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***In situ* imaging of gold nanocrystals during the CO oxidation
reaction studied by Bragg Coherent Diffraction Imaging.**

Thesis presented to the Institute of
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Supervisor: Prof. Dr. Sandra Helena Pulcinelli
Co-supervisor: Dr. Florian Meneau

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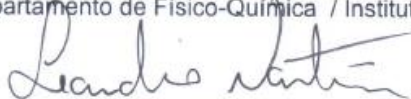
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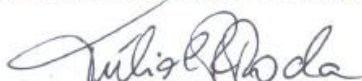
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“Life’s most persistent and urgent question is: What are you doing for others?”

Martin Luther King Jr.

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ABSTRACT

The fundamental aim of heterogeneous catalysis research is to understand mechanisms at the nanoparticle level, and then to design and synthesise catalysts with desired active sites. In this regard, the *in situ/operando* characterisation of defects is crucial as they are preferential catalytic sites for the reaction occurrence.

The main part of this thesis was the investigation of the morphology and structure evolution of gold nano-catalysts supported on titanium dioxide. We worked with different methods of preparation (seed-growth, ionic liquid stabilizer) to synthesise gold catalysts with controlled sizes. Those catalytic materials were evaluated for the model CO oxidation reaction, chosen for its environmental relevance and “simplicity” to be reproducible within our X-ray imaging study.

We used the Bragg Coherent Diffraction Imaging technique to follow *in situ* the 3D morphology changes under catalytic reaction conditions. A dedicated *in situ* heating reactor has been built. We correlated the 3D displacement field and strain distribution of the gold nanoparticles to the catalytic properties of the material. In particular, for a 120 nm gold nanoparticle, we quantified under working conditions the adsorbate-induced surface stress on the gold nanocrystal, which leads to restructuring and defects identified as a nanotwin network.

Finally, by using scanning X-ray nanodiffraction to characterise few tenths of nanometers single gold nanorods, we were able to obtain a strain map over the Bragg well oriented gold crystals. This characterisation revealed the presence of a strain pattern encoded in the nanorods structure consistent with the so-called Rayleigh Instability. This kind of study proved to be very important as the presence of instability does affect the properties of nanorods.

Keywords: *in situ* Bragg CDI, gold nanocrystals, CO oxidation reaction, strain, twin defects, nanodiffraction.

RESUMO

O principal objetivo da catálise heterogênea é entender os mecanismos de reação a nível nanométrico e planejar/sintetizar catalisadores com os sítios ativos desejados. A este respeito, a caracterização de defeitos *in situ/operando* é crucial, pois esses são sítios catalíticos preferenciais para a ocorrência da reação.

A parte principal desta tese foi a investigação da morfologia e evolução estrutural de nano-catalisadores de ouro suportados em dióxido de titânio. Trabalhamos com diferentes métodos de preparação (crescimento de “sementes”, uso de líquidos iônicos como agentes estabilizantes) para sintetizar catalisadores de ouro com tamanhos controlados. Esses catalisadores foram testados para a reação modelo de oxidação de CO, escolhida por sua relevância ambiental e "simplicidade" para ser reproduzível em nosso estudo de imageamento por raios-X.

Utilizamos a técnica Imageamento por Difração Coerente de Bragg para acompanhar *in situ* as alterações da morfologia em 3D nas condições da reação catalítica. Um reator que permite aquecimento, dedicado a experimentos *in situ*, foi construído. Correlacionamos o *strain* e *displacement field* em 3D das nanopartículas às propriedades catalíticas do material. Para uma nanopartícula de 120 nm em particular, nós quantificamos sob condições de funcionamento o *stress* superficial induzido pelo processo de adsorção no nanocristal, o que leva à reestruturação da nanopartícula e defeitos identificados como uma rede nanotwin.

Finalmente, usando nanodifração de raios-X para caracterizar *nanorods* de ouro individuais de algumas dezenas de nanômetros, pudemos obter um mapa de *strain* para os cristais de ouro bem orientados na condição de Bragg. Esta caracterização revelou a presença de um padrão de deformação codificado na estrutura dos *nanorods*, consistente com a chamada Instabilidade de Rayleigh. Esse tipo de estudo provou ser muito importante, pois a presença de instabilidade afeta as propriedades dos *nanorods*.

Palavras-chave: *in situ* Bragg CDI, nanocristais de ouro, reação de oxidação do CO, *strain*, defeitos twin, nanodifração.

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RESUMO EXPANDIDO

Em escala nanométrica, os materiais apresentam propriedades físico-químicas diferentes se comparadas com o estado bulk, devido à alta razão superfície/volume, característica de nanomateriais. Isso garante o emprego desses materiais em numerosas aplicações em áreas como sensores, na biomedicina, fabricação de dispositivos eletrônicos, etc. Por exemplo, nanopartículas de metais nobres suportadas em óxidos são bastante utilizadas em catálise heterogênea e são um tema amplamente estudado em nanociência.

A catálise é dita heterogênea quando a fase do catalisador é diferente da fase dos reagentes. Uma vez que esse tipo de catálise é extensivamente empregada em várias áreas da química e em muitos processos industriais, melhoras no desempenho de catalisadores heterogêneos são de suma importância no aprimoramento de processos industriais, no desenvolvimento de novas formas de energia e no controle da poluição ambiental. Um exemplo é o uso de catalisadores em veículos automotivos para a transformação química de gases poluentes que representam uma ameaça ao meio ambiente como hidrocarbonetos, monóxido de carbono (CO) e óxidos de nitrogênio (NO_x) em substâncias menos agressivas em termos de poluição ambiental, como CO₂, H₂O e N₂. Nesse cenário, o estudo da estrutura do catalisador e os mecanismos envolvidos na reação de catálise são passos importantes no processo de melhoramento no desempenho de catalisadores.

Dispersões coloidais de nanopartículas de ouro (Au NP) são muito estudadas devido as suas fascinantes propriedades físico-químicas: trata-se de dispersões estáveis que apresentam propriedades ópticas e magnéticas muito interessantes. O ouro quando no estado bulk é um metal inerte, mas quando nanoparticulado, apresenta excelentes propriedades catalíticas para uma ampla série de reações químicas. Esse fato é atribuído principalmente a abundância de átomos com menor número de coordenação em partículas pequenas, onde a adsorção dos reagentes, difusão e a dessorção dos produtos acontece.

Esses sítios ativos estão localizados nas bordas, esquinas e defeitos superficiais das nanopartículas. A reatividade dos catalisadores é ajustada pela deformação ("*strain*") presente na estrutura superficial, a qual é altamente dinâmica e consequentemente varia durante a ocorrência da reação. Nesse contexto, o *strain*

denota o deslocamento dos átomos na estrutura cristalina em relação às suas posições ideais. O desempenho catalítico pode ser melhorado através do entendimento da evolução do *strain* e a formação de defeitos tanto na superfície quanto na estrutura interna dos nanomateriais. Sob o ponto de vista da catálise, a fonte de *strain* durante o processo catalítico pode ser advinda da tensão (“*stress*”) induzida pela adsorção dos reagentes e da formação de defeitos internos/superficiais, os quais deslocam os átomos, resultando em compressão ou expansão da rede em relação à estrutura cristalina perfeita.

Além disso, as condições da reação afetam o comportamento dos catalisadores e seu desempenho. Assim, estudos sob condições controladas do ambiente reacional (“*in situ/operando*”) devem ser feitos. No entanto, técnicas de imageamento *in situ* em três dimensões (3D) que alcancem resolução nanométrica e determinação de *strain* simultaneamente são difíceis de serem aplicadas. Informações referentes a *strain* e defeitos em escala nanométrica podem ser obtidos com resolução atômica através de microscopia eletrônica, mas com severas restrições que incluem pressões reduzidas devido a profundidade de penetração curta dos elétrons, impedindo caracterizações *in operando*. Por outro lado, difração de raios-X de pó no regime de raios X duros permite a determinação de *strain* sob condições *in operando*; no entanto, as informações obtidas se referem a amostra como um todo, levando a informações que representam uma média de todas as estruturas presentes no pó.

A disponibilidade de raios X coerentes em fontes de luz síncrotron abre novos caminhos no campo de imageamento de nanomateriais, onde a técnica de Imageamento por Difração Coerente de Bragg (Bragg CDI) pode revelar a distribuição de *strain* de objetos nano e micrométricos em 3D em condições *in operando*. É importante destacar que a caracterização por Bragg CDI é possível em diversos ambientes realísticos (soluções aquosas, atmosferas reativas, altas temperaturas, etc.). Bragg CDI é uma técnica que se desenvolveu muito ao longo dos últimos 20 anos. Ela permite a reconstrução 3D de nano/micro objetos cristalinos e não cristalinos, como por exemplo, zeólitas, nanopartículas, tecidos biológicos, etc. Na técnica de difração, como a intensidade da radiação espalhada é o quadrado de sua amplitude, nós temos acesso a amplitude; no entanto, informações relativas a fase das ondas difratadas são perdidas nesse processo. Esse é o famoso “problema da fase”, bem conhecido na área de cristalografia. A radiação difratada pode ser

convertida na distribuição da densidade eletrônica do objeto espalhador através da aplicação de uma transformada de Fourier inversa. A amplitude da imagem obtida por Bragg CDI representa a densidade eletrônica da amostra e a fase corresponde a projeção do deslocamento dos átomos na estrutura cristalina. Assim, é possível reconstruir a partícula e obter informações referentes a morfologia e também sobre o deslocamento na posição dos átomos em relação as suas posições ideais na estrutura cristalina.

Neste trabalho, a técnica Bragg CDI é utilizada para revelar a dinâmica dos defeitos cristalinos e também o processo de facetamento que ocorre no sistema modelo sintetizado, isto é, nanopartículas de ouro suportadas em dióxido de titânio. Esse sistema foi estudado *in situ* durante a reação de oxidação de CO a pressão atmosférica. Essa reação catalítica é de suma importância ambiental uma vez que ela é utilizada no controle da poluição ambiental através da remoção de CO do sistema de exaustão de veículos motores, sendo considerada uma reação modelo.

Um reator dedicado para experimentos de Bragg CDI *in situ* e que pode funcionar a altas temperaturas também foi construído. Fazendo uso de um algoritmo para recuperar a fase através de um processo iterativo, a densidade eletrônica 3D de Bragg é reconstruída, sendo possível obter informações relativas a morfologia do objeto, e também ao campo de deslocamento dos átomos presentes na rede cristalina das nanopartículas de ouro. Para um dos experimentos, chegou-se a uma resolução espacial de 12 nm. As transformações superficiais que são induzidas pelo processo de adsorção e a quantificação do *stress* superficial também foram descritos, mostrando que a formação de redes geminadas de *nanotwins* desempenham um papel crucial nos mecanismos de deformação dos nanocristais e se correlacionam com o comportamento catalítico das nanopartículas de ouro suportadas em dióxido de titânio.

Outra parte desse trabalho consistiu na síntese de nanopartículas de ouro ultra-pequenas, extremamente relevantes do ponto de vista catalítico. As NP muito pequenas apresentam excelente performance catalítica para a reação de oxidação do CO: a taxa de conversão de CO para Au NP no intervalo de tamanho de 2-4 nm é aumentada em duas ordens de magnitude se comparadas com Au NP maiores, demonstrando que o tamanho da nanopartícula é extremamente relevante para a ocorrência do processo catalítico. Para o preparo dessas nanopartículas foram

utilizados líquidos iônicos como agentes estabilizantes. Essa classe emergente de materiais tem crescido e atraído bastante atenção devido as suas propriedades físicas únicas como baixa volatilidade, alta estabilidade, baixa toxicidade e biodegradabilidade. De fato, diversos líquidos iônicos têm sido vastamente utilizados nas áreas de síntese orgânica, catálise, eletroquímica, eletrólitos poliméricos, na síntese “verde” de nanomateriais estáveis em água, em diversas reações químicas empregadas na indústria, etc.

Por fim, uma outra parte do trabalho desenvolvido durante esse doutorado foi o estudo de nanobastões (“*nanorods*”) de ouro utilizando como técnica principal nanodifração. O estudo aprofundado da estrutura e morfologia de *nanorods* de ouro é extremamente relevante para o emprego dos mesmos em uma ampla gama de aplicações que inclui dispositivos nanoeletrônicos e na área de biologia. Nessa tese, através do uso de microscopia eletrônica de varredura e nanodifração de raios X para caracterizar pequenos *nanorods* de ouro individuais, foi possível obter uma projeção da distribuição de *strain* dos cristais bem orientados na condição de Bragg. Essa última caracterização revelou a presença de um padrão de *strain* codificado na estrutura cristalina dos *nanorods* consistente com a chamada instabilidade Rayleigh, que leva a uma posterior segmentação de sua estrutura em esferas. Nossa metodologia mostra que a instabilidade está intrinsicamente presente nos *nanorods* em escala atômica e traz informações sobre a estabilidade estrutural dos mesmos, fazendo emergir uma compreensão nova para a engenharia de dispositivos que utilizam esse tipo de nanomaterial.

A principal inspiração do trabalho desenvolvido durante esse doutorado é a necessidade de conhecimento científico sobre técnicas advindas de radiação coerente uma vez que a nova fonte de luz síncrotron brasileira, o SIRIUS, terá diversas linhas de luz que oferecerão técnicas que utilizam luz coerente. O SIRIUS será uma máquina de quarta geração e está em estágio final de construção em Campinas-SP, sendo capaz de funcionar como um grande microscópio que oferecerá para a comunidade científica uma ampla série de métodos de caracterização pioneiros. Isso com certeza irá permitir o desenvolvimento de pesquisas no estado da arte, com potencialidades para resolver problemas científicos em diversas áreas como saúde, agricultura, energia, etc. Nesse aspecto, o presente trabalho abriu novos caminhos em relação a experiência/conhecimento adquiridos pelas pessoas envolvidas nesse projeto em

relação a técnica utilizada, aquisição/tratamento dos dados, conhecimento teórico/prática experimental, etc.

A linha de luz Cateretê, no SIRIUS, será dedicada a performance de CDI e está planejada para começar a funcionar em 2019. Quando a linha de luz de Cateretê estiver em operação, as técnicas de imagem de difração de raios X coerentes alcançarão a resolução espacial e temporal necessária para o estudo de dispositivos reais e as técnicas poderão ser aplicadas durante medições *in situ/operando*: tratamento térmico; uso de células dedicadas em diferentes atmosferas; estudo de carga/descarga em sistemas de baterias; dentre muitas outras possibilidades. Sem dúvida, isso expandirá os horizontes para a comunidade científica uma vez que no SIRIUS o fluxo coerente de fótons será 2 a 3 ordens de grandeza maior do que os disponíveis hoje em dia, o que significa uma grande melhora nas resoluções espacial e temporal.

CHAPTER I: Introduction

1.1. INTRODUCTION

At the nanometric scale, materials present different properties from the bulk state, mostly due to the remarkable property of high surface/volume ratio. Colloidal dispersions of gold nanoparticles (Au NP) have been vastly studied due to their fascinating physicochemical properties: they are the most stable (1), and present very interesting optical and magnetic properties. Although gold is inert in the bulk state, when in nanosized regime, gold presents excellent catalytic properties in a wide range of reactions. This fact is attributed to the abundance of a high number of low coordinated atoms in small nanoparticles, where the reactants' adsorption, diffusion and the products' desorption take place.

These active sites are localised at corners, edges and surface defects (2,3). The reactivity of the catalysts is tuned by the inherently strained surface structure (4,5) that is highly dynamic under reaction conditions (6–8). The improvement of catalytic processes can be achieved through the fine understanding of the evolution of strain and the formation of defects in both the surface and the inner core structure of the nanomaterials. In this context, strain denotes to the displacement of atoms in the crystal structure in relation to their ideal positions. For a catalyst, the source of strain during the catalytic process can be caused by the stress induced by the reactants adsorption and from internal defects, which displaces the atoms, resulting in compression or expansion from the ideal crystalline lattice.

Moreover, reaction conditions affect the catalysts behaviour and their performances. *In situ/operando* studies under relevant and controlled environmental conditions must be performed (9,10). However, *in situ* three-dimensional (3D) imaging techniques enabling nanometer-resolution and strain determination simultaneously are lacking. To date, strain and defect information at the nanoscale is accurately obtained by electron microscopy (11,12) with restrictions to reduced pressures due to the short penetration depth of electrons, preventing *in operando* characterisations. On the other hand, powder X-ray diffraction in the hard X-ray regime, enables to get strain structure data *in operando* conditions but on a large assembly of particles, yielding solely averaged information. The availability of coherent hard X-rays from synchrotron light sources opens new opportunities for imaging studies of nanomaterials (13,14), where Bragg coherent X-ray diffraction imaging (Bragg CDI) can reveal the strain distribution of single micro- and nano-sized objects (15–20) in 3D and *in operando* conditions. It is

worth mentioning that Bragg CDI is feasible in several realistic environments (aqueous solutions, reactive atmospheres, high temperatures...). The amplitude of the image obtained by Bragg CDI represents the electron density of the sample and the phase corresponds to the projection of the displacement of the crystal lattice. Thus, it is possible to reconstruct the particle and obtain information about the morphology and also information regarding the displacement of the atom's positions in relation to their ideal positions in the crystal lattice.

In this PhD work, Bragg CDI is used to unveil the defects dynamics and facetting process occurring on model gold nanocrystals supported on titanium dioxide during the CO oxidation reaction at atmospheric pressure. Because of its use in pollution control, by removing toxic CO from the exhaust of motor vehicles, this catalytic reaction is of high environmental and societal importance but also considered as a prototypical reaction for heterogeneous catalysis (22). We built a dedicated *in situ* heating reactor for *in situ* Bragg CDI. Applying iterative phase retrieval for coherent diffraction imaging (21), we reconstructed the 3D Bragg electron density and lattice displacement field of the gold nanocrystals with a spatial resolution down to 12 nm. We describe the adsorbate-induced surface transformation, quantify the surface stress and further show that nanotwins formation play a crucial role in the nanocrystal deformation mechanisms and correlates with the catalytic behaviour of the gold catalyst.

In this work we also synthesised ultra-small gold nanoparticles, which are interesting from the catalysis point of view (23). Very small Au NP present excellent catalytic performance for the CO oxidation reaction: the conversion rate of CO for Au NP in the 2-4 nm size range is increased by two orders of magnitude if compared with larger Au NP, demonstrating that the size of the nanoparticle is extremely relevant to the reaction rate (23). The approach we followed to prepare the ultra-small Au NP was based on the use of ionic liquids (IL) as stabilizers. This emergent class of material has grown and has attracted much attention due to their unique physical properties such as nonvolatility, high stability, low toxicity and biodegradability (24–26). Therefore, IL have been widely used in the area of organic synthesis, catalysis, electrochemistry, polymer electrolyte, surface active agents, nanoparticles green synthesis in water stable, chemical reactions mostly used in industry (27) and so forth.

Another part of this work regards the study of pristine gold nanorods. Comprehensive knowledge of the structure and morphology of thin gold nanorods is

crucial for its reliable employment in a wide range of applications such as in the nanoelectronics devices area and in biology field. In this thesis, by using scanning electron microscopy (SEM) and then scanning X-ray nanodiffraction to characterise few tenths of nanometers single gold nanorods, we were able to obtain a projection of the strain distribution over the Bragg well oriented gold crystals. This characterisation revealed the presence of a strain pattern encoded in the nanorods structure consistent with the so-called Rayleigh Instability compatible with a mechanism that leads to further rod segmentation into spheres. Our approach shows that the instability is intrinsically present in the rods on the atomic-scale and provides insights on the structural stability in very thin gold nanorods which brings up novel opportunities for nano-devices engineering.

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CONCLUSIONS AND FUTURE WORK

Regarding the main part of this thesis, the characterisation of single gold nanoparticles under working conditions was done using Bragg CDI. We succeeded in following the changes in the internal and surface structure of the nanocrystals during the reaction occurrence by mapping the phase/strain of the reconstructed nanoparticles in the different measured conditions.

We developed an *in situ* cell (Chapter IV) to perform Bragg CDI under controlled gas/temperature environments, which is crucial for *in situ/operando* measurements.

The changes in the surface morphology of the gold nanocrystal discussed in Chapter V indicates that even at RT the adsorption gases strongly interact with the surface atoms. This interaction is evidenced by the compressive to tensile strain swap from air to CO/O₂ atmospheres at RT. The adsorption leads to a compressive surface stress, resulting in the smoothing curves seen for the reconstructed nanoparticles. During the reaction, there is the reconstitution of the sharper edges of the nanoparticles, which are regions of low-coordinated atoms and represent the catalytic sites for the reaction. As the temperature increases and the NP becomes active, there is the formation of ribbons seen as phase oscillation inside the particle and it was attributed to the formation of a nanotwin network, which was correlated with the increased catalytic activity of the gold nanocrystal.

The capability of Bragg CDI to observe changes in morphology/crystalline lattice under dynamic conditions is very powerful and fills up the gap for 3D characterisation under *in situ/operando* conditions to get atomic scale information.

The reconstructions shown in Chapter VI is a twinned Au NP, a very common type of defect in crystalline structures. As the presence of twin domains does influence the crystal properties, the investigation of twin domains is of paramount importance. The slight changes in the twin domain size between the parent crystal regions can influence the catalytic properties as the number of active sites may change in this case. As future work for this part of the thesis, the calculation of the stress, as was done for the particle in the previous chapter, would help to get insights about the link between the structure and the catalytic properties of this particle.

Another important additional work to do would be to study the crystalline structure of the seed particles to verify if they are single crystals or twinned particles.

Twinned nanoparticles can grow from either twinned or single-crystalline seeds. If single-crystalline, a nanoparticle seed can generate twin defects during the growth of the larger particle (or through a coalescence mechanism). Alternatively, if the nanoparticle seed has a twinned structure, it can grow layer-by-layer in the twinned sequence. Understanding the nanoparticle structure formation is important for controlling the reaction conditions so we can selectively enhance or suppress the single-crystalline/twinned nanoparticle growth, depending on the material's desired properties. We have evidences that the seed precursor is formed by twinned nanoparticles, but a deeper investigation is needed to draw a conclusion. If we consider that the seeds are in fact twinned, most probably the defected structure of the seed is somehow transferred to the entire larger particle, as already reported in few works. This could happen through epitaxial growth. In the case that the seed dispersion is composed by single crystals, it would be interesting to investigate when exactly the twin domains are formed in the crystalline structure: does it form during the wet synthesis procedure or during the calcination process? As it does affect the catalytic properties, this investigation is interesting for the future.

An important study regarding this topic would be to control the degree of twin domains in gold nanoparticles, having twin free crystals in one case and twinned nanoparticles in another case and investigate the structural differences between both and try to correlate this with the catalytic properties of the nanoparticles. Then, we can answer the question: is there any difference between the catalytic performance of defect free and twinned Au NP?

Although the resolution of the CDI techniques does not yet reach the atomic scale as in electron microscopy, this will be dramatically improved with the operation of 4th generation synchrotron sources like SIRIUS (under construction in Campinas, Brazil, where the Cateretê beamline will be dedicated to perform CDI and is planned to operate in 2019). When Cateretê beamline will be in operation, coherent X-ray diffraction imaging techniques will achieve the spatial and time resolution required to study real devices and the techniques could be applied during *in situ/operando* measurements: thermal treatment; use of dedicated cell under different atmospheres; study of charge/discharge in batteries systems; among many other possibilities. This will undoubtedly expand new horizons for the scientific community once in SIRIUS the coherent flux of photons will be 2 to 3 orders of magnitude higher than the available

ones, which means that time resolution in the second range will be possible with an improved spatial resolution.