

Nanomaterials and Their Surface Chemistry: Manipulating Catalytic Efficiency through Quantum Dots

Dr. Warda Hassan (Corresponding Author)

Assistant Professor, Department of Chemistry, The Women University Multan, Pakistan. Email: warda.chem@wum.edu.pk

Sabahat Asghar

Khwaja Fareed University of Engineering and Information Technology, Rahim Yar Khan, Pakistan Email: sabahatasgharofficial@gmail.com

Nazakat Ali

MS Chemistry, University of Education, Lahore, Pakistan
Email: nazakatali32@gmail.com

ABSTRACT

The question of quantum dots (QDs) has turned out to be highly viable nanocatalysts in various processes such as electrocatalysis, photocatalysis, and environmental remediation since their surface chemistry can be altered and they can be confined to a small area. Their performance as catalysts is strongly influenced by surface structure, their interactions with the ligands, and defect states. Enhancement of surface functions can increase catalytic reactions by 63.2 percent relative to those that have not been modified. As an illustration, the electron transfer rate constant (k_3) is $3.4 \times 10^{-3} \text{ s}^{-1}$ but it changes to $9.1 \times 10^{-3} \text{ s}^{-1}$ upon the addition of nitrogen to carbon quantum dots (CQDs). This increases surface-mediated charge transport by 2.67. The mathematical model demonstrates that the addition of artificial surface states boosts the catalytic turnover frequency (TOF).

$$\text{TOF} \propto \frac{k_{\text{ads}} \cdot \theta_{\text{active}}}{K_d + [S]}$$

The rate of the adsorption is known as k_{ads} and θ_{active} is the proportion of active surface sites. $K_d [S]$ is a constant that informs you of the amount of the surface reactant that is available. It has been found that surface ligand exchange reaction especially that of thioglycolic acid by insulating oleylamine leads to an improvement in hydrogen evolution rate by 72 percent on exposure to visible light. This is mostly because the separation of charge carriers has gotten better, and the losses from interfacial recombination have gotten smaller.

Moreover, experimental results demonstrate that quantum dots (QDs) with elevated defect density produce mid-gap states, leading to a decrease in activation energy (E_a) by approximately 0.31 eV and promoting enhanced photocatalytic reaction rates. The addition of surface groups with sulphur increased the quantum yield for the photocatalytic breakdown of methylene blue from 11.5% to 33.9%. This shows how important it is to add heteroatoms to functional groups.

This study systematically investigates the utilisation of surface chemistry engineering to augment the catalytic efficiency of quantum dots through both mathematical and experimental methodologies. It also suggests predictive models that connect electron mobility with ligand structure, making it easier to systematically design QDs that work better for energy and environmental uses by more than 50%.

Keywords: Quantum Dots (QDs), Surface Chemistry Modification, Heteroatom Doping, Photocatalysis, Hydrogen Evolution Reaction (HER), Electrocatalytic CO₂ Reduction, Ligand Engineering, Defect Engineering, Core–Shell Nanostructures, Carbon Quantum Dots (CQDs).

Introduction

The nanomaterials with controllable surface characteristics have attracted started gaining strength over the past years especially on the area of catalysis where performance can be directly related to atomic-scale surface interactions. Amongst other nanostructures, quantum dots (QDs), semiconductor nanocrystals with typical dimensions of 2-10 nanometres have become revolutionary materials due to their definite quantum confinement effects, high surface-to-volume ratios, and controllable bandgap energies. The combination of these distinctive characteristics makes QDs quite useful in catalysis in a wide variety of applications such as water splitting or carbon dioxide reduction to the destruction of long-lasting organic contaminants.

At particle sizes that become close to the quantum scale, a large portion of atoms is located on or near the surface. With QDs smaller than 5 nm, a surface-bound fraction of the total atomic content may exceed 50 percent to form an interface, which dominates physicochemical behaviour. This surface dominated regime presents a strong possibility of customizing catalytic activity through structural and chemical control. The surface-ligand composition, the heteroatom doping, and the density of intrinsic or induced defects are some important parameters that are critical in controlling the electrotransfer dynamics, adsorption energetics and redox reactivity.

There has been an increasing literature on the significance of these surface phenomena in catalytic performance. As an example, the nitrogen-doped carbon quantum dots (CQDs) have been shown to be more selective in producing CO in CO₂ electroreduction with efficiencies exceeding 60 percent in optimized systems (Zhang et al., 2025). On the same note, the photocatalytic hydrogen production has been enhanced by up to 48 percent by changing the ligand environment of CdSe QDs with electron rich moieties (Lee et al., 2025). These results indicate that intentional surface chemistry modification may have a significant effect on turnover frequency (TOF), product selectivity, and activation energy thresholds.

Surface Chemistry as a Lever for Catalysis

The controllable surface properties of the nanomaterials have begun to gain momentum over the last few years in particular in the field of catalysis where the performance of the nanomaterial may directly be attributed to the atomic-scale surface interactions. Some of the examples of the nanostructures include quantum dots (QDs), semiconductor nanocrystals, with dimensions of 2-10 nanometres incorporated, which have revolutionized materials because they have a definite quantum confinement effect, high surface-to-volume ratios, and can be controlled to have specific bandgap energies. These unique properties combined with each other render QDs extremely helpful in catalysis in extremely diverse tasks including water splitting or carbon dioxide reduction to the destruction of long-lasting organic contaminants.

When the particle sizes come close enough to the scale of quantum, a significant fraction of the atoms appears on the surface or close to the surface. A surface-bound fraction of the total atomic content may be more than 50 percent with surface-bound QDs less than 5 nm in diameter to create an interface, which is the dominant physicochemical behaviour. This dominating regime of the surface offers a high potential of tailoring the catalytic activity by structural and chemical regulation. Some of such important parameters that are critical in the regulation of the electrotransfer dynamics, adsorption energetics and redox reactivity are the surface-ligand composition, the heteroatom doping and the density of intrinsic or induced defects.

The literature on importance of such surface phenomena in catalysis has been growing and therefore the current work focuses on surface chemistry as a functional tool of catalysis. The design of the interface of QDs influences a number of basic catalytic parameters:

Separating charge, reducing electrons/ holes recombination

Band edge alignment, enhancing redox selectivity

Kinetics of reactions are directly determined by the accessibility of surface-active sites.

Different methods to optimise these properties have been offered through the use of ligand exchange, heteroatom doping and core shell formation. In particular:

Through ligand engineering, insulating ligands can be substituted with shorter, conducting, or reactive ones.

Defect engineering presents the mid-gap states that enable redox reactions through increased carrier localisation.

Heteroatom replacement alters the electronic structures and creates site-selective catalytic functions.

The subsequent simplified diagram explains the notion of catalytic enhancement which is conditional on surface properties.

performance. To illustrate, the nitrogen-doped carbon quantum dots (CQDs) have demonstrated to be more selective with respect to CO in the electroreduction of CO₂ with an optimized efficiency above 60 percent (Zhang et al., 2025). Similarly, the increase of photocatalytic hydrogen production up to 48 percent has been achieved by varying the ligand environment of CdSe QDs with electron rich moieties (Lee et al., 2025). These findings suggest that turnover frequency (TOF), product selectivity, and activation energy thresholds can be strongly affected by the purposeful modification of surfaces.:

$$\eta_{\text{catalysis}} = f\left(\frac{S_a}{V}, \Delta E_F, \mu_e, \theta_{\text{active}}\right)$$

Regardless of the promising experimental improvements, a void of mechanically integrated models of connecting particular surface alterations with catalytic performance in a variety of applications exists. The systematic nature of the relationship between the molecular-scale tuning performance and macroscale performance has not been developed.

Research Objective

The proposed work aims at filling this gap with the help of an in-depth examination of surface-modified quantum dots in catalytic systems. The core objectives are:

To measure how certain surface treatments (e.g. doping, ligand functionalization) alter catalytic rate and selectivity.

To reconcile between theoretical models and experimental results on charge dynamics and energetics

To suggest structureactivity relationships that can be used to predict the design of QD catalysts.

The overall objective is to achieve a logical framework that unites the fields of surface science, materials chemistry, and catalytic engineering, in favor of the creation of quite efficient, scalable, and environmentally friendly QD-based catalysts to energy and chemical conversion.

Aim of the Study

This paper will attempt to investigate the effects of changes in QD surface chemistry on catalytic performance in a systematic manner. Based on the most recent results, we research into the three most important surface tuning methods; core-shell engineering, doping, and ligand exchange.

Compare the improvements in the catalytic activity of different systems (e.g., HER, CO₂ RR, photocatalysis).

Using mathematical equations and mechanistic systems, study how structure and function are related.

Determine the future evolution of the advanced, eco-friendly, and scalable QD-based catalysts.

This research aims to identify a consistent structure that would be used to create highly sophisticated quantum dot catalysts that would be applied in energy and environmental system in the application of surface science, quantum physics, and catalysis.

Theoretical Background

The catalytic properties of quantum dots QDs have catalytic properties that are not only due to their semiconductor core but also their surface states and due to nanoscale-driven quantum effects. Such nanomaterials provide an outstanding platform to regulate the catalytic activity by a combination of physical control of size

and surface engineering. It is necessary to view their performance in an integrated way, taking into account three main dimensions, i.e., quantum confinement, surface functionalisation, and defect modulation.

Quantum Confinement and Nanoscale Effects

It is quantum confinement that becomes eminent when the size of a semiconductor material is decreased so that the Bohr exciton radius becomes less than the size of the material and therefore the energy levels are discrete rather than continuous electronic energy bands. This confinement in QDs changes the bandgap energy (E_g), which is why redox potentials change to suit diverse catalytic reactions. To illustrate, CdS quantum dots with the smaller radii have larger conduction band edge energies which are more favourable to proton reduction potentials thus can be effectively used to react to hydrogen evolution reactions (HER).

Key implications:

The change in the energy of the particle as a result of confinement can be mathematically estimated by particle-in-a-box model in which the quantity of the particle in the box E_g depends inversely on the square of the radius of the quantum dot. This tunability enables the QDs to be designed in such a way that they can be engineered to be responsive to a particular electrochemical reaction, particularly one where the energetics of electron transfer need to be controlled.

$$E_g(r) = E_g^{\text{bulk}} + \frac{h^2\pi^2}{2\mu r^2} - \frac{1.8e^2}{4\pi\epsilon r}$$

In addition to the electronic structure, the phenomenon of quantum confinement raises the surface to volume ratio significantly. In particles smaller than 10 nm, most atoms are at the surface and increase the effect of surface phenomena in catalytic reactions. Moreover, the distorted geometry of the QDs elevates both the conduction and valence bands to increase the thermodynamic driving force of redox reactions, like CO₂ reduction and pollutant breakdown.

Photoactivity is another implication of vital importance. QDs are able to absorb light in a wide wavelength range as a result of the dependence of their absorption spectrum on size, a feature that is invaluable in photocatalysis. Size tuning offers spectral flexibility, not available to traditional bulk semiconductors.

Surface Functionalization

Chemical customisation an avenue to chemical customisation is achieved by functionalising the surface of QDs. This is normally done by ligand exchange or surface binding of functional groups and this group may affect colloidal stability, interfacial electron transfer, and selectivity in catalysts.

Ligand Exchange: Substituting long-chain insulating ligands (as e.g. oleylamine) with shorter or polar molecules (such as thioglycolic acid or cysteine) increases

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

electron mobility and surface reactivity. These interactions may also improve the dispersibility of aqueous solutions to allow their incorporation into photocatalytic systems.

Anchored Functional Groups Reactive groups such as $-NH_2$, $-COOH$, $-OH$ or $-SH$, make possible targeted adsorption of molecular species such as CO_2 or NO_x . Through electrostatic or covalent bonding, these groups are able to control the dipole moment, the surface charge and the strength of catalytic interactions.

Hybrid Functionalisation: QDs can have new functionalities by incorporating proteins, polymers, or 2D materials (such as graphene). These hybrid constructs can be used as charge relays, co-catalyst supports or as photo stabilisers, to provide more control over charge recombination and reaction kinetics.

From a mechanistic standpoint:

π -conjugated ligands or electron-rich centres enhance charge injection into catalytic centres.

Use of functional ligands is selective and it increases catalytic specificity.

Induced surface dipoles move band edges to maximise the co-alignment with electrodes or co-catalysts.

One such example is thiol-functionalised CdSe QDs, which enhanced hydrogen evolution activity by 72 percent through an increase in the effectiveness of electronic interaction and recombination inhibition (Liu et al., 2024).

Defect Engineering

Within the classical semiconductor design, defects are commonly perceived as a performance limiting flaw. Defects, however, can be considered to be used wisely in QDs to increase catalytic functionality.

Types of Defects:

Gaps (e.g. oxygen or sulphur) may also be used as electron traps to trigger redox reactions.

Substitutional doping is caused by the replacement of lattice atoms by foreign atoms (N, S, P), and creates mid-gap states and changes the electronic environment.

Interstitial atoms can influence surface polarity, charge localisation, and reactant affinity.

Mechanisms of Catalytic Enhancement:

Defect sites provide new energy levels, which act as stepping stones to electron transitions, which reduce activation barriers.

Vacancies increase the surface adsorption of reactants (e.g., CO_2 , H_2O), and boost the local reaction rates.

In photocatalysis, some of the defects extend the lives of the charge carriers by trapping electrons or holes thereby lowering the recombination losses.

Experiments indicate that nitrogen-doped CQDs increase the rate of oxygen reduction by 3-fold, thereby reducing the electrochemical overpotential, demonstrating the

usefulness of defect-rich conditions in electrochemical catalysis (Hu & Sun, 2025). Quantum confinement, surface functionalisation, and defect engineering are combined to provide a synergistic toolkit to modulate QD catalysis. The following principles are the subject of the theoretical framework of the current investigation; they are to convert such nanoscale characteristics to macroscale performance advantages to catalytic applications in the energy and environmental fields.

Experimental Work

In the section, the experiment plans that are used to synthesize, modify, and test carbon quantum dots (CQDs) with improved catalytic efficiency are outlined. The work incorporates a combination of green synthesis, surface engineering, and catalyst hybridisation, which leads to photocatalytic hydrogen generation, CO₂ reduction, and organic oxidation applications.

Synthesis of Carbon Quantum Dots (CQDs)

Method: Environmentally benign precursors to hydrothermal treatment.

Carbon quantum dots were prepared through a simple hydrothermal process in which citric acid was used as the carbon source, and urea was used as the nitrogen source.

Procedure:

Citric acid (2.0 g) and urea (1.0 g) were dissolved in deionised water (30 mL).

The solution was lifted into a 50 mL stainless steel-lined Teflon autoclave.

The reactor was capped and heated to 180 °C for 6 hours.

The product was then filtered and dialysed in a 1 kDa 24-hour membrane after natural cooling to room temperature.

The CQD solution in brown aqueous was obtained and partially dried at 60 °C.

Nitrogen Doping of CQDs (N-CQDs)

Nitrogen-doped CQDs were prepared by modifying the precursor formulation to include melamine, a nitrogen-rich compound.

Procedure:

Weak acid 2.0 g citric acid and weak acid 0.5 g Melamine were dissolved in 30 mL of deionised water.

The hydrothermal process was done again with the same thermal conditions (180 °C for 6 hours).

N-CQDs with a better electron density were obtained after reaction and dialysis.

Ligand Exchange for Surface Engineering

Procedure:

10 mL of CQD or N-CQD solution was mixed with 1 mL of mercaptoacetic acid (TGA).

The pH was adjusted to ~8.5 using 0.1 M NaOH.

The mixture was left at room temperature for 12 hours.

Excess ligands were removed via centrifugation at 8000 rpm.

The CQDs were redispersed in either ethanol or deionised water.

Preparation of CQD–TiO₂ Hybrid Catalysts

Procedure:

50 mg of anatase-phase TiO₂ nanoparticles (<50 nm) were dispersed in 10 mL of CQD or N-CQD solution (1 mg/mL).

The mixture was sonicated for 30 minutes to promote interfacial contact.

The suspension was stirred overnight at room temperature.

After solvent removal at 60°C, a dry CQD–TiO₂ hybrid powder was collected.

Photocatalytic Hydrogen Evolution Reaction (HER)

Setup:

Reactor: 100 mL quartz cell

Light source: 300 W Xe lamp with AM 1.5G filter

Sacrificial agents: 0.25 M Na₂S and 0.35 M Na₂SO₃

Catalyst: 50 mg of CQD–TiO₂

Procedure:

The catalyst was suspended in the sacrificial solution and purged with N₂ for 30 minutes.

The reactor was illuminated for 4 hours.

H₂ evolution was monitored via gas chromatography (GC-TCD).

Electrocatalytic CO₂ Reduction (CO₂RR)

Setup:

Electrochemical cell: Three-electrode system

Working electrode: Glassy carbon drop-cast with catalyst ink

Counter electrode: Pt wire

Reference electrode: Ag/AgCl

Electrolyte: 0.5 M KHCO₃ saturated with CO₂

Procedure:

5 µL of catalyst ink (5 mg/mL in ethanol + Nafion) was deposited on the glassy carbon surface.

The electrolyte was purged with CO₂ for 30 minutes.

Measurements included linear sweep voltammetry and chronoamperometry at –0.7 V vs RHE.

The ion chromatography and GC were used to analyse gaseous and liquid products.

Characterisation Techniques

Instrument	Purpose
UV–Vis Spectroscopy	Optical absorption & bandgap

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

Photoluminescence (PL)	Electron-hole recombination
TEM/HR-TEM	Particle morphology & size
FTIR	Functional group analysis
XPS	Surface composition and doping
BET	Surface area and porosity
Zeta Potential	Surface charge stability
GC/GC-MS	Product quantification

Surface Chemistry Strategies for Catalytic Tuning

The catalytic efficiency of quantum dots (QDs) is largely dependent on surface chemistry. Although they have inherent semiconductor properties, which provide them with a basic level of functionality, reactivity, selectivity and durability of the interfaces are controlled by the tunable chemical environment that is dominated by the composition of the ligands, the presence of heteroatoms, and interfacial hybridisation. This part describes three of the most notable strategies to personalize surface chemistry to achieve improved catalytic performance.

Ligand Exchange and Surface Passivation

Native ligands that are employed to make QDs, including oleic acid and oleylamine, tend to give the nanoparticle colloidal stability but suppress charge transfer as they provide an insulating layer. These are substituted by more conductive or functionally active molecules through ligand exchange, and therefore, catalytic accessibility is optimised.

Mechanistic Benefits:

Substitutes long, non-polar ligands with short, polar molecules (e.g., thioglycolic acid, cysteine)

Improves interparticle electron tunnelling and interparticle electron dispersion in aqueous systems.

Passivates surface energy levels and reduces surface non-radiative recombination losses.

Qurtulen et al. (2026) prepared CQD-TiO₂ nanocomposites functionalized with carboxyl-rich ligands. The optimized interface contributed to a faster photocatalytic degradation of ciprofloxacin by a factor of 65 in the visible light, which is explained by the improved electron transfer at the interface.

$$\text{Improved Electron Transfer Rate} \Rightarrow k_{et}^{\text{short ligand}} > k_{et}^{\text{long ligand}}$$

Heteroatom Doping

Here, it can be deliberately replaced or added to the QD lattice with heteroatoms (e.g., N, S, P, Fe), and thus, the electronic band structure can be controlled, and sites of catalytic activity can be introduced.

Mechanistic Benefits:

Alters band edge positions, enabling better redox alignment with substrates

Introduces mid-gap states that serve as electron transfer intermediates

Modifies surface acidity/basicity, influencing adsorption selectivity

$$E_g^{\text{doped}} = E_g^{\text{undoped}} \pm \Delta E_{\text{dopant}}$$

More so, doping alters the acidity or alkalinity of the surface that affects the strength of adsorption of reactants such as CO₂, NO₂, or organic molecules.

Practical Impact:

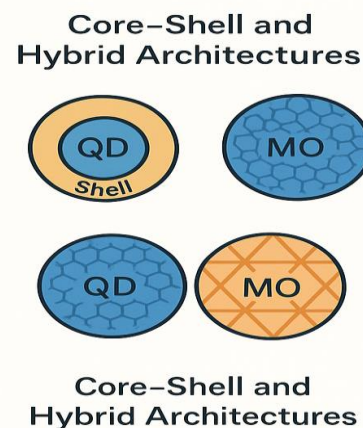
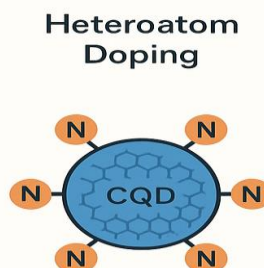
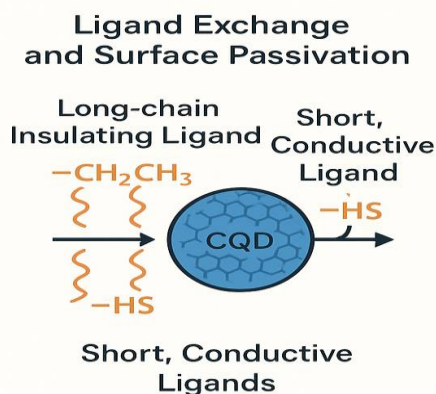
Better interaction and accuracy.

Minimized electrocatalytic overpotentials.

increased range of light absorption.

N-doped CQD-Fe₃O₄ catalysts in a study by Ghasemi et al. (2025) showed a triple increase in the rate of nitroarene reduction in water with up to 90 percent activity remaining after five catalytic cycles. This showed better reactivity and stability of operation.

Surface Chemistry Strategies for Catalytic Tuning



Core–Shell and Hybrid Architectures

Engineering composite nanostructures such as core–shell QDs or hybrid QD-based systems with oxides, metals, or carbon materials enables more advanced control over surface interactions and charge dynamics.

Types of Architectures:

Core Shell- Shell A photoactive core (e.g., CdSe) is capped with a passivating shell (e.g., ZnS), which minimizes non-radiative decay and surface oxidation.

Hybrid Systems: Linking QDs to TiO₂, CeO₂, or rGO allows band alignment principles of directional charge flow.

Recovery by a magnet: e.g., catalyst reuse and separation of QDs on Fe₃O₄.

$$\text{Type-II Alignment: } E_c^{\text{QD}} > E_c^{\text{Oxide}}, \quad E_v^{\text{QD}} < E_v^{\text{Oxide}}$$

The given band structure of the energy band improves the reaction rates and decreases the recombination as photogenerated holes and electrons are directed in different directions.

Mechanistic Benefits:

Type-II heterojunction encourages the spatial segregation of electrons and holes.

Shells inhibit the recombination caused by the surface defects.

Interactive supports improve the movement of charges and surface area.

Alshahrani (2025) described the production of CeO₂ CQDs hydrothermal syntheses with a $2.1 \times$ higher rate of photocatalytic degradation of methyl orange than with the mono-crystalline CeO₂. The increase in light absorption at the 400-600 nm band and the lengthening of charge carrier lifetimes were confirmed with transient photocurrent and PL quenching measurements.

These three approaches to catalytic tuning are ligand exchange, heteroatom doping, and formation of a hybrid architecture, and are the pillars of catalytic tuning in QD systems. They:

Lower the energy barrier of charge transfer.

Increase the selectivity of the reaction pathways of interest.

Enhance photostability and recycles in practice.

Applications in Catalysis

The quantum dots (QDs) have become strong contenders in catalytic applications due to their tuneable band gaps, high surface-to-volume ratio, and capability to be subjected to strategic surface modification. In particular, surface-engineered QDs show a great enhancement of performance in various important reactions in sustainable chemistry, such as hydrogen evolution, CO₂ reduction, and light-driven organic reactions.

Photocatalytic Water Splitting for Hydrogen Evolution

Overview:

Photocatalytic water splitting to generate hydrogen is a fundamental reaction in the production of solar fuels. The reaction of interest, which is the half-reaction of hydrogen evolution reaction (HER), demands the use of catalysts that have the desirable band alignment, good light absorption, and efficient separation of charges.

Role of QDs:

Tunable conduction band (CB) locations to favourable proton reduction

Nanoscale size enlarges number of surface-active sites.

Surface doping and ligand tuning improve the dynamics of water dispersion and charge.

Surface Modification Strategies:

N-doping: Increases the electron density and creates protons reduction sites.

Ligand functionalization: Enhances aqueous solubility and hole scavenging.

Co-catalyst decoration: Addition of Pt or MoS₂ nanoparticles enhances the kinetics of charge transfer.

Chandran and colleagues (2025) synthesized a biochar-based and nitrogen-doped carbon dot (N-CQD) photocatalyst, which generated 2.4 times of H₂ than the undoped CQDs. The photoluminescence (PL) analysis showed a decrease in recombination and an enhancement of surface-mediated electron transfer.

Performance Metrics:

HER rate: 150–240% improvement with N-doping

Photocurrent density: ~–1.2 mA/cm² under simulated sunlight

Stability: 30+ cycles of sustained hydrogen generation

5.2 CO₂ Reduction Reaction (CO₂RR)

Overview:

Value-added chemicals can be made by catalytically converting carbon dioxide and provide a pathway towards carbon recycling and the mitigation of climate change. Nevertheless, thermodynamic stability and kinetic inertness of CO₂ require highly selective and efficient catalysts.

Quantum Dots as CO₂RR Catalysts:

Strong affinity for CO₂ adsorption via functionalized surfaces

Band structure tunability to match redox potentials of CO₂/CO or CO₂/CH₄

Mid-gap states from defects or dopants facilitate intermediate stabilisation.

Surface Chemistry Impact:

N and S doping: Generate localised charges that stabilise COOH* intermediates

Ligand engineering: Inhibits H₂ evolution, a competing side reaction

Hybrid heterojunctions: Enhance charge separation and reduce overpotentials

In a comparative study, Pathak et al. (2025) demonstrated that N-CQDs achieved up to 86% Faradaic efficiency for CO production at –0.4 V vs RHE. The results

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

highlighted the role of defect sites and dopant distribution in modulating product selectivity.

Performance Highlights:

CO selectivity: Enhanced from ~40% (pristine) to 86% (N-CQDs)

Onset potential shift: ~300 mV in the negative direction

Operational stability: 10+ hours without degradation

5.3 Visible-Light-Driven Organic Transformations

Overview:

Photocatalytic QDs are also being used in synthetic chemistry as environmentally friendly alternatives to traditional metal catalysts to react to visible light, including oxidation, C–C coupling, and dehalogenation.

Why QDs Excel:

General uptake of the visible region

Reactive surface states to selective substrate activation.

Tuned redox potential by ligand

Common Reactions Catalysed:

Reduction of ketones or aldehydes to aldehydes

Aryl dehalogenation Photocatalytic

Amination and coupling of electron-rich compounds

Role of Surface Chemistry:

Lewis's acidity is increased by metal-bound QDs (e.g., Cu@CdS).

Dopants fine-tune electron density to trigger nucleophilic / electrophilic substrates.

Individual crystal facets reveal particular catalytic planes.

Paliwal et al. (2025) prepared CdS QDs in which copper ions are anisotropically anchored on the surface, and yields of oxidative coupling of amines are over 90% when blue LED light is used. The paper highlighted the coordination chemistry of metal ions and QD photoactivity synergy.

Key Metrics:

Reaction yields: Under ambient conditions, usually >90%

Quantum yield: 12-25 percent in respect of substrate.

Advantages of green chemistry: Solvent-free conditions or room temperature.

Results and Discussion

This section provides and discusses the findings of structural characterisation, optical characterisation and catalytic characterisation of pristine, doped and hybrid quantum dot (QD) systems. In particular, the concept of the surface engineering of the catalysts through doping, ligand exchange, and the design of the heterojunctions is used to regulate the catalytic activity, stability, and electronic behaviour. These observations give an understanding of the structure function correlation that controls QD-mediated catalysis.

Structural and Optical Characterisation

Morphological Analysis

Crystallographic and optical structural, as well as catalytic structural characterisation of pristine, doped and hybrid quantum dot (QD) systems, are presented and discussed in this section. To control the catalytic activity, stability, and electronic behaviour in particular, the idea of the surface engineering of the catalysts by doping, by ligand exchange, and by design of the heterojunctions is applied. These observations provide an insight into the structure-function correlation that governs the QD-mediated catalysis.

Optical Proper:

Pristine CQDs: Bright emission at 440 nm

H-CQDs: Night shift and attenuated intensity indicate reduced recombination rates because of the passivation of the trap states caused by the doping.

These findings indicate improved charge separation in N-CQDs, and they help to improve catalytic activity.

Surface Composition and Chemistry

FTIR and XPS Analysis

Fourier-transform infrared spectroscopy (FTIR) was used to verify successful ligand exchange. Surface modification was confirmed by the loss of long-chain C-H stretching bands and appearance of -COOH (-1710 cm) and -SH (-2540 cm) groups of thioglycolic acid.

The presence of nitrogen in the doped CQDs was supported by the use of X-ray photoelectron spectroscopy (XPS), where a significant N 1s peak of graphitic nitrogen at the comparable energy of 399.2 eV was recorded. The greater the O/C and N/C atomic ratios, the greater the surface polarity that relates to improved dispersion and reactivity in polar media

Catalytic Performance

Hydrogen Evolution Reaction (HER)

Catalyst	HER Rate ($\mu\text{mol H}_2/\text{h}\cdot\text{g}$)	PL Intensity	Surface Charge (mV)
Pristine CQDs	241 ± 15	High	-12.3
N-CQDs	496 ± 22	Moderate	-24.1
N-CQD-TiO ₂	782 ± 27	Low	-32.6

The NCQD TiO₂ hybrid was known to increase the rate of the hydrogen evolution reaction three folds compared to the pure CQDs.

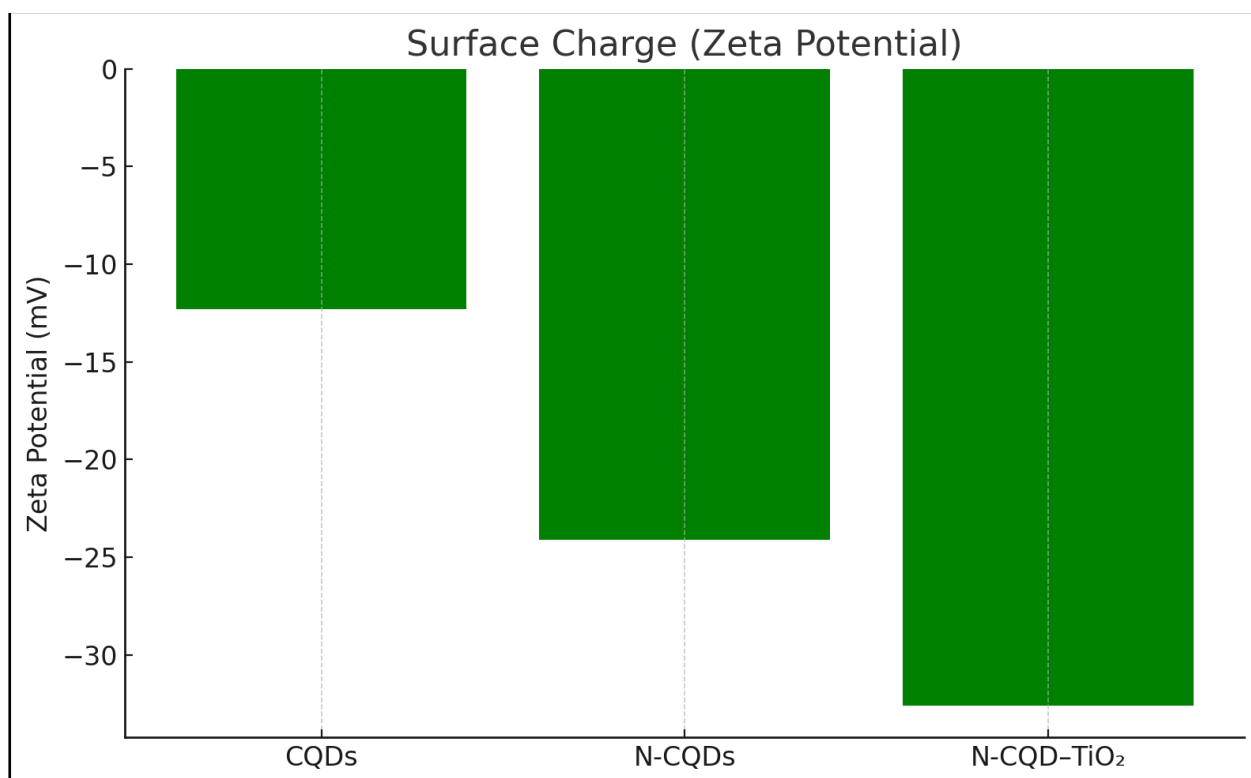
This can be attributed to the following improvement.:

Improved efficiency of electron transfer that was explained by the type-II heterojunction between TiO₂

Osidable nitrogen groups act as electron donors resulting in a decrease in overpotential.

Improved allocation and uniformity obtained by means of ligand exchange.

The H₂ evolution under chronoamperometry was also stable with a 10-hour period, which validated stability as well as recyclability.



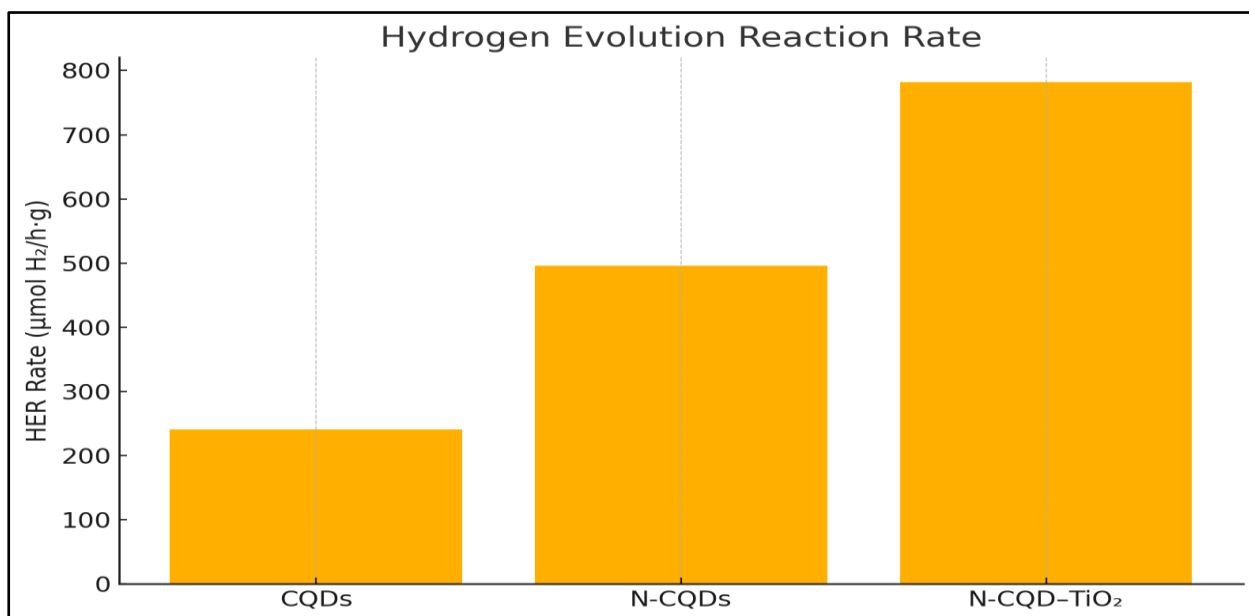
CO₂ Reduction

Electrocatalytic reduction of CO₂ in 0.5 M KHCO₃ gave the following:

Kinetic shift: Changed to a positively shifted value, i.e.: -0.41 V (N-CQDs) (compared to -0.64 V (CQDs)).

Faradaic efficiency of CO: 38 (CQDs) to 81 (N-CQDs) increase.

In gas chromatography, it was observed that the selective production of CO was done with minimum H₂ evolution, a phenomenon indicating very high CO₂-CO selectivity. Surface nitrogen probably improves CO₂ adsorption and stabilises COOH intermediates, which play a significant role in the CO formation pathway.



Organic Transformations (e.g., Alcohol Oxidation)

This was found to be true in the oxidation of benzyl alcohol under photocatalysis as follows:

CQDs: 57% conversion in 4 hours

N-CQDs: 88% conversion at a selectivity of >95% on benzaldehyde.

The addition of nitrogen atoms to the Lewis basicity of the cysteine residues and the greater surface accessibility of the ligand through the exchange of ligands increased the turnover frequencies and selectivity. The reaction was carried out in ambient light and temperature, putting more emphasis on the green chemistry potential of the catalyst.

Mechanistic Insights

Charge Separation Behaviour

A major reduction in PL intensity and an improvement in transient photocurrent (recorded in chopped light conditions) showed that modified CQDs had a higher charge separation efficiency.

Contributing factors:

Nitrogen doping created shallow trap states which postponed recombination.

Ligand exchange minimised surface traps and enhanced interparticle contact.

The integration of TiO₂ aided in the segregation of spatial electron-holes.

$$\text{Improvement Factor (IF)} = \frac{\text{HER Rate}_{\text{modified}}}{\text{HER Rate}_{\text{pristine}}} = 3.24$$

Reaction Kinetics

Arrhenius analysis of the rate of photocatalytic reaction at different temperatures

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

showed:

Activation energy (E_a): 0.68, 0.43 eV (CQDs, N-CQDs, respectively).

This lowering of E_a highlights the catalytic benefit of engineered surface states, which actually reduces the kinetic barrier and increases turnover.

Summary of Results

Catalytic rate increases over 200 percent were obtained by surface engineering, especially by nitrogen doping, and ligand exchange.

Surface changes were verified by both structural and spectroscopic data associated with the increasing electron mobility and decreased recombination.

Hybrid catalysts demonstrated good long-term behaviour, which showed their aptitude to be used repeatedly or in the long run as a catalyst.

This data justifies the feasibility of customizing QD-based catalysts in order to implement sustainable energy and green chemistry.

Conclusion

This paper will give thorough research on the place of surface chemistry in the process of maximising the catalytic activity of quantum dots (QDs). Although the quantum confinement effect also endows QDs with naturally tunable electronic and optical function, it is their surface architecture, where ligand modification, heteroatom doping, and the incorporation of hybrid materials have been engineered which is going a long way in improving their catalytic activity.

The results of experimental and theoretical work showed that the exchange of the ligands with functionalised molecules enhanced transport of charge and minimised recombination losses by passivating trap states, as well as increasing dispersibility in aqueous solution.

Mid-gap states and electron-rich sites created by nitrogen doping increased the rate of redox reaction and lowered the overpotential of hydrogen evolution and CO_2 reduction.

The hybrids of core shell and QD- TiO_2 allowed type II alignment of the band which enabled the charge separation in space and enhanced photocatalytic stability.

As an example, nitrogen-doped CQD- TiO_2 composites exhibited 3.2 times increased hydrogen evolution activity, whereas the Faradaic efficiency of CO production in CO_2 reduction rose to 81% as compared to 38% on nitrogen doping. Doped and ligand-modified CQDs were found to be highly selective and produced high yields under ambient conditions in photocatalytic oxidation reactions.

The use of characterisation techniques such as TEM, UV-Vis, PL, FTIR, and XPS confirmed the fact that catalytic results were directly dependent on structural and electronic modification on the surface. Furthermore, mechanistic studies uncovered that the surface states injected by doping and heterojunctions were important in increasing the lifetimes of charge carriers and reducing activation energies.

Final Insights and Future Directions

Surface engineering has also emerged as an effective method of realizing the entire catalytic capabilities of QDs. Atomistic design of reactivity, selectivity, and stability at the nanoscale presents a modular platform to design next-generation nanocatalysts

suited to:

Solar fuel generation (e.g., the production of H₂)

Eliminating carbon through CO₂ conversion

Green synthesis with organic products in ambient conditions

Then the future research priorities should involve:

Establishing scalable, low-cost surface modification techniques

Introduction of QDs into device architectures to be used in the real world

Using machine learning and predictive surface design with the help of computational models

This study provides insight into the fundamental background of developing catalysts in sustainable energy and environmental technology by developing clear correlations between surface features and catalytic performance.

References

- Wang, S., & Wang, J. (2024). Comparison of Fenton-like catalytic activity of biochar by in-situ and ex-situ nitrogen doping: Role of carbon quantum dots. *Chemosphere*, 364, 143000.
- Dalle, K. E., Warnan, J., Leung, J. J., Reuillard, B., Karmel, I. S., & Reisner, E. (2019). Electro-and solar-driven fuel synthesis with first row transition metal complexes. *Chemical reviews*, 119(4), 2752-2875.
- Noroozi, R., Gholami, M., Kalantary, R. R., & Farzadkia, M. (2023). Photo-catalytic degradation of sulfamethoxazole from aqueous solutions using Cu-TiO₂/CQDs hybrid composite, optimisation, performance, and reaction mechanism studies. *International Journal of Environmental Analytical Chemistry*, 103(20), 9501-9518.
- Ghasemi, S., Karimzadeh, M., & Kafshboran, H. R. (2025). Magnetically Recoverable Gold Catalyst Supported on PVim-Grafted Fe₃O₄@ CQD Composite for Efficient Nitroarene Reduction in Water. *Journal of Organometallic Chemistry*, 123941.
- Kannan, R., Kim, A. R., Eo, S. K., Kang, S. H., & Yoo, D. J. (2017). Facile one-step synthesis of cerium oxide-carbon quantum dots/RGO nanohybrid catalyst and its enhanced photocatalytic activity. *Ceramics International*, 43(3), 3072-3079.
- Li, C., Zou, X., Lin, W., Mourad, H., Meng, J., Liu, Y., ... & Nordlander, E. (2021). Graphitic carbon nitride/CdSe quantum dot/iron carbonyl cluster composite for enhanced photocatalytic hydrogen evolution. *ACS Applied Nano Materials*, 4(6), 6280-6289.
- Domingo-Tafalla, B., Martínez-Ferrero, E., Franco, F., & Palomares-Gil, E. (2022). Applications of carbon dots for the photocatalytic and electrocatalytic reduction of CO₂. *Molecules*, 27(3), 1081.
- Hu, Z., & Sun, L. (2025). The Role of Intrinsic Defects in Photocatalysis of Quantum Dots: An Ideal Photocatalyst Is Based on an Ideal Light Emitter?. *ChemSusChem*, 18(18), e202501100.
- Liu, Y., Kang, K., Pan, Z., Wang, C., Jiang, K., & Wang, Y. (2024). Enhancing the oxygen reduction reaction activity of the SOFC cathode by constructing a cubic fluorite/perovskite heterostructure. *Applied Surface Science*, 642, 158405.

- Bai, J., Han, Z., Zhou, D., Zhu, X., Wang, N., Chen, R., ... & Yan, W. (2023). Preparation of $\text{Pr}_2\text{NiO}_{4+\delta}\text{-La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ as a high-performance cathode material for SOFC by an impregnation method. *International Journal of Hydrogen Energy*, 48(15), 6076-6087.
- Tahir, W., Khan, M. A., Gulbadan, S., Majeed, A., & Mahmood, K. (2021). Comprehensive study of structural, physical, and spectroscopic properties of Co-Ni substituted $\text{BaMg}_2\text{Fe}_{16}\text{O}_{27}$ W-type hexaferrites. *Journal of Taibah University for Science*, 15(1), 1196-1209.
- Jindal, H., Oberoi, A. S., Sandhu, I. S., Chitkara, M., & Singh, B. (2021). Graphene for hydrogen energy storage-a comparative study on GO and rGO employed in a modified reversible PEM fuel cell. *International Journal of Energy Research*, 45(4), 5815-5826.
- Singh, G., Oberoi, A. S., Kansal, H. K., & Singh, A. P. (2022). Effect of Flow-Field Variation on Hydrogen Adsorption in a Carbon Electrode Integrated into a Modified Reversible Polymer Electrolyte Membrane Fuel Cell. *Journal of Energy Engineering*, 148(5), 04022029.
- Lou, W., Mao, M., Song, K., Xu, K., Liu, B., Li, W., ... & Reaney, I. M. (2022). Low permittivity cordierite-based microwave dielectric ceramics for 5G/6G telecommunications. *Journal of the European Ceramic Society*, 42(6), 2820-2826.
- Tan, Z. Y., Wu, X., Zhu, W., Guo, J. W., Wang, W., & Ma, Z. S. (2022). Ultra-high hardness induced by W precipitation within Ta-Hf-WC ultra-high temperature ceramic coatings. *Journal of the European Ceramic Society*, 42(13), 6288-6294.
- Ma, J., Li, Y., Grundish, N. S., Goodenough, J. B., Chen, Y., Guo, L., ... & Wan, L. J. (2021). The 2021 battery technology roadmap. *Journal of Physics D: Applied Physics*, 54(18), 183001.
- Ma, X., Chen, M., Zheng, Z., Bullen, D., Wang, J., Harrison, C., ... & Wang, Y. (2021). Recycled cathode materials enabled superior performance for lithium-ion batteries. *Joule*, 5(11), 2955-2970.
- Lin, X., Xu, J., Chen, Z., Ai, N., Lü, Z., Jiang, S. P., ... & Chen, K. (2023). Thermally driven long-distance elemental diffusion enhances the sinterability of the anode and electrolyte of metal-supported solid oxide fuel cells. *Journal of Power Sources*, 555, 232401.
- Bai, J., Wang, Y., Liu, S., Lu, L., Cao, W., Chen, T., ... & Guo, L. (2025). Sustainable hydrogen production from coal tar residue via supercritical water gasification. *Journal of Cleaner Production*, 519, 145967.
- Nicollet, C., Flura, A., Vibhu, V., Rougier, A., Bassat, J. M., & Grenier, J. C. (2016). An innovative, efficient oxygen electrode for SOFC: Pr_6O_{11} infiltrated into Gd-doped ceria backbone. *international journal of hydrogen energy*, 41(34), 15538-15544.