resulting in a chemical enhancement in the Raman signal. By monitoring changes in the Raman signal, the generation and healing of surface  $V_O$  can be monitored in real time on realistic textured substrates under operando conditions. In addition, the presence of  $V_O$  can be used for trace sensing application, allowing an additional enhancement pathway beyond conventional surfaced enhanced Raman (SERS).



**Fig. 1** a) Scheme showing the four stages of the PIERS sensing method: 1) As prepared photocatalytic metal-oxide semiconductor with NPs deposited on the surface. 2) UVC light photo-induces charge carriers leading to surface oxygen vacancy defects forming. 3) Raman band intensities of analyte molecule are enhanced via resonant charge transfer effects between the AuNP-semiconductor-vacancy-analyte system. 4) Under ambient conditions vacancy states are healed, where the Raman signal subsequently returns to the original SERS intensity. b) Average PIERS (orange) and SERS (blue) spectra for different Raman analytes (top – 4-mercaptobenzoic acid, bottom Rhodamine 6G) deposited on a  $\text{TiO}_2$  thin film with AuNPs.

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