



Short Communication

Evaluation of gold-decorated halloysite nanotubes as plasmonic photocatalysts



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ABSTRACT

Herein we report on the synthesis of gold-decorated halloysite nanotubes (HNTs) and their evaluation as photocatalysts in the degradation of a model organic contaminant. The combination of photo-thermally-induced local heating and charge transfer mechanisms between the nanostructured gold surface and the organic molecule results in the observed dye decomposition. The use of an inexpensive natural clay support with suitable surface chemistry and adsorption properties represents an eco-friendly method for light-induced oxidation reactions carried out at ambient temperatures.

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1. Introduction

The search for alternative strategies for conventional thermally-driven catalytic processes represents a scientific challenge of increasing interest. Greener routes involving more efficient reactors and the use of naturally available sources have boosted the research on photocatalysts able to drive chemical reactions in the presence of UV–Visible light. The most extended group of photocatalysts is based on semiconductor materials such as TiO₂ or ZnO, that are able to generate electron–hole pairs in their conduction and valence bands respectively and form reactive radicals for secondary processes [1,2]. In order to improve their photocatalytic activity or shift their efficiency towards the visible spectrum, different hybrid structures containing noble-metal nanocrystals or nanostructured quantum dots have been also successfully evaluated [3–7]. These nanostructured materials decorated onto photo-active semiconductor supports are used as photo-sensitizers that enhance the electron–hole pair's lifetime and the electron-transfer phenomena occurring at the nanoparticle–semiconductor interface.

Nevertheless, a renewed attention is currently being paid to the direct photo-catalytic effect of noble-metal nanoparticles [7–14]. Several activation mechanisms have been proposed to justify their

photo-active nature without incurring into the same photo-catalytic principles applied to semiconductors. The most extended so far involves the so-called Surface-Plasmon-Resonant (SPR) effect [15]. This SPR effect occurs when metal nanoparticles strongly absorb light at certain wavelengths (normally in the visible–NIR range) and the electromagnetic field of the incident light couples with the oscillation of the conduction electrons present in the metal nanoparticles. The SPR absorption may cause rapid heating of the nanoparticles when the electrons return to their basal states and release heat to the lattice and the surroundings [16]. This photo-thermal effect may strongly enhance reaction rates and selectivities. A second enhancement mechanism based on the injection of electrons into the unoccupied molecular orbitals of the targeted molecules has been also suggested and is currently under investigation [10].

In this work, we present a rationalized synthesis of gold-decorated halloysite nanotubes (HNTs) and their evaluation as photocatalysts. We prove that a careful selection of gold nanoparticle sizes is required to match the resonant frequency of the incident green laser. In addition, an efficient distribution of the gold nanoparticles deposited onto the HNTs is crucial to promote the photo-decomposition of the dye. Moreover, the HNTs, naturally occurring aluminosilicates with [Al₂Si₂O₅(OH)₄·nH₂O] nominal composition and a representative morphology where silica tetrahedrons and alumina with octahedral structure form hollow nanotubes are presented as a readily available

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and inexpensive support with suitable surface chemical composition for the attachment of nanoparticles.

2. Results and discussion

The amine-grafting of the halloysite nanotubes and the subsequent gold seeding process were confirmed by TEM as depicted in Fig. 1a–b (see Supporting information for further synthesis details). The electrostatic attraction between positively charged amine terminal groups and negatively charged Au NPs, especially at low pH values, favored a suitable coating and distribution of the pre-formed metal nanoparticles. The Au NPs were synthesized in advance with the aid of THPC as reducer and stabilizer [17,18] and the amination of the tubular clay support was carried out under mild conditions using a simple flask without any especial precaution with air or humidity, since inert conditions did not render a better anchoring of Au NPs despite possible self-polymerization events of APTES. Further details on the synthesis are fully described in Supplementary information and in previous works [19,20].

Fig. 1c shows the SPR absorption band for both Au-HNT samples centered at ca. 530 nm. Therefore, the optical maximum absorption of the catalysts perfectly matched with the incident green laser wavelength (532 nm) used in the photocatalytic experiments. The average diameter of the pre-formed Au NPs was ca. 5.3 ± 1.6 nm for the catalyst with 2% loading (see inset in Fig. 1a) and slightly higher for the HNTs with 4.2 wt.% Au (6.2 ± 2.7 nm; see inset in Fig. 1b). The main differences were based on the gold size distribution along the HNT support (see Fig. 1a–b). The HNTs with 4.2 wt.% Au loading contained bigger

agglomerates of nanoparticles and wider size dispersions, thereby coinciding with the partial broadening of the SPR band observed in Fig. 1c.

Both Au-HNT samples with different gold loadings and their respective control experiment in the absence of catalyst were tested for the degradation of Methyl Orange (MO) as organic contaminant, under different laser irradiation intensities. As shown in Fig. 1d, only the sample with 2 wt.% Au content increased the MO decomposition rate as the laser intensities increased from 0.2 to 2 W. A 16-fold enhancement of the MO degradation was observed at the maximum power in comparison with control conditions (Fig. 1d). The Au-HNT sample with 4.2 wt.% Au slightly decreased the initial MO concentration by only 4% at the maximum applied power of 2 W (see Fig. 1d). Additional experiments under similar experimental conditions were performed using different excitation sources such as a red laser (633 nm) and an UV Hg lamp with two bandpass filters at 254 and 365 nm, respectively. The absence of dye degradation further corroborated the plasmon-enhanced photocatalytic effect of the Au-HNTs when the SPR maximum absorption and the incident laser wavelength overlapped (green laser conditions).

The light-driven degradation mechanism of MO can be partly ascribed to thermal heating effects induced by the resonant excitation of the plasmonic electrons in the Au NPs. This resonating oscillation coupled with the incident low-power laser wavelength is converted into lattice vibrations and finally released as heat [16]. This principle has been previously observed for gold nanoparticles in phototherapy and remotely photo-triggered heating release experiments [19,21]. Moreover, the plasmon-mediated oxidation of carbon monoxide [22],

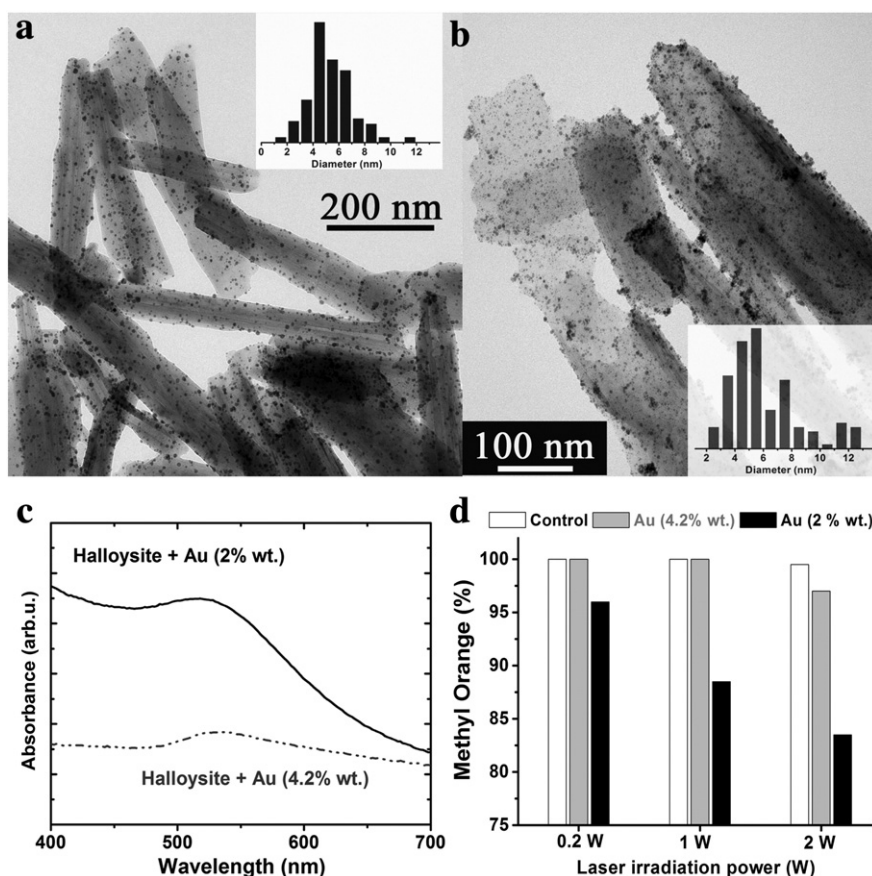


Fig. 1. TEM images corresponding to the amine-functionalized halloysite nanotubes after the seeding step with gold nanoparticles prepared with different volumes of the initial 1 wt.% HAuCl₄ salt precursor (see Section 2 for details). a) HNTs with 2 wt.% Au loading (inset includes the Au NP size distribution centered at 5.3 ± 1.6 nm); b) HNTs with 4.2 wt.% Au loading (inset refers to the Au NP size distribution centered at 6.2 ± 2.7 nm); c) UV-Vis spectra of the Au-HNT catalysts with different Au loadings; d) degradation of Methyl Orange in the absence (white column) and the presence of the Au-HNT catalysts under different laser irradiation power values (concentration of catalysts: 0.5 g L^{-1} ; concentration of dye: 20 mg L^{-1} ; volume of reaction: 1 mL; irradiation time: 1 h).

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