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Development of photochemical and electrochemical cells for *operando* X-ray absorption spectroscopy during photocatalytic and electrocatalytic reactions†

Rachit Khare, ^a Andreas Jentys*^a and Johannes A. Lercher^{ab}

Photochemical and electrochemical reactions are highly relevant processes for (i) transforming chemicals (e.g. photoreduction of isopropanol to acetone, electrochemical hydrogenation of benzaldehyde to benzyl alcohol, etc.), and (ii) sustainable energy production (e.g. photoreduction of CO₂ to methanol, electrocatalytic H₂ evolution reaction). It is therefore of importance to monitor the structural changes and to understand the properties of active sites under photocatalytic and electrocatalytic reaction conditions. *Operando* X-ray absorption spectroscopy (XAS) provides the means to investigate the nature of active sites under realistic reaction conditions. In this contribution, we describe the successful development of photochemical and electrochemical cells for *operando* XAS measurements during photocatalytic and electrocatalytic reactions. We have used the *operando* photochemical cell to monitor the formation of Pt nanoparticles on graphitic carbon nitride nanosheets (g-C₃N₄-ns) via photodeposition under visible light illumination and observed the formation of highly dispersed Pt nanoparticles with an estimated size of ~2.5 nm and >60% dispersion. We have also tested this cell to follow the oxidation state of Pt in Pt/TiO₂ and Pt/g-C₃N₄-ns during H₂ evolution reaction (HER). We observed that Pt predominantly existed as metallic (reduced) Pt⁰ species under HER conditions, and that PtO_x species were partially reduced from Pt^{IV} to Pt⁰ upon illumination with UV or visible light. The rates of H₂ evolution obtained in the photochemical cell (12.1 mmol g⁻¹ h⁻¹ on Pt/TiO₂ and 1.01 mmol g⁻¹ h⁻¹ on Pt/g-C₃N₄-ns) were comparable to that obtained in a standard top-irradiated photoreactor (16.6 mmol g⁻¹ h⁻¹ on Pt/TiO₂ and 1.76 mmol g⁻¹ h⁻¹ on Pt/g-C₃N₄-ns). The *operando* electrochemical cell was successfully tested to monitor the changes in the structure and oxidation state of Pd in Pd/C electrocatalyst during electrocatalytic hydrogenation (ECH) of benzaldehyde. It was demonstrated that Pd in Pd/C was present in a partially reduced state (~80% Pd⁰ and ~20% Pd^{II}) and Pd nanoparticles did not degrade upon the application of an external potential under ECH reaction conditions.

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1 Introduction

The development of cells for *operando* X-ray absorption spectroscopy (XAS) experiments is essential to follow the chemical state and the structural properties of catalytically active materials under realistic reaction conditions. A large number of designs have been developed and successfully applied for gas-phase and liquid-phase reactions,^{1–12} photochemical reactions,^{13–21} or electrochemical reactions.^{22–41} However, only a few designs

capable of performing *operando* XAS measurements for heterogeneous photochemical or electrochemical reactions have been discussed or described in detail. The main challenges associated with such cells is that the photocatalytic and electrocatalytic reactions are typically carried out in liquid phase at the solid–liquid interface and that the catalyst has to be exposed to UV/visible irradiation (in photocatalysis) or to an external potential (in electrocatalysis). The presence of the liquid phase on its own represents a challenge due to the high absorbing background, but the additional constraints due to the external excitation with UV/visible light or electrons leads to further constraints in the cell design.

Our design principle is based on a modular design, where the catalyst is deposited on an X-ray transparent glassy carbon window which can either be illuminated with a UV/visible LED lamp (for photocatalysis applications) or is directly used as a

^a Department of Chemistry and Catalysis Research Center, Technical University of Munich, Garching, Germany. E-mail: jentys@tum.de

^b Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, USA

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conducting electrode (for electrocatalysis applications). To supply the cell with reactants and to remove the products for online analyses, a gas-dosing and gas/liquid-recirculation setup was developed, which is highly modular and can be used either in the laboratory or directly at the beamline for *operando* XAS measurements. To demonstrate the potential of the photochemical cell, we studied photodeposition of Pt nanoparticles on graphitic carbon nitride nanosheets (Pt/g-C₃N₄-ns) under visible light irradiation, and monitored the changes in the oxidation state of Pt in Pt/TiO₂ or Pt/g-C₃N₄-ns under H₂ evolution reaction (HER) conditions. The *operando* electrochemical setup was tested for electrochemical hydrogenation (ECH) of aqueous benzaldehyde solution over Pd/C electrocatalyst. Our experiments successfully demonstrated that these *operando* cells can be reliably used to (i) determine the oxidation state of active species, and (ii) monitor structural changes in the active species, under photocatalytic or electrocatalytic reaction conditions.

2 Experimental section

2.1 Materials

Following materials and chemicals were obtained from commercial suppliers and were used as-received without further modifications: TiO₂ (Sigma-Aldrich, Degussa Aeroxide[®] P25, typically composed of ~75% anatase and ~25% rutile phases),^{42,43} dicyandiamide (Sigma-Aldrich, 99%), H₂PtCl₆ aqueous solution (Sigma-Aldrich, 8 wt% in H₂O), methanol (Sigma-Aldrich, 99.8% anhydrous), Pd/C (Sigma-Aldrich, 5 wt% Pd-loading, activated carbon support), Pt/C (Sigma-Aldrich, 5 wt% Pt-loading, activated carbon support), acetic acid/sodium acetate buffer solution (Sigma-Aldrich, pH ~4.6). The Nafion[®] proton exchange membrane (Sigma-Aldrich) was treated in H₂O₂ solution (3 vol%) and sulfuric acid (2 M) before use. The following materials were used as references in XAS measurements: Pt⁰-foil (Exafs Materials), Pd⁰-foil (Exafs Materials), Pt^{IV}O₂·H₂O (Sigma-Aldrich, 99.9% trace metal basis), and Pd^{II}O (Sigma-Aldrich, 99.97% trace metal basis).

2.2 Catalyst preparation

2.2.1 Synthesis of bulk graphitic carbon nitride. Graphitic carbon nitride (g-C₃N₄) bulk material was synthesized *via* thermal polymerization of dicyandiamide.⁴⁴ Typically, ~10 g dicyandiamide was placed in an alumina crucible (Sigma-Aldrich, CoorsTM) covered with a lid. The crucible was placed in a muffle furnace and heated to 823 K at a rate of 10 K min⁻¹. The temperature was held at 823 K for 4 h before naturally cooling down to room temperature. The obtained powder was yellow in color. It was washed with 0.1 M HCl, followed by 0.1 M NaOH, and then several times with deionized water. The powder was dried overnight in an oven at 353 K and crushed to a fine powder.

2.2.2 Synthesis of graphitic carbon nitride nanosheets. g-C₃N₄ nanosheets (g-C₃N₄-ns) were synthesized *via* thermal exfoliation of g-C₃N₄ bulk material.⁴⁵ In a typical synthesis,

~2 g bulk g-C₃N₄ was placed in an open alumina crucible without a lid. The crucible was then placed in a muffle furnace and heated to 773 K at a rate of 10 K min⁻¹. The temperature was held at 773 K for 3 h before naturally cooling down to room temperature. The obtained powder was light yellow in color and is denoted as g-C₃N₄-ns.

2.2.3 Synthesis of Pt-loaded photocatalysts. Pt was deposited on g-C₃N₄-ns or TiO₂ *via* photodeposition using a conventional top-irradiated photoreactor (see Fig. S1 in the ESI[†]). Typically, 100 mg g-C₃N₄-ns or TiO₂ was suspended in 45 mL deionized water. The suspension was ultrasonicated for 30 min to disperse the photocatalyst before being placed in the photoreactor. Appropriate amounts of H₂PtCl₆ (corresponding to 0.5 wt% Pt-loading) and methanol (corresponding to 10 vol%) were added. The catalyst suspension was stirred continuously. The photoreactor was sealed and flushed several times with Ar to remove any residual gases. The system was finally pressurized to 1 bar with Ar and reactor temperature was maintained at 298 K using cooling water supply. The gas-phase was analyzed using an online Shimadzu 2010 Plus gas chromatograph (GC) equipped with a Restek ShinCarbon packed column, a thermal conductivity detector (TCD), a flame ionization detector (FID), and a Ni-based methanizer unit. Illumination was provided with a 405 nm 4.4 W visible light LED lamp (for photodeposition on g-C₃N₄-ns) or with a 365 nm 5 W UV light LED lamp (for photodeposition on TiO₂). The photodeposition was typically carried out for 120 min or until the observed H₂ evolution rate was constant.

2.3 Catalyst characterization

The synthesized materials were characterized using elemental analyses, N₂ adsorption-desorption measurements, powder X-ray diffraction (XRD), and UV-visible diffuse reflectance spectroscopy (UV-vis DRS). The applied characterization techniques are described in detail in the ESI[†].

2.4 Photocatalytic activity measurements

The photocatalytic activity of Pt/g-C₃N₄-ns and Pt/TiO₂ were determined for HER in a conventional top-irradiated photoreactor (see Fig. S1 in the ESI[†]). In a typical experiment, ~50 mg photocatalyst was dispersed in 45 mL deionized water and ultrasonicated for 30 min. The catalyst suspension was placed in the photoreactor and 5 mL methanol was added. The entire setup was flushed several times with Ar to remove any residual gases. All reactions were carried out at 298 K and under 1 bar Ar pressure. Illumination was provided either by a visible light (405 nm 4.4 W) or a UV light (365 nm 5 W) LED lamp. Gas-phase was continuously analyzed using an online GC. Data points were collected at 20 min intervals for up to 120 min.

2.5 X-ray absorption spectroscopy measurements

X-ray absorption spectra were collected at the P65 beamline of the German electron synchrotron (DESY) in Hamburg, Germany. The PETRA III storage ring was operated at 6 GeV energy and 100 mA beam current in top-up mode. A water-cooled Si111 (for Pt L_{III}-edge) or Si311 (for Pd K-edge) double crystal monochromator (DCM) was used for obtaining

Fig. 1 Exploded view of the photochemical cell for XAS measurements during photocatalytic reactions or photodeposition studies. (A) PTFE back-cover, (B) PTFE front-cover, (C) 500 μm thick glassy carbon window (HTW Germany) coated with the catalyst, (D) UV or visible light LED lamp (Prizmatix) equipped with an optical guide, and (E) collimator lens (Prizmatix), (F and G) PTFE liquid inlet and outlet, (H) PEEK flangeless fittings (IDEX Optofluidic Systems), (I) stainless steel nuts, bolts, and washers, (J) UV/vis transparent quartz window (Edmund Optics), (1–3) rubber sealing gaskets, (4–6) flow path created using 2 mm thick PTFE sheets (Garlock).

monochromatic X-rays. Two Rh-coated plane mirrors were installed in front of the DCM to reject higher harmonics.⁴⁶ The DCM was calibrated for Pt L_{III} -edge measurements by measuring a Pt-foil and defining the first inflection point as 11 564 eV. Similarly, the DCM was calibrated for Pd K-edge measurements by measuring a Pd-foil and setting the first inflection point to 24 350 eV. The corresponding metal foils were placed between the second and third ionization chamber for the energy calibration of each measured spectrum.

The energy resolution of the beamline is estimated to be ~ 1.6 eV at the Pt L_{III} -edge and ~ 1.5 eV at the Pd K-edge. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were performed using Athena and Artemis software packages.⁴⁷

2.6 Operando photochemical experiments

XAS measurements during photochemical reactions were performed at Pt L_{III} -edge (11 564 eV) in fluorescence mode using a

passivated implanted planar silicon (PIPS) detector. The spot-size of X-ray beam at the sample was 1.4 mm (horizontal) $\times$ 600 μ m (vertical). XANES were measured between -100 eV and $+400$ eV around the Pt L_{III} -edge in continuous scanning mode. The spectra for EXAFS were measured between -150 eV and $+1000$ eV around the Pt L_{III} -edge in step scanning mode. For XANES analyses, E_0 was fixed at 11 564 eV and the spectra were normalized and flattened. For EXAFS analyses, spectra were background subtracted, normalized, k^3 -weighted, and Fourier-transformed in the k range of 3–15 $\text{\AA}^{-1}$. The EXAFS data was fitted to Pt fcc structure in R -space between 1.5–3.5 $\text{\AA}$ (corresponding to the first coordination shell).

2.6.1 The photochemical setup. A schematic of the photochemical cell used for *operando* XAS measurements is shown in Fig. 1. The cell comprises of a back-cover and a front-cover constructed out of PTFE. The back-cover features two ports for liquid inlet and outlet, and a UV/vis transparent quartz window for allowing illumination with UV or visible light. The front-cover features an X-ray transparent glassy carbon window coated with the photocatalyst for XAS measurements in fluorescence mode. Typically, 5 mg catalyst was dispersed in 200 μ L isopropanol and ultrasonicated for 30 min to create an ink. The ink was coated onto the glassy carbon window and the substrate was dried at 353 K for 2 h. The cell features a flow path constructed out of 2 mm thick PTFE sheets for liquid flow across the catalyst surface. The cell was sealed using rubber gaskets and stainless-steel nuts and bolts.

The *operando* XAS measurements were performed in the photochemical cell using a gas-dosing and gas/liquid-recirculation setup as illustrated in Fig. 2. The setup consists of a liquid reservoir placed inside an aluminum cooling jacket. A recirculating chiller unit was used to continuously circulate cooling water (CW) and maintain the desired reaction temperature.

The reservoir was covered with a lid featuring several inlet and outlet ports. Gas flow rates were controlled using mass flow controllers, and a pressure meter was used to monitor the pressure. The gases were recirculated using a double diaphragm gas pump. The liquid was recirculated between the liquid reservoir and the photochemical cell using a liquid gear pump.

2.6.2 Photocatalytic reactions. For photocatalytic reactions, Pt/g-C₃N₄-ns or Pt/TiO₂ were coated onto the glassy carbon window. Typically, 50 mL methanol aqueous solution (10 vol%) was added to the liquid reservoir. The system was flushed with Ar several times to remove any residual gases. The setup was pressurized with Ar to 1 bar. All reactions were carried out at 298 K in recirculation mode. XANES spectra were measured every 90 seconds in continuous scanning mode. Several measurements were taken before illumination. The LED light source was switched on remotely and several spectra were measured during illumination. The measurements were stopped when no spectral changes were observed upon further illumination. In separate experiments carried out in the laboratory, photocatalytic activity of Pt/g-C₃N₄-ns and Pt/TiO₂ for HER was determined using the *operando* photochemical setup. During these experiment, gas-phase was continuously analyzed using an online GC. Data points were collected at 20 min intervals for up to 120 min.

2.6.3 Photodeposition studies. For photodeposition, g-C₃N₄-ns was coated on the glassy carbon window. H₂PtCl₆ aqueous solution was used as a metal precursor. The cell was assembled using the same procedure as described in Section 2.6.2. XANES spectra were continuously measured before and during illumination. Measurements were stopped when no significant changes were observed in the spectra upon further illumination. The cell was then drained of the residual

Fig. 2 Gas-dosing and gas/liquid-recirculation setup for *operando* XAS measurements during photocatalytic reactions and photodeposition studies. (A) PTFE liquid reservoir, (B) aluminum cooling jacket connected to a recirculating chiller unit (Julabo), (C) PTFE lid with several inlet and outlet ports, (D) mass flow controllers (Bronkhorst), (E) pressure meter (Bronkhorst), (F) double diaphragm gas pump (KNF Neuberger), (G) switching valve (VICI Valco), (H) online GC (Shimadzu 2010 Plus), (I) magnetic stirrer (ThermoFischer), (J) K-type thermocouples (Omega), (K) UV or visible light LED source equipped with an optical guide and a collimator lens (Prizmatix), (L) 500 μ m thick glassy carbon window (HTW Germany) coated with the catalyst, (M) liquid sampling port, (N) liquid gear pump (Ismatec), and (O) quartz window (Edmund Optics).

Fig. 3 Exploded view of the electrochemical cell for *operando* XAS measurements during electrocatalytic reactions. (A) PTFE counter electrode cover, (B) PTFE working electrode cover, (C) titanium electrical connectors, (D) PEEK flangeless fittings (IDEX Optofluidic Systems), (E–H) PTFE electrolyte inlets and outlets, (I) stainless-steel nuts, bolts, and washers, (J) flangeless fitting (IDEX Optofluidic Systems), for (K) Ag/AgCl leakless reference electrode (eDAQ), (L and M) 500 μm thick glassy carbon windows (HTW Germany) coated with electrocatalyst, (N) Nafion[®] perfluorinated proton-exchange membrane (Sigma-Aldrich), (2–7) flow path constructed out of 2 mm thick PTFE sheets (Garlock), and (1 and 8) rubber sealing gaskets.

solution, and EXAFS measurements were performed on dry Pt/g-C₃N₄-ns catalyst.

2.7 *Operando* electrochemical experiments

XAS measurements during electrochemical reactions were performed at the Pd K-edge (24 350 eV) in fluorescence mode using a 7-element high purity germanium (HPGe) detector. The spot size of the X-ray beam at the sample was 1.4 mm (horizontal) $\times$ 200 μm (vertical). All spectra were measured between -100 eV and $+400$ eV around the Pd K-edge in step scanning mode. For XANES analyses, E_0 was fixed at 24 350 eV and spectra were

normalized and flattened. For EXAFS analyses, spectra were background subtracted, normalized, k^3 -weighted, and Fourier-transformed in the k range of 3–10 $\text{\AA}^{-1}$. The data was fitted to Pd fcc structure in R -space between 1.5–3.0 $\text{\AA}$ (corresponding to the first coordination shell).

2.7.1 The electrochemical setup. With a few modifications, the photochemical cell together with a modified gas-dosing and gas/liquid-recirculation setup was used for *operando* XAS measurements during electrochemical experiments. Fig. 3 shows a schematic of the *operando* electrochemical cell. The cell comprises of a working-electrode and a counter-electrode

chamber separated by an ion-exchange membrane. The working-electrode cover contains two ports for inlet and outlet of the electrolyte and one port for inserting a reference electrode. The counter-electrode cover also contains two ports for the inlet and outlet of the electrolyte. The cell features an X-ray transparent glassy carbon window coated with an electrocatalyst (acting as the working electrode) and a similar counter electrode. The glassy carbon electrodes were connected to a voltage supply unit using titanium electrical connectors. The cell also features a flow path in the working- and counter-electrode chambers constructed out of 2 mm thick PTFE sheets. The cell was sealed using rubber gaskets and stainless-steel nuts and bolts.

A schematic of the modified gas-dosing and gas/liquid-recirculation setup for electrochemical experiments is shown in Fig. 4. The setup features two electrolyte reservoirs for the working electrode and the counter electrode chambers, respectively. The reservoirs are constructed out of PTFE and feature several ports for gas and liquid inlet and outlet. The reservoirs are enclosed inside aluminum cooling jackets connected to a recirculating chiller unit. The electrolyte was recirculated between the liquid reservoirs and the electrochemical cell using liquid gear pumps. Gases were supplied to the reservoirs using mass flow controllers. A switching valve was used to switch between recirculation mode and flow-through mode. Temperature of the liquid and gas phase was monitored using K-type thermocouples. The pressure was continuously monitored using pressure meters. The electrolyte reservoirs also feature ports for sampling the liquid during the reaction for further analyses.

2.7.2 Electrochemical hydrogenation of benzaldehyde. For electrochemical reactions, a glassy carbon window coated with Pd/C was used as the working electrode (cathode) and a Pt/C coated glassy carbon window was used as the counter electrode (anode). Acetic acid/sodium acetate buffer solutions (~ 50 mL) were used as catholyte and anolyte solutions and were placed in the respective liquid reservoirs. The system was flushed with Ar several times to remove any residual gases. All reactions were carried out at 298 K in flow-through mode. Prior to the reaction, cathode was polarized under constant current of -40 mA for 30 min. Benzaldehyde was added to the catholyte before the reaction to obtain a final concentration of 20 mmol L^{-1} . The uncompensated resistance (iR drop) was determined by potentiostatic electrochemical impedance spectroscopy (PEIS). The applied potentials were corrected using the value obtained therein. Electrochemical hydrogenation (ECH) of benzaldehyde was carried out at a constant applied potential of up to -600 mV (vs. Ag/AgCl reference electrode). XANES and EXAFS measurements were performed under open circuit voltage (OCV) conditions and under ECH reaction conditions.

3 Results and discussion

3.1 Catalyst characterization

The results of elemental analyses, N_2 adsorption-desorption measurements, powder XRD, and UV-vis DRS measurements, are presented in detail in the ESI.†

Fig. 4 Gas-dosing and gas/liquid-recirculation setup for *operando* XAS measurements during electrocatalytic reactions. (A) PTFE electrolyte reservoirs, (B) aluminum cooling jackets connected to a recirculating chiller unit (Julabo), (C) PTFE lid with several inlet and outlet ports, (D) mass flow controllers (Bronkhorst), (E) pressure meters (Bronkhorst), (F) double diaphragm gas pump (KNF Neuberger), (G) switching valve (VICI Valco), (H) online GC (Shimadzu 2010 Plus), (I) magnetic stirrer (ThermoFischer), (J) K-type thermocouples (Omega), (K) 500 μ m thick glassy carbon windows (HTW Germany) coated with electrocatalyst, (L) liquid gear pumps (Ismatec), (M) liquid sampling ports, (N) voltage supply unit (BioLogic VSP-300), and (O) Nafion[®] perfluorinated proton-exchange membrane (Sigma-Aldrich).

Fig. 5 H_2 evolved (in mmol g^{-1}), as a function of time, during HER, on (a) Pt/TiO₂, (b) Pt/TiO₂ (in the *operando* photochemical cell), (c) Pt/g-C₃N₄-ns, and (d) Pt/g-C₃N₄-ns (in the *operando* photochemical cell). The initial rates of H_2 evolution (in $\text{mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$) are also reported.

3.2 Photocatalytic activity

The photocatalytic activity of Pt/g-C₃N₄-ns and Pt/TiO₂ was determined for HER in a conventional photoreactor as well as in the *operando* photochemical setup. Fig. 5(a) and (c) show the photocatalytic activity of TiO₂ and g-C₃N₄-ns, respectively, in the conventional photoreactor. The measured rates of H_2 evolution were $16.6 \text{ mmol g}^{-1} \text{h}^{-1}$ on Pt/TiO₂ under UV light illumination and $1.76 \text{ mmol g}^{-1} \text{h}^{-1}$ on Pt/g-C₃N₄-ns under visible light illumination. Fig. 5(b) and (d) show the H_2 evolution activity in the *operando* photochemical cell. The rate of H_2 evolution was $12.1 \text{ mmol g}^{-1} \text{h}^{-1}$ on Pt/TiO₂ and $1.01 \text{ mmol g}^{-1} \text{h}^{-1}$ on Pt/g-C₃N₄-ns. The H_2 evolution rates obtained in the *operando* cell were slightly lower than those obtained in the conventional photoreactor. A possible reason for this is that in the photochemical cell, only the exposed surface of the catalyst is activated and there may be part of catalyst not illuminated by UV/visible light. In the conventional top-irradiated photoreactor, on the other hand, the catalyst is suspended in the solution and is continuously stirred during the reaction. This results in a more uniform illumination of the photocatalyst. The rates obtained in the *operando* photochemical cell are however comparable to those obtained in the conventional photoreactor.

3.3 Operando XAS measurements

3.3.1 Photodeposition of Pt nanoparticles. The XANES and EXAFS at Pt L_{III}-edge (11564 eV) were measured during the photodeposition of Pt nanoparticles on g-C₃N₄-ns using the *operando* photochemical cell. The XANES of Pt before illumination, during illumination, and after illumination, are shown in Fig. 6(a). The XANES of Pt before illumination was similar to that of Pt^{IV} in H₂PtCl₆ aqueous solution. Upon illumination with visible light, the XANES measurements suggest reduction of Pt from Pt^{IV} to Pt⁰, indicating the formation of Pt nanoparticles on the surface of g-C₃N₄-ns. Illumination was continued for 20 min, after which, no significant changes in XANES were observed for five consecutive measurements. A linear combination fitting (LCF) was performed between -30 eV and +50 eV around the Pt L_{III}-edge, using Pt⁰ and Pt^{IV} references as standards, and the results are shown in Fig. 6(b).

Fig. 6 (a) XANES of Pt nanoparticles at Pt L_{III}-edge (11564 eV) during photodeposition of Pt on g-C₃N₄-ns using H₂PtCl₆ aqueous solution as a metal precursor. (b) Fraction of Pt^{IV} and Pt⁰ before illumination, during illumination, and in the dry sample, obtained from linear combination fitting.

Before illumination, Pt was present as $\sim 90\%$ Pt^{IV} and $\sim 10\%$ Pt⁰, suggesting partial reduction of Pt^{IV} to Pt⁰ even before illumination was started. This observation can be attributed to the low band gap of g-C₃N₄-ns ($E_g \sim 2.7 \text{ eV}$). It is possible that g-C₃N₄-ns was activated under natural light, thereby

Fig. 7 k^3 -Weighted EXAFS and Fourier-transformed EXAFS of: (a and b) Pt-foil, and (c and d) Pt/g- C_3N_4 -ns (dry sample). Experimental data is shown as open symbols while the fitted curves are shown as solid lines.

Table 1 EXAFS fitting parameters: Pt–Pt coordination number (CN_{Pt-Pt}), Pt–Pt interatomic distance (d_{Pt-Pt}), ΔE_0 , and σ^2 , for (i) Pt-foil, and (ii) Pt nanoparticles deposited on g- C_3N_4 -ns via photodeposition (Pt/g- C_3N_4 -ns). The correlation between parameters (greater than 0.4) are also reported. E_0 was set to 11572 eV

	CN_{Pt-Pt}	$d_{Pt-Pt}/\text{\AA}$	$\Delta E_0/\text{eV}$	$\sigma^2 \times 1000/\text{\AA}^2$
Pt-foil	12.0 ± 0.5	2.764 ± 0.002	0.1 ± 0.4	4.67 ± 0.16
Pt/g- C_3N_4 -ns (dry)	9.4 ± 1.0	2.745 ± 0.005	-0.8 ± 1.0	5.69 ± 0.53

Correlation between parameters: σ^2 and $CN_{Pt-Pt} = 0.81$ – 0.83 , Δd_{Pt-Pt} and $\Delta E_0 = 0.75$ – 0.76 .

reducing Pt^{IV} and resulting in the formation of Pt nanoparticles under *ex situ* conditions prior to illumination. After illumination, Pt^{IV} content continuously reduced and reached 36% when the measurements were stopped. The high Pt^{IV} content is likely due to remaining H_2PtCl_6 aqueous solution in the cell. The cell

was therefore drained of the remaining aqueous H_2PtCl_6 solution and XANES was measured once more (referred to as the dry sample). Upon decantation, Pt^{IV} content further reduced to $\sim 13\%$ with $\sim 87\%$ Pt^0 . The remaining Pt^{IV} can be attributed to H_2PtCl_6 solution retained/absorbed on the g- C_3N_4 nanosheets. It can however be concluded that Pt nanoparticles were formed on the surface of g- C_3N_4 -ns upon illumination with visible light.

Fig. 7 shows the k^3 -weighted EXAFS and Fourier-transformed EXAFS of Pt-foil and Pt nanoparticles formed on g- C_3N_4 -ns as a result of photodeposition. The corresponding EXAFS fitting parameters are reported in Table 1. The Pt-foil was first fitted to Pt fcc structure. The Pt–Pt coordination number (CN_{Pt-Pt}) in the Pt-foil was set to 12 (theoretical value based on the fcc structure) to obtain the amplitude reduction factor $S_0^2 = 0.79$, which was subsequently used to fit Pt–Pt coordination shell in the Pt nanoparticles deposited on g- C_3N_4 -ns via photodeposition. The E_0 for Pt-foil measurement was set to 11572 eV in order to obtain $\Delta E_0 < 1$ eV and the same value of E_0 was used in the fitting of Pt nanoparticles. The Pt–Pt interatomic distance (d_{Pt-Pt}) in Pt-foil fitted to 2.764 ± 0.002 Å, which is slightly lower than the theoretical value of 2.772 Å. The CN_{Pt-Pt} in Pt nanoparticles was found to be 9.4 ± 1.0 with d_{Pt-Pt} equal to 2.745 ± 0.005 Å. A CN_{Pt-Pt} of 9.4 corresponds to a spherical particle size of ~ 2.5 nm and a dispersion $> 60\%$.^{48,49} These results show that photodeposition resulted in the formation of highly dispersed nanoparticles on the surface of g- C_3N_4 -ns.

3.3.2 Photocatalytic H_2 evolution reaction. XANES measurements were performed on Pt/TiO₂ and Pt/g- C_3N_4 -ns under photocatalytic HER conditions using the *operando* photochemical cell. Fig. 8(a) and (b) show the XANES of Pt in Pt/TiO₂ and Pt/g- C_3N_4 -ns, respectively, under HER conditions. The Pt nanoparticles in Pt/TiO₂ and Pt/g- C_3N_4 -ns remained in metallic (reduced) Pt^0 state during the reaction and there was no change observed in XANES upon illumination with UV or visible light. These results suggest that the active Pt-species during

Fig. 8 XANES at Pt L_{III} -edge (11564 eV) of (a) Pt/TiO₂, (b) Pt/g- C_3N_4 -ns, and (c) PtO_x/TiO₂, before and after illumination under HER conditions.

photocatalytic HER conditions is Pt^0 . To further confirm the oxidation state of active Pt-species during HER, XANES measurements were also performed on $\text{PtO}_x/\text{TiO}_2$ photocatalyst. $\text{PtO}_x/\text{TiO}_2$ was synthesized by treating Pt/TiO_2 in synthetic air (20% O_2 in N_2) at 573 K for 8 h. The temperature was increased from room temperature to 573 K at 1 K min^{-1} and held at 573 K for 8 h before cooling down naturally to room temperature. Fig. 8(c) shows the XANES of Pt in $\text{PtO}_x/\text{TiO}_2$ under HER conditions. It was observed that Pt reduced from Pt^{IV} to Pt^0 upon illumination with UV light. Linear combination fitting using Pt^0 and Pt^{IV} reference spectra as standards showed that Pt^{IV} content decreased from $\sim 96\%$ before illumination to $\sim 33\%$ after illumination, while Pt^0 content increased from $\sim 4\%$ to $\sim 67\%$. This suggests that Pt did not completely reduce from Pt^{IV} to Pt^0 upon illumination. It is possible that only the surface Pt atoms were reduced and the non-surface atoms within the Pt nanoparticles remained in the Pt^{IV} oxidation state as PtO_x . These results, however, confirm that the active Pt-species during photocatalytic HER is indeed metallic Pt^0 . The obtained results show that the *operando* photochemical cell can be used to (i) study photodeposition of nanoparticles, and (ii) determine the oxidation state of active species under photocatalytic reaction conditions.

3.3.3 Electrochemical hydrogenation of benzaldehyde. The *operando* electrochemical setup was used to investigate the oxidation state of Pd in Pd/C during ECH of 20 mM benzaldehyde aqueous solution. XANES measurements at Pd K-edge (24 350 eV) were performed on Pd/C electrocatalyst under OCV and ECH reaction conditions (-100 mV or -600 mV vs. Ag/AgCl reference electrode) and the results are reported in Fig. 9. It can be observed that Pd predominantly existed as metallic (reduced) Pd^0 species under OCV as well as ECH reaction conditions. Linear combination

Fig. 9 XANES measurements at Pd K-edge (24 350 eV) of Pd nanoparticles in Pd/C at (i) OCV, (ii) -100 mV (vs. Ag/AgCl reference electrode), and (iii) -600 mV (vs. Ag/AgCl reference electrode), during ECH of benzaldehyde.

fitting was performed on the experimental spectra between -30 eV and $+50 \text{ eV}$ around the Pd K-edge (24 350 eV) using Pd^0 and Pd^{IV} reference spectra as the two standards. The Pd in Pd/C was observed to be mixture of $\sim 80 \pm 10\%$ Pd^0 and $\sim 20 \pm 15\%$ Pd^{IV} . There was no significant difference in the observed $\text{Pd}^0/\text{Pd}^{\text{IV}}$ composition in Pd/C under OCV or ECH reaction conditions.

Fig. 10 shows the k^3 -weighted EXAFS and Fourier-transformed EXAFS of Pd-foil and Pd/C under OCV and ECH reaction conditions. The EXAFS fitting parameters are reported in Table 2. The Pd-foil was fitted to Pd fcc structure. The Pd-Pd coordination number ($\text{CN}_{\text{Pd-Pd}}$) in the Pd-foil was set to 12 (theoretical value based on fcc structure) to obtain the amplitude reduction factor (S_0^2) of 0.74. The same value of S_0^2 was used in the fits for Pd/C under OCV and ECH reaction conditions. The E_0 for Pd-foil measurement was set to 24 352 eV in order to obtain $\Delta E_0 < 1 \text{ eV}$ and the same value of E_0 was used in all subsequent fits. The Pd-Pd distance ($d_{\text{Pd-Pd}}$) in Pd-foil

Fig. 10 k^3 -Weighted EXAFS and Fourier-transformed EXAFS of: (a and b) Pd-foil, (c and d) Pd/C at OCV, (e and f) Pd/C at -100 mV (vs. Ag/AgCl reference electrode), and (g and h) Pd/C at -600 mV (vs. Ag/AgCl reference electrode), during ECH of benzaldehyde. Experimental data is shown as open symbols while the fitted curves are shown as solid lines.

Table 2 EXAFS fitting parameters: Pd–Pd coordination number (CN_{Pd-Pd}), Pd–Pd interatomic distance (d_{Pd-Pd}), ΔE_0 , and σ^2 , of (i) Pd-foil, (ii) Pd/C at OCV, (iii) Pd/C at –100 mV (vs. Ag/AgCl reference electrode), and (iv) Pd/C at –600 mV (vs. Ag/AgCl reference electrode), during ECH of benzaldehyde. The correlation between parameters (greater than 0.4) are also reported. E_0 was set to 24 352 eV

	CN_{Pd-Pd}	$d_{Pd-Pd}/\text{\AA}$	$\Delta E_0/\text{eV}$	$\sigma^2 \times 1000/\text{\AA}^2$
Pd-foil	12.0 ± 0.5	2.735 ± 0.002	0.4 ± 0.3	4.44 ± 0.36
Pd/C (OCV)	10.1 ± 26.0	2.756 ± 0.173	0.2 ± 17.7	8.64 ± 25.62
Pd/C (–100 mV)	10.4 ± 24.5	2.750 ± 0.157	0.2 ± 16.2	8.44 ± 23.28
Pd/C (–600 mV)	10.6 ± 21.9	2.763 ± 0.136	0.4 ± 14.2	8.41 ± 20.25

Correlation between parameters: σ^2 and $CN_{Pd-Pd} = 0.86\text{--}0.90$, Δd_{Pd-Pd} and $\Delta E_0 = 0.80\text{--}0.81$.

fitted to 2.735 ± 0.002 Å, which is lower than the theoretical value of 2.751 Å. The CN_{Pd-Pd} in Pd/C was determined to be ~ 10.1 at OCV and only increased slightly to ~ 10.4 at –100 mV (vs. Ag/AgCl reference electrode) and to ~ 10.6 under –600 mV (vs. Ag/AgCl reference electrode) external potential. These results suggest that the Pd nanoparticles were stable during ECH of benzaldehyde.

3.4 Further applications

The *operando* electrochemical cell and the gas-dosing and gas/liquid-recirculation setup, being modular in nature, can be further modified for *operando* XAS measurements for photo-electrochemical experiments. The modified photo-electrochemical setup is described in detail in the ESI.†

4 Conclusions

We have successfully developed and tested a photochemical cell and an electrochemical cell for *operando* XAS measurements during photocatalytic or electrocatalytic reactions. The *operando* photochemical setup was used to monitor the formation of Pt nanoparticles on graphitic carbon nitride, and the formation of highly dispersed Pt nanoparticles (~ 2.5 nm with $>60\%$ dispersion) was observed. We also utilized this cell to determine the oxidation state of Pt under HER conditions and showed that the active Pt-species in Pt/TiO₂ or Pt/g-C₃N₄-ns were predominantly metallic (reduced) Pt⁰, and that PtO_x partially reduced from Pt^{IV} to Pt⁰ under these reaction conditions. We also showed that the rates of H₂ evolution obtained in the *operando* photochemical cell ($12.1 \text{ mmol g}^{-1} \text{ h}^{-1}$ on Pt/TiO₂ and $1.01 \text{ mmol g}^{-1} \text{ h}^{-1}$ on Pt/g-C₃N₄-ns) were comparable to those obtained in a standard top-irradiated photoreactor ($16.6 \text{ mmol g}^{-1} \text{ h}^{-1}$ on Pt/TiO₂ and $1.76 \text{ mmol g}^{-1} \text{ h}^{-1}$ on Pt/g-C₃N₄-ns). The *operando* electrochemical cell was also successfully utilized to determine the oxidation state of Pd in Pd/C during electrochemical hydrogenation (ECH) of benzaldehyde. It was observed that Pd predominantly existed as metallic (reduced) Pd⁰ in the form of stable Pd nanoparticles, which did not degrade upon the application of negative potential (–100 mV or –600 mV vs. Ag/AgCl reference electrode) under ECH reaction conditions.

Conflicts of interest

The authors declare no conflicts of interest.

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