

Extension of optical properties of ZnO/SiO₂ materials induced by incorporation of Au or NiO nanoparticles



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ABSTRACT

Incorporating noble metal nanoparticles (NPs) and oxides has been proved to be an effective method to tune the optical properties of silica based materials. In this paper the optical and photocatalytic properties have been studied for ZnO/SiO₂ modified with Au or NiO nanoparticles. Changes in the optical properties of semiconductor ZnO particles have been observed due to the deposition of coloured Au and NiO nanoparticles by reducing the band gap energy and thus extending light absorption to visible domain. The excellent surface characteristics of NiO/ZnO/SiO₂ and Au/ZnO/SiO₂ favour the adsorption behaviour of these materials and limit the recombination of electron–holes pairs. Crystal Violet degradation under VIS light proved to have higher efficiency in the presence of Au/ZnO/SiO₂ (97%) than for NiO/ZnO/SiO₂ (60%).

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1. Introduction

Silica and silica-modified materials have found widespread application for industrial, technological and domestic purposes. The demand for improved silica types with specific properties such as mechanical strength, pore volume and size distribution, surface area or reactivity is very high for the search of innovative materials [1]. For many years, silicates have attracted great attention due to their special physicochemical properties, low cost and abundant supply, and have been widely applied in many fields, e.g. as molecular sieves [2], catalyst supports [3], for gas absorption and separation [4], and as raw materials for the glass industry [5].

Surface decoration of silica has been demonstrated as an effective method to tailor the optical properties of silica modified nanostructures. Various nanoparticles, such as ZnO [6], NiO [7], mixed oxides [8], various kinds of noble metals [9] have been investigated in this regard. Among them coloured nanoparticles have been intensively studied as they have the ability to extend light absorption in the visible region of the spectrum, by reducing the band gap energy and thus improving the photocatalytic properties.

In this study optical, adsorptive and photocatalytic properties of NiO/ZnO/SiO₂ and Au/ZnO/SiO₂ were investigated. Silica matrix has

the benefit of being a very good adsorbent, preserves the properties of the incorporated structures and facilitates the contact between the dye and the photoactive centres generated by NiO, ZnO and Au nanoparticles. The photocatalytic performance of these materials was tested on Crystal Violet.

2. Materials and methods

ZnO-modified with Au or NiO–silica materials were synthesized by microemulsion assisted sol–gel procedure (MAPR) [10] that can be shortly described as follows: (i) gold nanoparticles (AuNP) were synthesized by using a water-in-oil microemulsion template: polyoxyethylene-4-lauryl ether (Brij 30)/2, 2, 4 – trimethylpentane/HAuCl₄ aqueous solution [10]; (ii) hydroxide nanoparticles were obtained in Brij 30/2, 2, 4 – trimethylpentane/metallic (Zn²⁺ and/or Ni²⁺) salt basic aqueous solutions. Then the sol–gel process was carried out in the pristine microemulsion in the presence of tetraethoxysilane in acidic media (Scheme 1 from supporting information). Crystal Violet dye (CV) (Loba Feinchemie) stock solutions (1000 mg L⁻¹) were prepared in double distilled water and the working solutions were obtained by successive dilutions. The final materials studied were: (i) ZnO, (ii) Au and ZnO, (iii) NiO and ZnO nanoparticles incorporated in silica composites (ZnO/SiO₂, Au/ZnO/SiO₂ and NiO/ZnO/SiO₂).

The spectral characterization of the materials, as powders, was performed by diffuse reflectance UV–VIS–NIR measurements on a

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JASCO V-550 spectrophotometer equipped with an integrating sphere. Nitrogen adsorption/desorption measurements were carried out on a Quantachrome instrument NOVA 2200e.

3. Experimental

For the adsorption experiments a series of samples were prepared by contacting 10 mL Crystal Violet (CV) dye solutions ($2\text{--}250\text{ mg L}^{-1}$) with a fixed amount of solid material (20 mg) at 298 K, under continuous stirring. Then, the supernatant was filtered through a membrane (pore size $0.45\text{ }\mu\text{m}$), followed by recording its spectrum on a UV–VIS spectrophotometer (Ocean Optics HR 2000+).

The photochemical degradation of Crystal Violet was carried out in a Luzchem LZC-4X photoreactor equipped with eight lamps, each of 12 W. Typical intensity within the chamber was 0.024 W/m^2 per each lamp used. The photocatalytic experiments were carried out at a fixed dye concentration (20 mg L^{-1}) and material loading (0.2 g L^{-1}), under VIS light ($\lambda = 580\text{ nm}$) irradiation. The colour degradation was followed by spectral changes of 3 mL aliquots using a JASCO V-670 Spectrophotometer.

4. Results and discussion

4.1. Optical properties of the composites

Changes in optical properties as function of composition were revealed by VIS electronic spectra performed on all oxide – modified silica nanocomposites, as powders (Fig. 1). By comparing ZnO/SiO₂ with Au/ZnO/SiO₂ and NiO/ZnO/SiO₂ one can notice that the absorption edge becomes more slanted and shifts toward the lower energies due to the influence of Au and NiO coloured nanoparticles [11,12].

One may notice that unlike Au NPs materials those with NiO show multiple visible absorption peaks, 385 nm from ZnO inside silica and 440, 640 and 720 nm specific for NiO, which favours a better exploiting of light in Visible domain. These peaks in the visible region are the result of different types of NiO NPs produced during nucleation. The last more intensive band is specific for green colour of this compound, which combined with significant absorbance at 650 nm (blue) and 400 nm (orange) results in various tints of turquoise–bluish. By incorporating Au and NiO NPs in the structure of silica, the absorbance intensity significantly increases compared to ZnO/SiO₂ and the formation rate of electron–hole pairs on the composite surface is also higher [13]. These

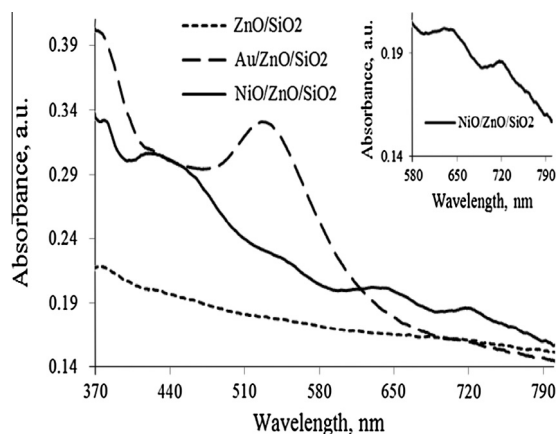


Fig. 1. VIS absorbance spectra of oxide – modified silica nanocomposites. The inset shows the spectrum of NiO/ZnO/SiO₂ on a more restricted wavelength domain.

characteristics suggest an improved photoactivity of the modified silica nanocomposites.

As expected, Au/ZnO/SiO₂ showed the characteristic surface plasmon absorption band centred around 530 nm, indicating that very small Au NPs were prepared by photo-reduction of Au (III) precursor.

A narrowing of the band gap energy from 3.28 eV, for ZnO/SiO₂, to 2.25 eV, for Au/ZnO/SiO₂, was observed (Table 1), values that were also reported for Au nanoparticles deposited onto ZnO surface by a hydrothermal process [14]. Au/ZnO/SiO₂ has small band gap energy and accordingly its capacity to absorb light significantly increases on the entire VIS range. This observation is also available for NiO/ZnO/SiO₂ as it has also reduced band gap energy (2.50 eV). The decrease of band gap energies can be attributed to the co-catalyst effect of Au or NiO nanoparticles inside ZnO/SiO₂ which increases the number of surface oxygen vacancies and/or surface defects. Therefore materials with small band gap energies were obtained by combining the properties of NiO, which is a *p*-type semiconductor with a wide band gap of 3.5 eV [10,7], or Au nanoparticles with that of ZnO, that is a multifunctional *n*-type semiconductor, also with a wide band gap of 3.37 eV [14,15] and by their incorporation into an insulator silica matrix (details about the band gap energy determination are found in Supporting Information).

As a consequence, a good strategy to extend ZnO absorption to visible domain is the modification of its valence band position by incorporating coloured nanoparticles like Au and NiO NPs.

4.2. Adsorption properties of the composites

The specific surface areas and the mean pore size, calculated with Barrer Joiner Hallenda (BJH) equation [16] according to the size distribution curve for the nitrogen desorption branch of the three nanomaterials are collected in Table 1. The surface area of the materials increased in the series of ZnO/SiO₂ < NiO/ZnO/SiO₂ < Au/ZnO/SiO₂ due to additional active sites provided by the presence of metal and oxide into the silica modified materials [17]. The surface characteristics of NiO/ZnO/SiO₂ and Au/ZnO/SiO₂ favour the adsorption behaviour of these materials and limit the recombination of electron–holes pairs. As a result, based on these observations corroborated with their small band gap energies, NiO/ZnO/SiO₂ and Au/ZnO/SiO₂ have photoactive adsorptive properties.

The adsorption capacity of ZnO/SiO₂, NiO/ZnO/SiO₂ and Au/ZnO/SiO₂ for CV is illustrated in Fig. 2. It was found that the amount of dye adsorbed (γ) for Au/ZnO/SiO₂ exhibited higher values. This may be attributed to the comparative values of the specific surface areas of these materials (Table 1). The adsorption capacities of the tested materials increased with increasing the CV dye concentration from 10 to 250 mg/L.

Since a good adsorbent possesses high porosity and large surface area one of the crucial aspects in the adsorption capacity of different organic and inorganic compounds is the availability of the surface area. The equilibrium adsorption isotherms are an important tool to study the mechanism of physical interaction between different compounds and nanocomposites. In the present

Table 1
Physico-chemical parameters of oxide-modified silica nanocomposites.

Sample name	Specific surface area ($\text{m}^2\text{ g}^{-1}$)	Pore diameter (nm)	Band gap energy (eV)
ZnO–SiO ₂	131.97	2.64	3.28
Au/ZnO/SiO ₂	583.33	4.89	2.25
NiO/ZnO/SiO ₂	388.34	2.57	2.50

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