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The effect of gold shape and size on the properties and visible light-induced photoactivity of Au-TiO_2

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ABSTRACT

In the present investigation, TiO_2 modified with a different geometry and size of gold particles, such as nanospheres (NSPs), nanostars (NSTs) and nanorods (NRs), were prepared by the immobilization method. The effect of the gold shape, size and TiO_2 matrix type (TiO_2 microspheres or rutile TIO-6_TiO_2) were systematically investigated. The obtained photocatalysts were thoroughly characterized by UV–vis diffuse-reflectance spectroscopy (DRS), BET surface area measurements, scanning electron microscopy (SEM), scanning transmission microscopy (TEM), X-ray diffraction analysis (XRD), and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity under visible light ($\lambda > 420$ nm) has been estimated in phenol degradation reaction in an aqueous phase. The significantly high photocatalytic activity under visible light irradiate as demonstrated by the TiO_2 sample modified by spheres of gold. The average rate of phenol decomposition was 1.9 μmol dm^{-3} min^{-1} and was three-times higher compared to the pristine TiO_2 amorphous microspheres. On the other hand the photocatalytic activity was relatively lower and was 0.38 and 0.27 μmol dm^{-3} min^{-1} for nanorods and nanostars deposited on the amorphous form of TiO_2 microspheres, respectively. The visible light activity decreased in following order: (NSPs)> (NRs)> (NSTs). The obtained photocatalytic efficiency of samples was ascribed to the geometry and the size effect of the enhanced and the possible mechanism for this was discussed in detail. Furthermore, in this work we show the effect of calcination temperature on the structure of gold NPs, NRs and NSs before and after modification on the morphology and photocatalytic activity of Au-TiO_2.

1. Introduction

The noble metal nanoparticles (NPs) have been extensively studied for an application in areas such as spectroscopy [1–3], catalysis [4–6], photocatalysis [7–9], energy [10–12], biology [13–16] and biomedicine [17–19]. Gold particles are of a broad interest due to their unique optical properties [20,21]. The gold nanoparticles interaction with an electromagnetic radiation resulted in the free electrons oscillation in response to the electric field component. At a specific wavelength (frequency) of light, collective oscillation of electrons on the gold nanoparticle surface cause a phenomenon called localized surface plasmon resonance (LSPR) resulting in strong extinction of light (absorption and scattering). The optical properties of gold particles are strongly affected by the size and mainly by the geometry [22]. Recently, many different shapes, such as nanospheres [23], nanorods [24], nanowires [25], octahedral NPs [26], cubes NPs [20], branched crystal nanogold [27], nanostars [28] and nanotriangle [29] have been identified to be of a special interest in relation on their optical properties. Under resonant excitation, Au nanocrystals have the unique ability to concentrate the free-space optical field within subwavelength regions adjacent to their surfaces [30]. In this context the gold nanoparticles, exhibiting plasmonic properties, may activate wide band gap semiconductors, such as TiO_2, under visible light irradiation [31]. Kowalska et al. [32] investigated photocatalytic properties and influence of gold size and shape on visible-light-inducted activity. They suggested that the spherical/hemispherical shape of gold NPs in comparison with rod-like ones is beneficial for a higher level of photoactivity

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under visible light irradiation. They also observed that the wide size/shape distribution of gold NPs and thus ability of absorption of light in a broad wavelengths range are responsible for the high level of photoactivity. Liu et al. [33] reported that the TiO_2 modified by Au-nanorods exhibited high activity in an oxidation process of 2-propanol under the wide range of visible irradiation resulting from the longitudinal and transversal plasmon. Nishijima et al. [34] stated that the NRs on the surface of TiO_2 single crystal have a larger optical field and effective generation of LSPs and, consequently, can be used in a highly efficient photoelectric conversion system. They suggested that the intense optical near-field locally increased by plasmonic enhancement effects obtained due to the spatial and temporal confinement at the edge of AuNRs (especially the AuNRs/TiO_2 interface in this case) may assist the electron excitation of gold even with near-infrared wavelengths as a result of the successful electron transfer from Au NRs to the conduction band of TiO_2. Tanabe et al. [35] investigated the effect of the Au nanospheres size on the photocatalytic activities of TiO_2. It was found out that the smaller Au nanoparticles induce a larger electronic state changes a hence high photocatalytic activity in degradation process under UV light (300–400 nm) of methylene blue. Additionally, the authors observed that the gold shape had a slight effect on the electronic states of the TiO_2. Kaur et al. [36] compared co-catalytic activity of various Au nanostructures (nanorods and nanospheres) deposited on TiO_2 surface-commercially available P-25, as well as, the size effect of the obtained spheres on the photocatalytic activity. The Au-TiO_2 showed a higher photocatalytic activity in oxidation of salicylic acid under the UV light than the pure TiO_2. The highest activity was observed for TiO_2 loaded with spherical Au nanoparticles. Moreover, it was found out that the TiO_2 modified by the smallest spherical Au shows the highest catalytic activity compared to the TiO_2 modified by large spheres. Pap et al. [37] investigated the correlation between different geometries of nano-gold (spheres, triangles and wires) deposited on the surface of the commercial TiO_2 and physical properties on the photocatalytic activity of the obtained Au-TiO_2. They observed that all gold-shape loaded on TiO_2 performed the better photocatalytic activity of oxalic acid under the UV light irradiation compared to commercial P-25. Thus, according to the literature data, only few papers [35–38] deal with photocatalytic properties of TiO_2 loaded with the gold nanoparticles differing in shape, however, the effect of gold particles shape on visible light induced photocatalytic activity of Au-TiO_2 is still unclear.

In this context, TiO_2 decorated by the different shape of gold nanostructure, such as nanostars (NSTs), nanospheres (NSPs) and nanorods (NRs), were recently obtained. In this paper we show both the effect of the gold particles shape and size and TiO_2 matrix type (amorphous TiO_2 microspheres, anatase TiO_2 microspheres and rutile TIO-6 TiO_2) on the optical properties as well as visible light induced photocatalytic activity of Au-TiO_2 composites. TiO_2 microspheres were chosen due to their low density, high surface-to-volume ratio, high surface area, good surface permeability and adsorption capacities resulting in high photocatalytic activities [39–42]. It is speculated that pores in the mesoporous structured sample benefit from the penetration of vis light [43]. For the first time, the correlation between the photoactivity under visible irradiation and shape of gold nanoparticles deposited on the TiO_2 has been systematically studied. Furthermore, the effect of the application of thermal treatment step (before or after the gold nanoparticles deposition a TiO_2 microspheres) on the morphology and photocatalytic activity of the TiO_2-Au nanostars (NSTs-TiO_2), TiO_2-Au nanospheres (NSPs-TiO_2) and TiO_2-Au nanorods (NRs-TiO_2) has been investigated. The role of the different size and geometry of gold deposited on various titania matrix and the possible mechanistic aspects have also been discussed in this paper.

2. Experimental

2.1. Materials and instrument

Gold(III) chloride trihydrate ($HAuCl_4 \times 3H_2O$) and titanium(IV) n-butoxide (TBT) (>99%) from Alfa Aesar was used as gold and TiO_2 precursor in the preparation procedure. Commercial titania photocatalyst, TIO-6 (Supplier CSJ, Catalysis Society of Japan), was used as the titania source. Sodium borohydrate (98%, $NaBH_4$), silver nitrate (≥99%, $AgNO_3$), Cetyltrimethylammonium bromide (99%, CTAB), L-ascorbic acid (≥98%, AA), tannic acid ($C_{76}H_{52}O_{46}$), potassium chloride (99%, KCl) were purchased from Sigma Aldrich. Deionized water was used in all the experiments. All glassware was washed with an aqua regia (3:1 hydrochloric acid to nitric acid by volume) and rinsed copiously with water.

The surface area of the samples were evaluated from the adsorption-desorption isotherms of liquid nitrogen (77 K) detected using a Micrimeritics Gemini V (model 2365). A photocatalysts samples were dried and degassed in a sample cell at 200 °C for at last 2 h before the adsorption. The specific surface areas of the photocatalysts were determined by Brunauer-Emmett-Teller (BET) method. Powder X-ray diffraction (XRD) studies of photocatalysts samples were carried out on a Empyrean (PANalytical) diffractometer using Cu Kα radiation (1.54 Å), reflection-transmission spinner (sample stage) and PIXcel 3D detector, operating in the Bragg–Brentano geometry. The 2 Theta scans were recorded at the room temperature (300 K) in the angles ranging from 5 to 90 (°2Theta) with a step size of 0.013 (°2Th.) and continued scan mode. The XRD estimation of the crystallite size was based on the Scherrer formula: $D = 0.89\lambda/(Be - Bt)\cos\theta$, where λ is the X-ray wavelength, Be indicates the measured breadth of the peak profile, while Bt is the ideal, non broadened breadth of a peak and θ is the diffraction angle. The value of Bt was estimated on the basis of the measurements performed for a standard sample of polycrystalline Si with large crystalline grains. The X-ray photoelectron spectroscopic (XPS) measurements were performed using the PHI 5000 VersaProbe (ULVAC-PHI) spectrometer with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV) from an X-ray source operating at the 100 μm spot size, 25 W and 15 kV. The high-resolution (HR) XPS spectra were collected with the hemispherical analyzer at the pass energy of 23.5 eV and the energy step size of 0.1 eV. The CasaXPS software (version 2.3.16) was used to evaluate the XPS data. The deconvolution of all HR XPS spectra, except Au 4f, was performed using a Shirley background and a Gaussian peak shape with 30% Lorentzian character. However the best fitting of Au 4f spectra was performed with the 80% Lorentzian character of the Gaussian peak shape. The binding energy (BE) scale of all detected spectra was calibrated by centering the peak $Ti2p_{3/2}$ of TiO_2 supported with BE values equal to 459.0 eV.

The morphology and distribution size of the TiO_2 nanocomposites were observed using SEM Jeol 7001TTLS microscope operated at 12 kV and Cs-corrected STEM (High Angle Annular DarkField, HAADF). The diffuse reflectance UV–vis absorption spectra of the samples was obtained using a spectrophotometer UV–VIS Double Beam, UVD-3500, Labomed, Inc. equipped with an integrating sphere where the baseline was recorded using a bare titania powders.

3. Preparation of the Au-TiO_2 nanocomposites

3.1. Synthesis of gold nanoparticles (Au NPs)

The gold nanoparticles in the shape of spheres, stars and rods, dispersed in aqueous solution, were prepared by the reduction