Creation and Tuning of Defects in Nanomaterials using Ion Beam Implantation

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1) Scientific Background and Rationale

The transition to a carbon-neutral economy necessitates the development of advanced technologies capable of converting CO_2, into sustainable fuels and valuable chemicals, to combat climate change and meet the growing energy demand. Among various strategies, photocatalytic conversion utilizing solar energy stands out for its potential to address both climate change and the increasing global energy demand. The heart of this technology lies in photocatalysts, materials designed to absorb sunlight and activate CO_2 molecules for conversion into useful products. Extensive effort is going on for the development of photocatalyst with desirable optical, surface and electronic properties. The efficiency of the photocatalytic processes lies in the development of a suitable semiconductor as a photocatalyst having extensive absorption in the visible region of solar light, a low rate of recombination of charge carriers and stability. (*Polshettiwar & coworkers*, Nature Communications **2024**, 15, 713; Nature Communications **2023**, 14, 2551; ACS Nano, **2023**, 17, 4526; Chemical Science, **2019**, 10, 6594].

Defect engineering holds a promise as the presence, concentration and distribution of defects play a key role in tuning the electronic, chemical and surface properties of TiO_2. The light absorption property of photocatalyst can be extended up to IR region and also, the defect sites assist in adsorption and activation of the CO_2 molecule. It is not only the oxygen vacant site but also the uncoordinated bonds near the oxygen vacant sites that helps in the activation of CO_2 molecule (*Polshettiwar & coworkers*, Chemical Science, **2021**, 12, 4267-4299.).

Recently we showed that defects in nanosilica (E'-centres, oxygen vacancies, and non-bridging oxygen hole centres) convert CO_2 to methane with excellent productivity and selectivity (Figure 1). Neither metal nor complex organic ligands were required, and the defect alone acted as catalytic sites for carbon dioxide activation and hydrogen dissociation and their cooperative action converted CO_2 to methane. Unlike metal catalysts, which become deactivated with time, the defect-containing nanosilica showed significantly better stability. Notably, the catalyst can be regenerated by simple heating in the air without the need for hydrogen gas. Surprisingly, the catalytic activity for methane production increased significantly after every regeneration cycle, reaching more than double the methane production rate after eight regeneration cycles. This activated catalyst remained stable for more than 200 h. Detailed understanding of the role of the various defect sites in terms of their concentrations and proximities as well as their cooperativity in activating CO_2 and dissociating hydrogen to produce methane was achieved. (*Polshettiwar & coworkers,* Proc. Natl. Acad. Sci. U.S.A **2020**, 117, 6383-6390; Nature Communications **2020**, 11, 3828; J. Am. Chem. Soc. **2023**, 145, 8634-8646.).

2) Motivation and Novelty of the Proposal

Building on the premise that defect characteristics profoundly influence photocatalytic performance, this proposal seeks to advance the field by employing ion beam technology to precisely engineer defects in a range of nanomaterials. The use of ion beams represents an innovative and largely unexplored method for tailoring material properties at the nanoscale, offering unparalleled control over the type, concentration, and distribution of defects.

The proposed research focuses on a diverse set of materials, including novel composites and nanostructures, each selected for their potential to contribute uniquely to the understanding and optimization of defective photocatalysis. By extending ion beam implantation techniques to these materials, we aim to uncover new mechanisms of CO_2 activation and conversion, ultimately leading to more efficient and sustainable photocatalytic processes.Understanding defect evolution and structural transformations is a prominent research frontier for ultimately governing the photochemical properties of defective nanocatalyst.

Conventionally defect creation was carried out by either high-temperature Hydrogen treatment or magnesiothermic techniques, although few examples of Ion Beam Implantation were also reported.[3-9] In this proposal, we like to use ion beams, to generate the defects (vacancy or adatoms/single atom) in the materials and study the effect of defects on their various properties (catalytic, optical, acidity etc.)
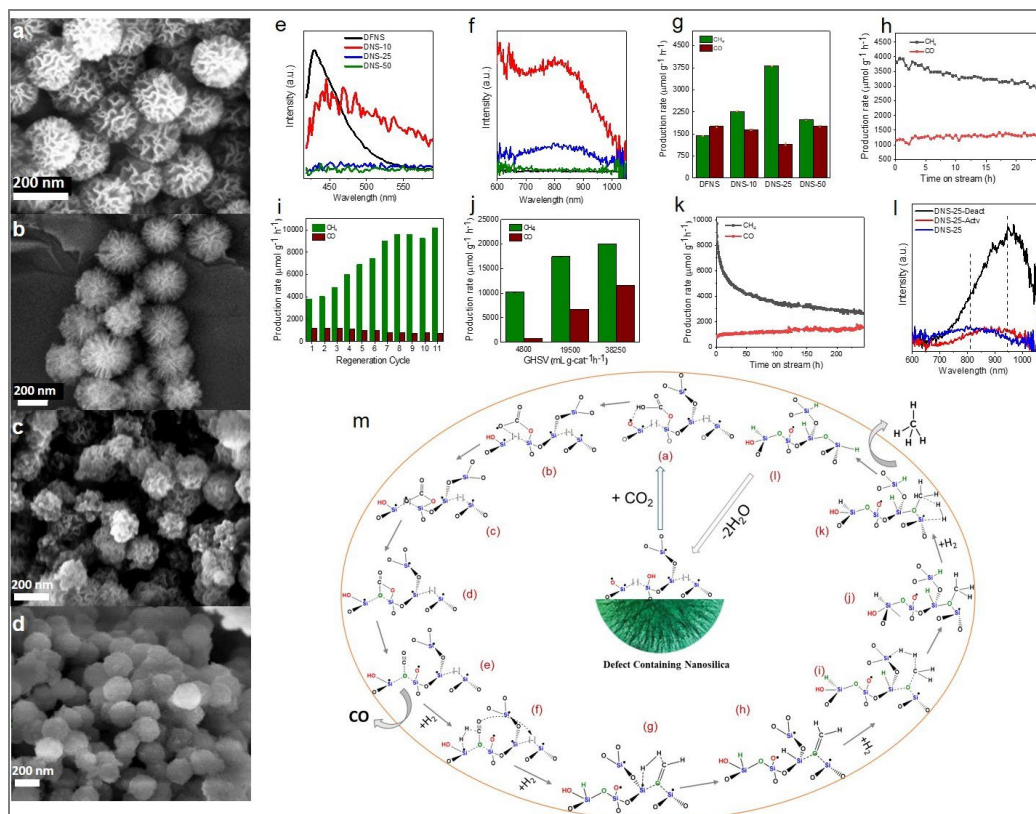
Figure 1. SEM images of (a) DFNS, (b) DNS-10, (c) DNS-25, and (d) DNS-50; (e, f) Photoluminescence emission spectra with an excitation wavelength (λexc)= 374 nm; (g) production rates of CH_4 and CO for various catalysts at 400 °C and 1 bar; (h) stability test of DNS-25 at 400 °C and 1 bar; (i) regeneration of catalysts in air at 400 °C and 1 bar for 11 cycles; (j) production rate of CH_4 and CO with the activated DNS-25 at various GHSVs, (k) stability test of activated DNS-25 at 400 °C and 1 bar for 200 h; (l) PL and (i) EPR, spectra of as-prepared DNS-25, activated DNS-25-Actv and deactivated DNS-25-Deact; (m) Schematic of the proposed mechanistic pathway. Here, [ ] indicates O-vacancy (ODC centre). All defects are shown only in one siloxane network for simplicity, although defects from various other siloxane networks of amorphous silica could also participate in the catalytic cycle.

3) Comprehensive Experimental Plan

We aim to introduce defects into a selection of our recently synthesized materials, as detailed below:

1. Dendritic Fibrous Nanosilica (DFNS) *[Chemical compsotion-SiO_2 (100%)]*
2. DFNS/TiO_2 *[Chemical compsotion-SiO_2 (80%) & TiO_2 (20%)]*
3. Black Gold *[Chemical compsotion-SiO_2 (70%) & Au (30%)]*
4. Ni_3N nanosheets *[Chemical compsotion- Ni_3N (95%) & -OH (5%)]*
5. Ceria *[Chemical compsotion- CeO_2 (100%)]*

We plan to employ various ion beams for this purpose:

Nickel (Ni), Vanadium (V), Silver (Ag), Aluminium (Al) and Boron (B)

Our foundational hypothesis is predicated upon the notion that the deliberate bombardment of these specified nanomaterials with a selection of ionic species will catalyze the genesis of bifurcated defect modalities: i) vacancies, and ii) adatoms (doping), or a sophisticated amalgamation of both, contingent upon the interplay between the ion's type and its kinetic energy dynamics. The strategic incursion of selected metallic ions into the lattice structures is postulated to precipitate the emergence of discrete atom dopants intricately embedded within the host material matrix, potentially revolutionizing its catalytic properties. Consequently, our predilection gravitates towards the employment of Nickel (Ni), Silver (Ag), Vanadium (V), or Aluminium (Al), predicated on the supposition that these <u>metallic ions</u>, by virtue of their distinctive electronic configurations and propensities for facile integration into the nanomaterials' frameworks, are highly suitable for creating the desired defects that are crucial for improving catalysis.

Should technical or practical limitations at the TIFR Pelletron facility preclude the use of these preferred elements, we are prepared to adapt by incorporating Boron (B). This tactical flexibility is motivated by the acknowledgment that Boron, notwithstanding its <u>non-metallic</u> character, may still contribute to the inducement of vacancy defects within the lattice frameworks of the materials. Such vacancies are instrumental in modulating the electronic properties of the materials and augmenting their catalytic efficiency, albeit via a mechanistic pathway distinct from that facilitated by metallic doping. This strategic adaptability and nuanced approach underscore our profound understanding of the intricate interdependencies governing material properties and our commitment to optimizing experimental paradigms to elucidate the transformative effects of ion-induced defects on the realm of nanomaterial catalysis.

4) Methodology

Our samples are powder which will be transformed into pallets, which can withdtsand the high vaccum. These samples are fully characterized by electron microscopy, UVDRS, N_2 sorption analysis and catalytic CO_2 conversion.

Defects can be generated by bombarding the sample with a say 50 MeV ion beam. However, at this stage we do not know the best optimum beam energy and sample exposure time, which need to be optimized. Hence, more detailed experimental planning for Ion Beam Implantation will be carried out with the help of Pelletron experts.

Sample Preparation: Transforming nanopowders into compact pellets designed to endure the high vacuum environment of the ion beam apparatus.

Sample Characterization: Employing advanced characterization techniques (e.g., HRTEM, XPS, UV-Visible spectroscopy, BET surface area analysis) to establish a comprehensive baseline of the physical, chemical, and optical properties of the materials prior to defect engineering.

Ion Beam Selection and Optimization: Experimentation with ion beams, optimizing parameters such as ion type, ion energy, and irridation time to achieve targeted defect structures.

Collaborative Optimization: Working in concert with Pelletron facility experts to refine ion beam parameters based on initial results, aiming for optimal defect configurations that enhance photocatalytic efficiency.

Photocatalytic Testing for CO_2 Conversion: Assessing the photocatalytic performance of each material in CO_2 reduction reactions under simulated sunlight, measuring product yield and selectivity.

Mechanistic Studies: Conducting in-depth analyses (e.g., transient absorption spectroscopy, electron paramagnetic resonance) to elucidate the mechanisms by which engineered defects facilitate CO_2 activation and conversion.

5) Justification for the use of Pelletron Accelerator

This study will provide information about how to create defects in nanomaterials using beamline and how to control their type and concentration. Their photocatalytic study and defect-activity relationship will provide very critical mechanistic understanding, which may take this defective photocatalysis field to the next level. Our questions are unique and have the potential to answer several unknown and critical questions about defective catalysis-based CO_2 to fuel conversion under ambient conditions.

The proposed use of the Pelletron Accelerator is pivotal for this research, as it offers an unmatched capability to precisely manipulate material properties at the atomic level through ion beam implantation. This project is positioned to make significant contributions to the field of photocatalysis by delivering a deeper understanding of the role of defects in catalytic processes, fostering the development of novel, efficient, and sustainable solutions for CO_2 reduction.

Our questions are distinct and hold the potential to unveil answers to numerous vital and yet-to-be-answered questions regarding the the defective catalysis.The outcomes of this research promise not only high-impact publications but also a tangible advancement in the defect based catalyst.

References:

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Some of the reported experimental details where ion beams are used;

1. The 100 MeV Ni^{7+} ions beam was used for SHI irradiation. Ion Irradiation was carried out in vacuum (10^{-6} Torr) and beam current of high energy ions was sustained at 1 pnA throughout the irradiation. Te samples were irradiated at room temperature with a range of fuence 5× 1012, 1× 1013, 1× 1014 and 2× 1014 ions/cm^2 . Te ion beam was focused using magnetic scanner to obtain fuence uniformity across the sample area. Te fuence values were determined by collecting the charge falling on sample mounted on metal ladder. Ref. Scientific Reports | (2021) 11:17672

2. Defect-engineered samples irradiated SLM with 91 MeV Xe ions under grazing incidence at an angle of $\Theta = 1°$ with respect to the surface and with a fluence (number of ions per area) of 15 ions per μm^2. The corresponding energy deposited per track length was Se = 19 keV nm^{-1} into MoS_2, Se = 12 keV nm^{-1} into SiO_2, and Se = 9.3 keV nm^{-1} intoglassy carbon. Ref. Nanoscale, 2018, 10, 22908

3. Proton implantation was carried out at an energy of 30 keV and a nominal dose of 1016 ions/cm^2 using a Varian 350 D ion implanter, ref. Nano Lett. 2015, 15, 6815−6820

4. Nitrogen ion implantation of the annealed samples was carried out in a multipurpose implanter designed by Öchsner et al. 20 at 60 keV accelerating energy and a nominal dose of 1 × 1016 ions/cm^2. https://pubs.acs.org/doi/10.1021/nl0600979]

5 Implantation energies of typically 40–60 keV were selected. NWs were implanted with Mn doses of 2 × 1015 to 1 × 1016 ions/cm^2 resulting in total Mn concentrations from 0.5 to 2.9% (corresponding to a stoichiometry of Ga1–xMnxAs with x from x = 0.01 to x = 0.058) as calculated with the iradina code. https://pubs.acs.org/doi/10.1021/nl2021653

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