

Layered Double Hydroxides and Metal Nanoparticles

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Artificially designed heterostructures formed by close conjunctions of plasmonic metal nanoparticles (PNPs) and non-plasmonic (2D) lamellar nanostructures are receiving extensive interest. The synergistic interactions of the nanounits induce the manifestation of localized surface plasmon resonance (LSPR) in plasmonic metals in the specific environment of the 2D-light absorbing matrix, impacting their potential in plasmon enhanced catalysis. Specifically, layered double hydroxides (LDH) with the advantages of their unique 2D-layered structure, tuned optical absorption, ease of preparation, composition diversity, and high surface area, have emerged as very promising candidates for obtaining versatile and robust catalysts. In this research, researchers cover the available PNPs/LDH heterostructures, from the most used noble-metals plasmonic of Au and Ag to the novel non-noble metals plasmonic of Cu and Ni, mainly focusing on their synthesis strategies toward establishing a synergistic response in the coupled nanounits and relevant applications in plasmonic catalysis.

layered double hydroxides

plasmonic nanoparticles

hybrid plasmonic catalysis

1. Introduction

1.1. Hybrid Plasmonic toward Optimized Photothermal-Photocatalytic Performances

Solar-to-chemical energy conversion by plasmon-driven photocatalysis is one of the sustainable approaches for obtaining intense electric fields, highly energetic electrons and local heating as tools to develop performant solutions to efficiently solve the environment pollution and improve the usage of solar energy. Among various promising routes, plasmonic hybrid nanocatalysts feature prominent solar driven surface plasmon resonance (SPR) ^[1]. SPR is related to the collective oscillations of the conduction electrons in metals and it can be classified into two modes: propagating surface plasmons (PSP) and localized surface plasmons (LSPR) ^[2].

By engineering the LSPR responses on a catalyst-molecule interface, a surface electronic state with an optimized energy can be created to selectively modulate solar-to-chemistry conversion capabilities in catalytic processes ^{[3][4]}. Recent investigations have shown that it is possible to broaden the functionality of LSPR characteristics in multicomponent catalysts formed by close conjunctions of a plasmonic nanounit, which amplifies and concentrates the photons energy within the material, and a non-plasmonic nanocomponent that is able to play the role as support and, furthermore, to extract the plasmon energy in the form of electronic excitations to perform a targeted catalytic function ^[5]. On such a plasmonic/non-plasmonic interface the light energy harvested by the plasmonic

metal can modulate specific interactions (MSI) with the support [6][7] that are entangled with the rearrangement of electrons, transfer of photogenerated carriers and their prolonged lifetime, and the extended light-response range [8] within heterostructured components. Moreover, the photogenerated carriers can promote shorter diffusion length with less recombination probability and enable superior photo-thermal-photocatalytic performances [9][10].

Currently, examples of heterostructured plasmonic photocatalysts include plasmonic-metal/metal [11] plasmonic-metal/2-D materials [12], plasmonic metal/carbon-based nanostructures [13], plasmonic metal/ metal-organic frameworks (MOFS) [14], or plasmonic-metal/molecule systems [9][15][16][17].

2. 2-D Nanoarchitectures of Layered Double Hydroxides as Light Absorbers

Layered double hydroxides materials are a class of anionic clays with well-defined 2D lamellar structures and special characteristics, which makes them very attractive for many applications, e.g., as stable and recyclable adsorbents, heterogeneous catalysts, or catalyst supports for a variety of reactions with high industrial and academic importance. LDH-type materials are recognized to provide eco-friendly and low-cost solutions for today's problems related to pollution or energy requirements [18]. Most of the LDH are synthetic and relatively simple and cheap to prepare on both the laboratory and industrial scale, respectively [19][20].

LDH are conventionally described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} \cdot A^{n-}_{x/n} \cdot mH_2O$, where the divalent M^{II} and trivalent M^{III} cations may be Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , Al^{3+} , Fe^{3+} , etc., and the A^{n-} can be almost any organic or inorganic anion [21][22]. LDHs may also be composed of M^I or M^{IV} , for example, Li^+ [23][24] or Ti^{4+} [25][26], Sn^{4+} [27][28], respectively. In such structures, the metallic cations are octahedrally coordinated to hydroxyl ions and form infinite layers of edge-shared MO_6 units.

Considerable research efforts are continuously realized into the design of different LDH-type structures for photocatalytic purposes due to their unique properties, i.e., their great adsorption capacity, which may be extended to visible light absorption via compositional variation, well dispersed MO_6 units, and O-H surface bonds that can react with holes of valence bands to produce hydroxyl radicals, unique layered morphology and high specific surface area, possibility of transformation to mixed metal oxide special structures and unique memory effect features, and last but not least, the availability of cheap and scalable synthesis procedures. All these valuable features indicate their advantageous application as photocatalytic materials (in the form of non-calcined LDH, mixed metal oxides, or as supports in hybrid nano-assemblies) for various applications, such as in renewable energy production and storage (water splitting, CO_2 reduction, alcohol photo reforming, batteries) [12][29][30][31] or pollutant degradation/removal in wastewater management [32][33][34][35][36][37][38][39].

LDH allow a very flexible choice in the nature of the metallic cations type to be inserted in the brucite-like sheets, resulting in binary, ternary, or multicomponent LDH, which together with the facile exchangeability of intercalated anions, facilitate their nanoscale tailoring for boosting the photocatalytic reactions. The cations in the MO_6 octahedral units are distributed in a uniform manner without clustering, offering a good metal dispersion,

facilitating a wider separation of the electron–holes pairs, and thus, enhancing the photocatalytic activity by reducing the recombination. The combination of widely dispersed octahedral units sharing edges in a specific configuration in LDHs with variation of the nature of the metallic cations specifically identified as active in photocatalytic processes is of high importance. Various photocatalytic functionalities can be introduced by the isomorphous substitution of key metallic cations, as these can act as light absorbers and/or co-catalysts. In this context, the maximization of light harvesting (with extension to visible light) can be mentioned to generate sufficient energetic electrons and holes with high mobility, suppressing their bulk recombination and allowing sufficiently strong redox power to induce the targeted reactions. The effect is similar as the one achieved by coupling semiconductor nanoparticles having different band gap positions [40][41][42][43]. By tuning the LDH composition, the newly developed LDH materials may be regarded as nano assemblies of semiconductor nanoparticles where the advantageous layered network provides highly distributed metal cations in which the contact between the semiconductor active centers/sites is realized at the atomic level rather than at the particle level. This is of particular importance, as such highly uniformly dispersed catalytic active sites are not easily obtained in practice, where the control of homogeneity, consistency, and reproducibility is still a major issue, even at the laboratory scale.

Many research reports are demonstrating the importance of the mixed metal oxides derived from LDH structure as highly efficient photocatalysts as well as photocatalytic supports. The unique memory effect property is advantageously employed in heterostructuring of nanoparticles, e.g., of metals (PNPs) or oxides, stabilizing the PNPs onto the LDH surface or in the interlayer, controlling their morphology. The obtained heterostructures show the synergistic effects of the individual nano-units, with modified electronic structure, enhancement of light harvesting and improved photocatalytic efficiency [12][39].

As mentioned above, an important strategy of shifting the photoresponsive properties of the LDH-type materials and harvesting the visible light is to isomorphously insert key cations, e.g., Cu^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , Cr^{3+} or Y^{3+} within the hydroxylic 2D [31][42][43][44]. ZnCr-LDH is recognized for its potential of harvesting visible light irradiation [30][45]. Further, the hybridization of ZnCr-LDH with Au PNPs was reported to promote the degradation of gaseous volatile organic compounds and the nano-structuring of AuPNPs onto the LDH surface increased the photodegradation efficiency under visible light up to 83.6% [38]. Zhong-zhu Yang et al. describe that, in water splitting reactions, the transition metal-LDH or its nanocomposite is spatially separating the oxidation and reduction reaction sites due to the presence of both anions and cations in LDH which are both acting as reaction sites [43]. The tuning of the visible light absorption was also demonstrated for ternary LDHs composed of ZnCuAl or ZnCuGa [29] for which a red shift of their light absorption was observed. It was concluded that the insertion of Cu extended their absorption towards visible range based on the generation of an electronic state induced by Cu ions, leading to the narrowing of the LDH band gap. Furthermore, the same study, which focuses on the CO_2 conversion, reports that the insertion of Cu ions also influenced the selectivity towards methanol formation due to the fact that the Cu sites are also acting as binding sites for the CO_2 molecules, thus, interacting with the photogenerated electrons, protons and the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ redox couple. As a consequence, the CO_2 molecules undergo a series of reduction reactions, forming CH_3OH selectively. The narrow band gap is aligning with the redox level of $\text{CO}_2/\text{CH}_3\text{OH}$, which is favorable for the production of CH_3OH under light irradiation. CoAl-LDHs manifest also a narrowed band gap

with consequent absorption in visible range. By measuring the UV-Vis absorption spectrum of CoAl LDH, it was demonstrated that the light absorption lies in the visible range and the photocatalyst has an estimated band gap of 2.1 eV [29]. Such a photocatalyst was used in the conversion of very low concentrations of atmospheric CO₂ and water to CH₄ [46]. The improved photocatalytic conversion and CH₄ generation was based on (i) the ability of to capture the visible light, (ii) the enhanced CO₂ adsorption by the surface OH groups, and (iii) the unique effect of divalent Co. Bai et al. studied the effect of the various cations (Mg²⁺, Ni²⁺, Co²⁺, or Zn²⁺) in the conversion of CO₂ under visible light irradiation and using the [Ru(bpy)₃]Cl₂ · H₂O as photosensitizer. Among the studied photocatalysts, the CoAl-LDH exhibited the highest CO conversion rate and H₂ production, and the NiAl-LDH showed the highest CH₄ production due to the selectivity of Ni towards CH₄. These photocatalytic performances were associated with (i) the improved light absorption and capturing the maximum of visible light region, (ii) the defects on the photocatalyst surfaces promoting CO₂ adsorption, and (iii) well matched energy levels of the LDH with the photosensitizer molecules, thus, under light irradiation, the photogenerated charges are drained towards the LDH surface where they can efficiently react with the adsorbed CO₂ [47].

The anions in LDH were demonstrated as having a positive influence also due to the effect on the LDH light absorption range, enlargement of the specific surface area, and modulating the interlayer spacing among the LDH layers, which improves the photocatalytic performance by facilitating the essential reaction between the reactants and the photoinduced charge carriers [48][49]. It was demonstrated that the interlayer space within the LDH layers act as an active site when Cu is present, such as in the situation when the CO₃²⁻ anions were exchanged with [Cu(OH)₄]²⁻ anions. An increased CO₂ conversion with selective CH₃OH formation was demonstrated when [Cu(OH)₄]²⁻ anions were intercalated, mainly assigned on the band gap narrowing and light absorption shifting after the intercalation of the [Cu(OH)₄]²⁻ anions [50]. Fluorine anions were found to enhance the photocatalytic activity based on the increased surface area of fluorinated LDH, while Cl⁻ anions were demonstrated as acting as hole scavengers in a photocatalytic reduction of CO₂ using Cl intercalated NiAl-LDH, owing to the strong reducing character of Cl⁻ which is rapidly oxidized by holes, yielding HClO and selective formation of CO [51]. Intercalated organic anions, e.g., acetate anions, were also found to be advantageous in photocatalytic CO₂ conversion owing to the decomposition of the acetate anions absorbed on the LDH surface, which facilitates the electron transfer towards the CO₂ sites within the LDH [52].

In addition, the hydroxylated brucite-like layers are also advantageous for photocatalytic reactions. The surface-OH groups in LDH participate in the photocatalytic reactions in two different ways. First, the hydroxyl groups may be converted to hydroxyl radicals, which may be considered as the most effective reactive species responsible for photocatalysis [31][53]. Second, they may facilitate the formation of the ligand to metal charge transfer (LMCT) complexes on the surface of the semiconductor inorganic matrices, which favor the electron transfer and reduce the recombination, which promotes the process and enhances the photocatalytic efficiencies [54].

3. Heterostructures of Plasmonic Metal Nanoparticles/Support

3.1. Plasmon Excitation in Metal Nanoparticles

Certain metal nanoparticles own unique optical properties that lead to the manifestation of SPR. Essentially, there are two experimental signatures of SPR: propagating surface plasmons (PSP) and localized surface plasmons (LSPR). Herein, researchers define metal plasmon nanoparticles as nanoparticles of metals that interact with photons through an excitation of LSPR. LSPR concentrates electromagnetic fields to the surfaces and its relaxation processes lead to convert photon energy to energetic charge carriers or heat, which can be harvested in photocatalysis [55]. It was revealed that LSPR response (intensity) is a function of both the nature of the metal and the size/shape of the nanoparticles [56]. However, most PNPs suffer from instability, aggregation behavior, and susceptibility to various “poisoning” issues, limiting their use in catalysis through deactivation and poor reusability [57]. To address these challenges, heterostructures of plasmonic metals stabilized on a support is an important approach. The support has the role to confine and stabilize the PNPs and, furthermore, to modulate the evolving plasmonic energy within the heterostructure [58]. Notably, representative progress in the field points to the high impact of the synthesis strategies in establishing the characteristics associated with LSPR and MSI (metal–support interaction) in hybrid nanostructures [59].

In recent years, nanosized Au, Ag and Cu received most of the attention because they exhibit resonant behavior when interacting with ultraviolet and visible (UV-Vis) photons in the condition that a large fraction of light consists of UV-Vis photons. Additionally, non-noble PNPs (e.g., Ni) are newly emerging as an alternative to noble-metal-based ones due to their advantages, such as earth-abundance, cost effectiveness and application capabilities, and until now, they were investigated to a much lesser extent. Therefore, herein, researchers shortly point out some recent achievements regarding the fabrication of noble (Au, Ag) and non-noble (Cu, Ni) plasmonic nanoparticles/support heterostructures.

3.2. Heterostructures of Noble Plasmonic Metals/Support

Since they were discovered, noble plasmonic nanoparticles have attracted the attention of researchers from all over the world due to their special optical properties. Most studies were conducted on AuPNPs, AgPNPs, due to their unique features, such as great stability, simplicity in chemical synthesis, and controllable surface modification [60].

Wang et al. fabricated 0D/2D Au/TiO₂ in a two-step process. First, TiO₂ was prepared by a hydrothermal method and further decorated with AuNPs using the in situ growth method. They obtained square-shaped TiO₂ nanosheets decorated with 5 nm size AuNPs recognized in the heterojunction. This type of 0D/2D heterojunction is ideal for separating photogenerated charges [61]. One-step synthesis was used by Kunthakudee et al. [56] to synthesize Au/TiO₂ with a simple photo-deposition method. They mixed commercial TiO₂ with a HAuCl₄ solution and irradiated it with UV-visible light. During the irradiation, the temperature of the reaction was kept constant at 30 °C. A 0.5M NaOH solution was used to regulate the pH to the desired range (3.2–10). The obtained precipitate was separated by centrifugation, washed with water, and dried at 80 °C. The morphology showed semi-spherical AuNPs with a large average diameter of the particles. They proved that pH during the synthesis played a key role in tailoring the particle size of AuNPs, respectively, oxidation state. Thus, a decrease in the size of gold nanoparticles (from 34–77 nm to the range of 2.53–7.85 nm) was observed with increasing pH (from 3.2 to 10). Additionally, they found that at

a lower pH (3.2), gold nanoparticles were deposited in metallic (Au⁰) and ionic (Au^{III}) states, while at higher pH (10) they were only in the metallic state [62]. Furthermore, Chang et al. reported the decoration of carbon nanorods (CN) and g-C₄N₃ by AuNPs using the hydrothermal reduction method. Primarily, they obtained carbon nanorods by the solvothermal method. Furthermore, the CN was mixed with an aqueous solution comprising the gold precursor (HAuCl₄) and glucose and stirred for 30 min. The obtained mixture was hydrothermally treated in an autoclave at 120 °C for 12h. As final steps, centrifugation, washing with water, and drying of the precipitate were performed. Au/g-C₄N₃ was synthesized by the aforementioned method. XPS measurements confirmed the presence of Au in the metallic state on the surface of CN and g-C₃N₄. UV–vis-NIR diffuse reflectance also confirmed the metallic state of AuNPs by the presence of the peak from 550 nm due to the LSPR effect of AuNPs [63]. An in situ method was used by Kashyap et al. to obtain AuNPs/CN nanosheets with high catalytic activity in Rhodamine B photodegradation. The CN nanosheets were obtained at 520 °C from urea with a 224 nm flake size. Spherical shaped AuNPs covering the CN nanosheets with a diameter 10.8 nm were noticed by HRTEM analysis. The XPS measurements revealed the presence of metallic Au⁰ and Au^{δ+} species. Due to the –OH adsorbed groups that bind with the oxidized Au⁺ species, the Au₂O was formed [64]. A novel type of support for plasmonic metal nanoparticles widely used in photocatalysis are metal-organic frameworks (MOFs). In comparison to more conventional materials such as zeolites and clays, MOFs perform better because they are a revolutionary type of porous material with tunable pore size, improved specific surface area, and outstanding porosity [65]. Thus, Liang et al. reported the immobilization of AuNPs on MIL-100(Fe) by a facile photodeposition method. They obtained homogenously dispersed AuNPs on MIL-100(Fe) in the metallic state Au (0) with an average size diameter of 15 nm [66]. By the same method Cure et al. diffused ultra-small AuNPs (1 nm) into the MOFs (thiol-functionalized MOFs, including MIL-101 (Cr), MOF-808-SH) pores. They found out that thiol groups stabilize the AuNPs firmly into particular pores, maintaining their nucleation, and keep them apart. During the synthesis, AuNPs were completely reduced from Au(III) to Au(0) in the methanol solution, a fact that was confirmed by XPS analysis and the presence of the peak at 550 nm in the UV-vis spectrum due to the LSPR effect of AuNPs [67].

Silver nanoparticles deposited on different supports have demonstrated their potential in photocatalysis for more than three decades. A study by Stucchi et al. reported the preparation of Ag/TiO₂ by an ultrasound-irradiation-assisted reduction method with high photocatalytic activity in acetone degradation. AgNO₃ salt was used as the silver precursor and NaBH₄ as the reducing agent. Their findings showed an effect from ultrasound treatment on the silver nanoparticles morphology. The ultrasound treatment favors the agglomeration of AgNPs on the TiO₂ surface. Thus, not well distributed and different sizes of AgNPs (between 1 and 10 nm) were obtained. XPS analysis showed the formation of different species of Ag, such as metallic Ag⁰ and Ag₂O [68]. Rabhi et al. doped TiO₂ with Ag using the sol-gel method as a photocatalyst in pharmaceutical effluent degradation. XRD results showed the formation of a tetragonal anatase-rutile phase and the Ag metallic phase. They noticed that increasing the concentration of Ag promotes the increasing of the rutile phase amount in the material [69]. Recently, a low-cost modified combustion method for synthesizing Ag/TiO₂ was reported by Cruz et al. They obtained a tetragonal rutile phase decorated with metallic AgNPs. TiO₂ with a granular morphology was obtained with a size ranging from 0.1µm to 1µm, as well as Ag with a size between 0.294 µm to 0.506 µm. The morphology of the obtained materials did not change after use in the photocatalytic degradation of methylene blue [70]. The deposition of AgNPs onto the

g-C₃N₄ were also reported. Chen et al. synthesized Ag/P-g-C₃N₄ in a 2 step method. In the first step, P-g-C₃N₄ was fabricated by thermal polymerization. Furthermore, the AgNPs were loaded by a photo-deposition route. The presence of (111), (220), and (311) planes show a cubic structure of AgNPs with a diameter size between 5 to 10 nm and non-uniformly distributed [71].

3.3. Heterostructures of Non-Noble Plasmonic Metals/Support

In the last few years, non-noble metals (Cu, Ni)-based plasmonic nanoarchitectures have attracted tremendous attention in the field of photocatalysis. Compared to the limited number of counterpart noble metals, the non-noble metals are considerably cheaper, highly available, and offer a broader spectral range of photoactivity, expanding the application area. Regarding the synthesis approaches, the discussion is similar to the many catalysts that require a specific nanoarrangement in terms of particles size, shape, or design (sandwich-like, nanotubes, nanosheets, nanoflakes, etc.) and the bottom-up method is by far preferred to the detriment of the top-down option. Furthermore, the non-noble metals are considerably more prone to form an oxide layer on the surface or even in the bulk regions, which may affect directly the photoresponse. In this regard, and taking into account the already extended focus on the preparation of noble metals plasmon nanoparticles (MeNPs), it is important for the future to draw the level between the advanced noble metal nanoparticles syntheses and, for the moment, primitive non-noble metal plasmons obtaining methods [9][72]. The current section targets the construction methodologies of photocatalysts consisting of non-noble metal nanoparticles (Cu, Ni), coupled with different inorganic or organic semiconductors or supports.

As one of the most studied materials in the photocatalysis field, TiO₂ represents a viable support for plasmonic MeNPs due to its outstanding long-known properties. Wei et al. designed an interesting heterostructure containing Cu NPs deposited on TiO₂ hollow spheres following a series of steps. First, carbon spheres (CS) were decorated with Cu NPs (Cu/CS) via a hydrothermal process. The resulted system was coated with TiO₂ using a controlled hydrolysis approach to obtain the Cu/CS@TiO₂ heterostructure. Finally, the Cu/CS@TiO₂ was calcined to remove the carbon spheres, and the catalyst was photoreduced. The electron microscopy investigations revealed that the resulting material was composed of Cu NPs of around 10 nm and TiO₂ hollow spheres with a diameter between 500–800 nm [73]. A simple and efficient Cu deposition on TiO₂ aerogels was employed by DeSario et al. involving a sol-gel method followed by a classical photodeposition of Cu NPs. Herein, the resulting composite revealed TiO₂ aerogels NPs of 10.3 ± 2.3 nm, while the Cu NPs, consisting of a mixture of Cu⁰, Cu¹⁺, and a very small amount of Cu²⁺, have a relative diameter of 3.2 ± 0.7 nm [74]. Dai et al. built up a photocatalyst consisting of Cu₂O octahedrons decorated with Cu NPs, to form an ohmic junction photocatalyst Cu@Cu₂O. In their study, the synthesis of the Cu₂O octahedrons was the first step, followed by an in situ chemical reduction with Cu⁺. The octahedra-like Cu₂O crystals had diameters between 400 and 800 nm, while the tiny Cu NPs were anchored on the surface of the parental Cu₂O [75].

In addition to Cu plasmonic NPs, remarkable results in environmental photocatalysis were observed also in the presence of Ni plasmons containing catalysts. As such, He et al. created a Ni-TiO₂ heterostructure following an adapted mediated nanosphere lithography method. The results showed a homogeneous layer of 200 nm

TiO₂ deposited on silica nanospheres, on top of which another layer of 100 nm of Ni was attached. The size of the Ni-TiO₂ top layers with the SiO₂ nanosphere as a core can be tuned specifically to influence directly the optical properties [76]. Wang et al. developed a system consisting of black TiO₂ nanowire arrays, on top of which size-controlled NiNPs were deposited. The black TiO₂ was obtained via a hydrothermal approach, followed by the thermal hydrogen treatment, while the NiNPs were deposited via atomic layer deposition (ALD). Black titania nanowires characteristics were found to be around 25 nm in diameter and approximately 3.2 μm length. At the same time, NiNPs size could be controlled from the cycles of the ALD applied [77]. Tudu et al. designed another type of heterostructure consisting of a non-noble-metals bimetallic alloy, Cu-Ni, integrated in a TiO₂ thin film. The Cu-Ni alloy synthesis followed a classical hydrothermal approach, using hydrazine hydrate and NaOH solution as a reducing agent and alkali environment, respectively. In order to obtain the Cu-Ni/TiO₂ nanohybrid, the authors used a simple impregnation pathway by suspending the well-known P25 (TiO₂) in ethanol and mixing it with the Cu-Ni alloy suspension in ethanol. The textural investigations revealed the formation of an alloy-semiconductor heterojunction between spherical Cu-Ni NPs with a homogeneous particle size distribution (20–30 nm) and irregular TiO₂ crystals [78]. Kumar et al. had a similar idea to employ the synergistic effect of Cu and Ni in Cu-Ni alloy NPs dispersed in the same P25 (TiO₂) matrix. The synthesis procedure was reported to involve the co-impregnation of TiO₂ with Cu and Ni nitrates, with the formation of the Cu-Ni alloy during the photocatalytic tests as a result of the mild photoreduction conditions. The electron microscopy analysis revealed the intimate contact between Cu-Ni alloy NPs a few nm in size and irregularly shaped anatase/rutile nanocrystals [79].

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