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Two-step photochemical inorganic approach to the synthesis of Ag-CeO₂ nanoheterostructures and their photocatalytic activity on tributyltin degradation



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ABSTRACT

Herein, we report a simple, sustainable and low-cost approach to design Ag-CeO₂ nanoheterostructures in pure aqueous and ethanol containing aqueous solutions *via* photochemical UV-light driven process with no capping agents nor stabilizers required. To this end, photochemically synthesized CeO₂ nanoparticles were applied as photoactive compounds in order to generate formation of metallic silver nanoparticles. Irradiation of deaerated CeO₂ suspensions in the presence of Ag⁺ resulted in the rise of a strong surface plasmon resonance band with a maximum at 393–422 nm in the absorption spectra of the solutions, indicating formation of small metallic silver particles. Faster formation of Ag nanoparticles with the lower amount of silver precursor being required was observed when ethanol was introduced to the reaction solution before the irradiation. This implies that oxidative reactions can be strongly suppressed in deaerated ethanol containing solutions with respect to the pure aqueous media. Not only was the overall efficiency of the process remarkably increased by the use of alcohol, but also smaller and more uniform silver nanoparticles with a size comparable to that of ceria nanoparticles (around 15 nm) were formed when compared to those synthesized without radical scavengers as revealed by TEM analysis. The proposed photochemical approach enables the production of silver-semiconductor system without employing organic stabilizers, thus resulting in formation of nanoparticles with “clean”, highly reactive metal surface. The as-synthesized silver-ceria nanoheterostructures demonstrated enhanced visible light driven photocatalytic activity on tributyltin (TBT) degradation if compared to pure ceria nanoparticles.

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1. Introduction

The enduring attention towards nano-dimensional metal nanoparticles (NPs) is basically raised by their ability to be applied in relevant processes, such as molecular diagnostics [1–4], catalysis, electronics [5], wastewater treatment [6], to mention just a few. Moreover, so-called plasmonic nanoparticles, such as Ag, Au, Cu and Al, also became enablers for a completely different set of applications that involve light [7–10]. Because of the unique capacity of plasmonic metals to scatter electromagnetic radiation,

concentrate electromagnetic fields or convert the energy of photons into heat, they are suitable to use in solar cells [10], single-molecule and surface-enhanced Raman spectroscopy [11–13], heat-induced selective tissue targeting [4] or in environmental processes, i.e., for photocatalytic decomposition of organic pollutants [14].

Heterogeneous photocatalysis has been considered as a cost-effective alternative for the destruction of persistent toxic organic compounds [15]. Some photocatalytic activity arising from the excitation of surface plasmons has been reported for plasmonic nanostructures [16,17]. However, direct plasmonic photocatalysis is generally regarded as improbable due to the short lifetimes of plasmon derived charge carriers as well as extremely fast quenching of electronically excited adsorbates on metal surfaces [18]. Photocatalysts for various chemical transformations induced

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by UV light are almost exclusively wide bandgap semiconductors, such as TiO₂ and ZnO [19]. The main disadvantage of such photocatalysts is, however, their limited solar energy conversion efficiency as UV region represents only ~4% of the solar spectrum at the sea level [20]. One of the possible attempts to overcome this problem could be the incorporation of plasmonic metal nanostructures into semiconductors thus extending light absorption to longer wavelengths, increasing light scattering, and exciting electron-hole pairs in the semiconductor by transferring the plasmonic energy from the metal to the semiconductor [21–23].

There are several approaches for the preparation of plasmonic NPs, supported on the semiconductor nanostructures. One of the most popular routes would be a two-step method that involves the initial synthesis of noble metal nanoparticles, which are further combined to a suitable support [24,25]. Co-impregnation and co-precipitation are probably the second most commonly applied techniques for the preparation of supported nanoparticles [26]. However, aggregation and a difficult size control of the noble metal particles are the main problems attributed to these methods.

The use of semiconductor nanoparticles provides the possibility to apply completely different route to the formation of noble metal NPs. It was observed by many researchers that irradiating semiconductor nanoparticles (TiO₂, ZnO, CdS, etc.) in the presence of metal (Ag, Au, Cu, Pb or Cd) ions can result in reduction of the metal cations and that this process is accompanied by formation of nanosized metal-semiconductor structures [27–30]. Light-assisted synthesis, if comparing to standard chemical approaches, (i.e. precipitation or solvothermal methods), provides advantages of a uniform distribution of the reducing agent in the entire solution, rather mild reaction conditions, and high reproducibility [31]. Whereas organic solvents or photoactive compounds are usually essential components of photochemical synthesis [32,33], the use of inorganic semiconductive nanostructures as photoactive compounds provides a possibility to carry out the process in aqueous solution. This is a huge advantage considering that organic compounds, employed in colloidal synthesis, would be able to block a number of active sites of catalytic materials due to the strong interaction with the metal surface and to the sterical hinders, thus leading to the loss of catalytic activity to a great extent. In addition, organic ligands are expected to exhibit susceptibility to chemical oxidation on the surface they protect, and exposure to UV radiation should accelerate this process [34,35].

Ceria is known for its structural stability up to 650 °C, the ability to absorb UV radiation, and, most interesting, the oxygen storage activity [36–38]. Because of the latter property, CeO₂ modifies the catalytic performance of the elements in contact by either providing to or withdrawing oxygen from them [39]. This can result in improved catalytic performance of the material in contact. For instance, it was observed that Pt supported on ceria trends to form Pt–O–Ce bond in the interface region between Pt particles and ceria. The existence of oxidized Pt is assumed to accelerate methanol decomposition by withdrawing the electron from the methoxy group to Pt and thus weakening the C–H bond [40]. Different behavior of ceria was reported in the silver-ceria system. It is found that ceria accelerates desorption of the lattice oxygen of Ag₂O, facilitating silver conversion to metallic state. Such Ag–CeO₂ catalyst demonstrated high catalytic activity in the process of carbon monoxide oxidation [39].

Despite demonstrating these unique and outstanding properties, ceria nanoparticles have not been extensively studied by the means of supported metal nanoparticles photochemical synthesis yet. Neither is CeO₂ frequently applied for photocatalysis like other wide bandgap semiconductors, such as TiO₂ and ZnO, although being reported to be less toxic than the latter compounds [41,42]. A photochemical approach to the formation of supported silver

catalysts on ceria was briefly presented by Scirè et al., albeit more stress was put on the Ag–TiO₂ system in the latter study. Moreover, both TiO₂ and CeO₂ were only studied as metal NPs supports, not taking into consideration their reductive properties under UV light [24].

The motivation of this work is to prepare Ag–CeO₂ nanoheterostructure *via* photochemical inorganic synthesis and to characterize this potential photocatalyst with visible light activity. Metallic silver was photocatalytically generated upon UV illumination of deaerated aqueous CeO₂ dispersion containing AgNO₃. The proposed photochemical approach enables the production of silver-semiconductor heterostructures without employing organic stabilizers and additives, thus resulting in formation of nanoparticles with “clean”, highly reactive metal surface. The photocatalytic properties of the products obtained were checked on photocatalysis of tributyltin.

2. Experimental

Synthesis of both ceria nanoparticles and CeO₂–Ag nanocomposites were performed using a 40 W low pressure mercury discharge lamp NIQ 40/18–45000024 (Heraeus – Amersil, Germany), emitting a spectrum with lines at 185, 254, 313, 365, 405, 436, 546, 579 nm.

2.1. Preparation of the CeO₂ nanostructures

CeO₂ nanoparticles were synthesized *via* photochemical route using sodium azide as a photoactive compound. Similar synthesis procedure is reported elsewhere [43], yet some essential modifications were applied this time. Although both Ce(NO₃)₃·6H₂O and CeCl₃·7H₂O could be used as starting materials for CeO₂ formation with no significant differences in the final products being observed [43], even a small amount of residual chloride ions would participate in a reaction with silver ions because of the low solubility product constant of AgCl ($K_{sp}(\text{AgCl}) = 1.77 \times 10^{-10}$) [44]. Unavoidable formation of some AgCl was observed in our studies, even if CeO₂ particles were washed numerous times before the reaction with silver salt (Supplementary information Figs. S1, S2). Considering this, cerium nitrate was chosen as the cerium source. Also, irradiation time was increased considerably if compared to the previous process, where the maximum irradiation time was 90 min only. In order to obtain larger nanoparticles with a better yield, the photochemical reaction has been carried out for 300 min this time. Lower concentrations of ceria precursors were applied than in the previous case with a goal to decrease the agglomeration ratio of uncoated nanoparticles.

Typically, 1.500 g of Ce(NO₃)₃·6H₂O (99.99%; Sigma-Aldrich) was dissolved in 50 mL of deionized water. After stirring the solution for 10 min, 0.200 g of sodium azide (99.95%; Sigma-Aldrich) was added to the solution, which was then diluted up to 250 mL. Subsequently, the homogeneous solution was transferred into a 250 mL volume home-made glass reactor and stirred in the dark vigorously for 30 min before the irradiation was started. The nitrogen gas was flushed through the solution at this stage as well as during the reaction. After irradiating the reaction mixture for 300 min, the finely dispersed solid phase was centrifuged for 60 min at 7000 rpm (Eppendorf 5804), the particles obtained were washed with deionized water five times and dried at 60 °C overnight.

Caution

Although sodium azide is a valuable substance in photochemical synthesis, it is nonetheless a toxic, reactive and energetic material and appropriate safety precautions should be taken. Care should be taken whenever working with metal azides which are

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