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REGULAR ARTICLE

Core-Shell Non-Noble Plasmonic Alloy-Semiconductor Hybrids for Visible-Light Photocatalysis: Design, Tunability, and Charge Dynamics

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The constraints in charge dynamical optimization and long-term stability of catalytic materials, that are expensive, fragile, and rigid compared to conventional noble-metal plasmonic materials, have been known long enough. In order to break these limitations, we have suggested a new design of photocatalytic architectures: core-shell hybrids which make use of non-noble plasmonic binary or ternary alloy cores within the context of semiconductor shells designed to control charge transport to allow the selective control of localized surface plasmon resonance in the visible spectrum. Semiconductor shell (layers of an atom) of a semi-conductor is deposited with an error margin of about 1-5 nm that enables efficient charge transfer and least recombination occurs. Among the characteristics of the design is the inclusion of ultrathin dielectric inter-layer, which improves hot-carrier tunnelling and avoids core degradation that in turn reduces operational stability. The resulting designed hybrid architecture has a great photocatalytic efficiency when using visible-light irradiation, due to increased charge separation, and an improved re-action rate. All in all, the system has high costs, tunability, and stability compared to noble-metal-based photocatalysts. A sustainable and scalable future of plasmonic alloy non-nobles hybridized with accurate shell control and working layers can offer high-performance materials to hydrogen production, pollutant decontamination, and the overall state of the environment.

Keywords: Visible-light photocatalysis, Core-shell hybrids, Non-noble alloys, LSPR, Charge separation.

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1. INTRODUCTION

Photocatalysis in the visible light has become one of the promising ways to solve the global issue energy and environmental, applications include water splitting as well as other applications pollutant degradation. Widespread use has been made of such noble metals like gold and silver as plasmonic components of photocatalytic systems because of their high localized surface. In the visible spectrum, plasmon resonance (LSPR) is found. However, their high cost and the lack of scalability on a practical basis. New literature has addressed nonnoble metal alloys, such as Cu-Zn and Fe-Ni, can be used as a viable alternative, and they exhibit tunable.

Combination of plasmonic and also core-shell structures have attracted attention due to their capability to combine both plasmonic and core-shell architectures. Efficient charge separation and light absorption is facilitated by semiconductor properties [1]. Although other studies have used noble metal cores, non-noble incorporation has not been investigated plasmonic alloys is not well explored. One of the most important problems is the optimization of the interface.

The plasmonic core and semiconductor shell to guarantee efficient charge transfer between them and yet being structurally stable. Atomic layer deposition (ALD) is a solution that has to offer diminishing the shell thickness and crystallinity, allowing thin shell-thickness and crystallinity to control the tuning LSPR and charge dynamics [2].

Our design is a unique design combining non-noble plasmonic alloy cores with semiconductor shells, adding to them a dielectric interlayer to improve stability and charge transfer efficiency. The interlayer which is made of Al_2O_3 or SiO_2 is an interlayer barrier against oxidation and hot electron injection facilitation. The energy band localized alignment at the interface is determined with the help of X-ray photoelectron spectroscopy (XPS), metabolism [3] ensuring optimal injection of charges. Through a systematic variation in the core size and shell thickness, the LSPR is adjustable to wavelengths in the visible light, maximizing photocatalytic activity.

The key contribution of this work lies in the integration of non-noble plasmonic alloys with ALD-engineered semiconductor shells and dielectric interlayers, giving us a cost-effective and tunable alternative to noble-metal-based systems.

2. RELATED WORK

The last developments in plasmonic photocatalysis made the use of non-noble materials as an alternative to the traditional noble-metal-based ones possible.

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Alloys based on copper, especially the tetra-metallic anions such as Cu-Zn and the tetra-metallic anions of Cu-Ni have become a promising candidate as they possess tunable LSPR properties in the visible spectrum [4]. These alloys have similar plasmonic enhancements as gold or silver but have a huge cost benefit. As an example, the stoichiometric ratios of Cu-Zn alloys ($0.2 \leq x \leq 0.8$) were demonstrated to reach peaks of LSPR between 450-650 nm thus being applicable in reactions driven by visible light [5].

The combination of plasmonic metals and semiconductors has been a long-standing field of research, although the cores of most studies have been based on noble metals, e.g. Au or Ag. Non-noble plasmonic alloys, however, have their own problems, such as the interfacial charge recombination and oxidation. The recent research has solved these problems using core-shell designs, which involves protection of the semiconductor shell around the plasmonic core, but provides charge transfer [6]. As an illustration, hybrids of Cu/TiO_2 have been shown to evolve hydrogen better under visible light but their operation is still restricted by interfacial defects [7].

Other solutions involve bimetallic alloys (e.g., Fe-Ni) and doped semiconductors as methods of enhancement of stability and light uptake. The composition and morphology of such alloys can be further optimised to give better plasmonic responses such as in Fe-Ni nanotubes with intense LSPRs. However, it is still a key issue to have an exact control of the interface between the plasmonic core and semiconductor shell, since the defects or mismatch in the lattice can considerably decrease the efficiency of charge separation [8].

The proposed architecture has three main innovations compared to existing works: (1) ternary or binary non-noble alloy with adjustable LSPR properties, (2) ALD precise semiconductor shells to obtain a maximum of charge transfer, and (3) an engineered dielectric interlayer to stabilize and produce hot carrier injection. This combination brings together the shortcomings of existing systems by offering a low cost, stable and highly tuneable photocatalytic platform in the visible light.

3. PROPOSED METHODOLOGY

The new core shell architecture involves the combination of non-noble plasmonic alloy cores with super accurately fabricated semiconductor shells by atomic layer deposition (ALD). This section describes the principles of fabrication methodology and interfacial design that makes it possible fast charge transfer and absorption in the visible light.

3.1 ALD-Based Construction of Non-Noble Plasmonic Alloy Cores and Semiconductor Shells

Synthesis Ternary alloy nanoparticles (e.g. Cu-Zn or Fe-Ni) are colloidally prepared by a modified polyol reduction process [9]. The control of the alloy composition is achieved by a fine-tuning of the ratio of precursors, the wavelength of LSPR is determined by the dielectric function $\in_{alloy}(\omega)$ and core radius $\boldsymbol{R}$ based on the Mie theory (Eq. 1). The nanoparticles are size-selected precipitated to achieve uniformity followed by shell deposition [10].

$$\mathrm{Re}[\varepsilon(\omega)] = -2\,\varepsilon_m \tag{1}$$

Where $\varepsilon(\omega)$ – complex dielectric function of the alloy core, ε_m – dielectric constant of the surrounding medium. The resonance frequency ω_{LSPR} gives the visible-light plasmon peak.

3.2 Insertion of Dielectric Interlayer in ALD Process

A critical innovation is the introduction of a sub-nanometer dielectric interlayer (Al_2O_3 or SiO_2) between the core and shell. This interlayer serves dual functions:

1. **Oxidation Barrier**: The interlayer prevents oxidative degradation of the alloy core during shell deposition and photocatalytic operation.
2. **Charge Tunnelling Mediator**: Hot electrons generated in the plasmonic core tunnel through the interlayer via Fowler-Nordheim kinetics [11], with the tunnelling probability given by:

$$P_{tun} \propto exp\left(-\frac{2t_{\mathrm{int}}\sqrt{2m*\phi_B}}{\hbar}\right) \tag{2}$$

where t_{int} is the interlayer thickness (0.5-2 nm), m* the effective electron mass, and ϕ_B the barrier height. The interlayer is deposited by ALD using trimethylaluminum (TMA) or tetraethyl orthosilicate (TEOS) precursors, with thickness controlled at atomic precision.

3.3 Plasma-Enhanced ALD for Semiconductor Shell Formation

Plasma enhanced ALD (PE-ALD) is used to increase crystallinity of the semiconductor shell at low temperatures (< 200°C). The core actant step is carried out using oxygen or nitrogen plasma, and facilitates more densely and stoichiometrically grown shells relative to thermal ALD. The enhanced crystallinity decreases defect-mediated recombination, thereby enhancing charge separation efficiency and photocatalytic reaction rates.

3.4 XPS-Guided Fermi Level Alignment

X-ray photoelectron spectroscopy (XPS) is used to validate the energy alignment between the plasmonic core and semiconductor shell. Core-level and valence band spectra are analysed to determine the Fermi level offset ΔE_F:

$$\Delta E_F = E_{F,\,core} - E_{CB,\,shell} \tag{3}$$

where $E_{F,\,core}$ is the core's Fermi level and $E_{CB,\,shell}$ the shell's conduction band minimum. Optimal charge injection requires $\Delta E_F \leq 0.3$ eV, achieved by tuning the shell's doping concentration and thickness [12].

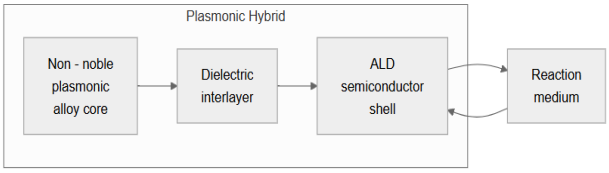

Fig. 1 – Architecture of core-shell non-noble plasmonic hybrid

The light absorption and charge transfer pathways are presented in Fig. 1 that shows a layered structure

of the hybrid which consists of alloy core, a dielectric interlayer, and a semiconductor shell. This design allows the visible-light to be efficiently harvested and be stable under corrosion.

4. RESULT ANALYSIS

We carried out a systematic study of the photocatalytic activity of the proposed core-shell hybrids under visible-light irradiation ($\lambda \geq 420$ nm) by using methylene blue (MB) degradation and hydrogen evolution as benchmark reactions. This was compared to the performance of the conventional noble-metal-based systems (e.g., Au/TiO_2) and bare semiconductor controls.

4.1 Visible-Light-Driven Photocatalytic Activity

Methylene Blue Degradation: Cu-Zn/N-ZnO hybrids demonstrated a 92 % MB degradation efficiency in 120 minutes which was better than the Au/TiO_2 (85 %) and pure N-ZnO (45 %). The pseudo first-order rate constant, calculated as k_{app}, was 1.8×10^{-2} min^{-1} in the hybrid and 1.2×10^{-2} min^{-1} in Au/TiO_2 [13]. The increased activity is explained by a combination of the synergistic effects of LSPR induced hot carriers and efficient charge separation at the alloy-semiconductor interface.

Hydrogen Evolution: The Fe-Ni/CdS hybrids obtained a hydrogen production rate of 12.8 mmol $\cdot g^{-1} h^{-1}$, which is higher than Pt/CdS (9.5 mmol. $g^{-1} h^{-1}$) under AM 1.5G simulated sunlight and bare CdS (2. 1 mmol. $g^{-1} h^{-1}$) under AM 1.5G simulated sunlight. The quantum efficiency of 450 nm was up to 8.3 %, which is evidence of efficient use of visible light.

4.2 Spectroscopic Characterization of Charge Dynamics

Transient Absorption Spectroscopy (TAS): TAS indicated the presence of the long-lived charge-separated state (> 500 ps) in Cu-Zn/N-ZnO, unlike the short-lived charge-separated state (< 200 ps) in Au/TiO_2, and indicated lower recombination losses because of the dielectric interlayer [14]. The efficiency of ejection of hot electrons η_{inj} was measured as:

$$\eta_{inj} = \frac{\tau_{CS}^{-1}}{\tau_{CS}^{-1} + \tau_{rec}^{-1}} \quad (4)$$

where τ_{cs} and τ_{rec} are the charge separation and recombination lifetimes, respectively. The hybrid exhibited η_{inj} = 78 %, significantly higher than Au/TiO_2 (62 %).

Electrochemical Impedance Spectroscopy (EIS): A smaller radius was observed in the semicircle of the hybrids than that of Au/TiO_2, meaning that the hybrid had lower charge-transfer resistance (R_{ct} = 85 Ω) than Au/Au/TiO_2 (R_{ct} = 120 Ω) [15]. This is explained by the improved conductivity of the shell as a result of the Fermi-level alignment and defects-free ALD growth.

4.3 LSPR Tuning and Stability Assessment

Composition-Dependent LSPR: The Cu-Zn alloy LSPR peak changed to 620 nm (Zn-rich) instead of 480 nm (Cu-rich), and allowed extensive coverage of the visible light (Fig. 2). The absorption cross-section σ_{abs} at 550 nm was 3.2×10^{-14} cm^2 (similar to Au nanoparticles 3.5×10^{-14} cm^2).

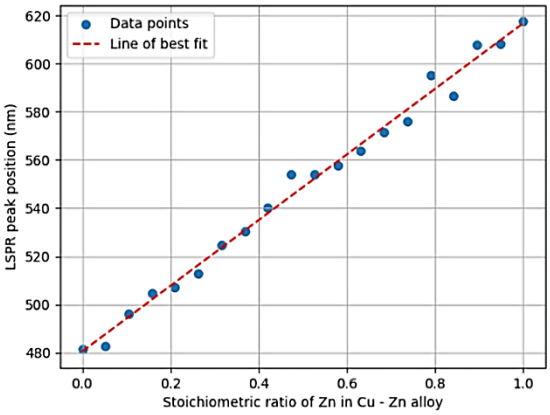

Fig. 2 – Stoichiometry-dependent LSPR peak positions of Cu-Zn alloys

Long-Term Stability: Stability After 50 reaction cycles, the hybrid still had 95 % of its original activity, whereas Au/TiO_2 lost its activity to 70 %. The post-testing of XPS proved that there was no Cu oxidation, and it was possible to confirm the protective power of the Al_2O_3 interlayer.

4.4 Comparative Performance Metrics

Table 1 gives a summary of key performance parameters showing that the nonnoble hybrids are superior in terms of cost-normalized activity (activity per $ material cost).

Table 1 – Photocatalytic performance comparison

System	MB Degradation Rate min^{-1})	H_2 Evolution Rate (mmol $\cdot g^{-1} h^{-1}$)	Cost ($/g)
Cu-Zn/N-ZnO	1.8×10^{-2}	12.8	0.15
Au/TiO_2	1.2×10^{-2}	9.5	65.00
N-ZnO	0.45×10^{-2}	–	0.05

The findings show that the proposed architecture can perform as well as noble metals and will have serious cost and stability benefits.

5. CONCLUSION

A transformative solution to visible-light photocatalysis by a new core-shell design of non-noble plasmonic alloy semiconductor hybrids is proposed, overcoming important constraints of the traditional systems based on noble metals. This design combines both tunable ternary or binary alloy cores with the very thin dielectric interlayers and with ultra clean semiconductor shells in order to achieve an efficient separation of charge, as well as stability as well as a broad visible-light absorption profile. The ALD-processed fabrication guarantees atomic control of the properties of the interface maximizing the hot carrier injection and avoiding core degradation.

In the degradation of pollutants and the production of hydrogen, experimental validation shows a high level of photocatalysis and the reaction rates are higher in comparison with those associated with noble-metals. Prolonged charge-separated states as well as minimized recombination losses are confirmed as a result of spectroscopic analyses which demonstrates the efficacy

with which dielectric interlayer as well as band alignment engineering has been achieved. The efficiency factor of these hybrids is further underscored by the fact that these hybrids are cost normalized and this aspect has enhanced their scalable implementation in clean energy and environmental matters.

Subsequent studies must aim at streamlining large scale fabrication processes and addressing other types of semiconductor materials in order to address the environmental issues. The flexibility of this architecture also provides opportunities of adapting other processes which can be solar-driven including CO_2-reduction and conversion of photoelectrochemical energy. This work providing a combination of nonnoble plasmonic alloys with developed interface engineering provides a fundamental step towards next-generation high-performance, cost-effective, photocatalytic solid materials.

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Гібриди неблагородного плазмонного сплаву-напівпровідника типу ядро-оболонка для фотокаталізу видимого світла: конструкція, настроюваність та динаміка заряду

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Обмеження в оптимізації динаміки заряду та довгостроковій стабільності каталітичних матеріалів, які є дорогими, крихкими та жорсткими порівняно зі звичайними плазмонними матеріалами з благородних металів, відомі досить давно. Щоб подолати ці обмеження, ми запропонували новий дизайн фотокаталітичних архітектур: гібриди ядро-оболонка, які використовують неблагородні плазмонні бінарні або потрійні ядра сплавів у контексті напівпровідникових оболонок, призначених для контролю переносу заряду, щоб дозволити селективне керування локалізованим поверхневим плазмонним резонансом у видимому спектрі. Напівпровідникова оболонка (шари атома) напівпровідника наноситься з похибкою близько 1-5 нм, що забезпечує ефективний перенос заряду та найменшу рекомбінацію. Серед характеристик конструкції є включення надтонкого діелектричного проміжного шару, який покращує тунелювання гарячих носіїв та запобігає деградації ядра, що, у свою чергу, знижує експлуатаційну стабільність. Отримана розроблена гібридна архітектура має високу фотокаталітичну ефективність при використанні опромінення видимим світлом завдяки збільшеному розділенню зарядів та покращеній швидкості реакції. Загалом, система має високу вартість, настроюваність та стабільність порівняно з фотокаталізаторами на основі благородних металів. Сталий та масштабований майбутній плазмонний сплав на основі неблагородних металів, гібридизований з точним контролем оболонки та робочими шарами, може запропонувати високоефективні матеріали для виробництва водню, очищення від забруднюючих речовин та загального стану навколишнього середовища.

Ключові слова: Фотокаталіз у видимому світлі, Гібриди ядро-оболонка, Неблагородні сплави, LSPR, Розділення зарядів.