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Comparative analysis of photocatalytic activity of aqueous colloidal solutions of $ReVO_4:Eu^{3+}$(Re = La, Gd, Y), $CePO_4$:Tb, CeO_2 and C_{60}

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ABSTRACT

Photocatalytic activity of aqueous colloidal solutions of nanoparticles of different nature at UV-irradiation was determined. 2 nm $GdYVO_4$:Eu, 8×25 nm $GdVO_4$:Eu, 6×40 nm $LaVO_4$:Eu, 2 and 9 nm CeO_2, 5×10 nm $CePO_4$:Tb and 62 nm C_{60} nanoparticles were used. Rare earth orthovanadate nanoparticles as well as fullerenes induce radical formation in water. It was shown that intensity of photocatalytic process increases with increase of the linear sizes of orthovanadate nanocrystals. Rare earth orthophosphate nanoparticles do not participate in photocatalytic processes at all. Cerium dioxide nanocrystals inactivate radicals in the water playing a role of a radical sponge.

1. Introduction

Nowadays a lot of attention is paid to the photocatalytic processes taking place in the presence of inorganic nanoparticles (NPs) in water solutions [1,2]. Especially interesting is the possible practical application of nanoparticles in biology and medicine. On the one hand, photosensitive nanomaterials under the action of an external light source are able to active generation of free radicals providing the necessary condition for their application in photodynamic therapy [3–5]. On the other hand, nanoparticles are widely used as a base for sunscreens [6,7]. The sunscreens are developed for protection of human skin from sunburns and harmful impact of UV, i.e. collagen damage, DNA mutations and dysfunctions of immune system following sometimes by cancer deceases. The sunscreen action of nanoparticles is based on the physical principles of reflection, absorption and Rayleigh scattering of UV radiation or its conversion to the radiation in the different spectral range. The necessary conditions for effective photoprotectors are the following: absorption of UV and neutralization of radicals and active oxygen formed at irradiation of water and biological molecules. As the photosensitive inorganic materials semiconductors (for instance, $SrWO_4$, TiO_2, YVO_4 and CeO_2 [8–11]) are usually used.

The photocatalytic properties of semiconductor materials are determined by the features of their electronic structure. The photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs generating thereby free radicals able to take part in the secondary reactions.

An evaluation of an ability of some photosensitive material to posses the properties of the heterogenic photocatalyst requires consideration of peculiarities of its band structure. Bandgap of an effective photocatalyst must, on the one hand, be narrow enough to provide an effective transfer of electrons from the valence band to the conduction band and, on the other hand, be wide enough to prevent an instant recombination of the free charge carriers. Average lifetime of free charge carriers in the common crystal photosensitive materials is $(30 \div 100) \times 10^{-12}$ s for free electrons and $(10 \div 250) \times 10^{-9}$ s for holes [12,13].

Electron–hole pair exists until the moment of recombination or until capture of either electron or hole by an alien agent—for instance, by molecule of oxygen, water or different substance adsorbed on the surface of NP.

Absorption of a photon by NP leads to the formation of free electrons (e^-) and free holes (h^+) that either recombine instantly or migrate through the material and are able to localization on the defects of the crystal structure:

$$NP + h\nu \rightarrow NP(e^-_{CB} + h^+_{VB})$$

where CB means conduction band, VB—valence band.

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In the aqueous media free charge carriers localized near the surface of nanoparticles can easily interact with water molecules forming thereby free radicals:

$$H_2O_{ads} + h^+_{VB} \rightarrow HO^{\bullet}_{ads} + H^+$$

$$OH^-_{ads} + h^+_{VB} \rightarrow HO^{\bullet}_{ads}$$

$$O_{2ads} + e^-_{CB} \rightarrow O_2^{\bullet -}{}_{ads}$$

$$O_2^{\bullet -}{}_{ads} + H^+ \rightarrow HO_2.ads$$

$$O_2^{\bullet -}{}_{ads} + e^-_{CB} + 2H^+ \rightarrow H_2O_{2ads}$$

At UV irradiation hydrogen peroxide dissociates with formation of hydroxyl radicals:

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet}_{ads}$$

The hydrogen peroxide as well as dissolved oxygen is an effective scavenger of photogenerated electrons:

$$H_2O_2 + e^- \rightarrow H_2O_2^{\bullet -} \rightarrow HO^{\bullet} + OH^-$$

Presence of the ions with variable valence in the crystal lattice leads to the reversible process:

$$Ce^{4+} + e^-_{CB} \rightarrow Ce^{3+}$$

$$Ce^{3+} + h^+_{VB} \rightarrow Ce^{4+},$$

which can cause either migration of free charge carriers within the volume of the crystal or their interaction with the molecules or radicals adsorbed on the surface of NPs. These processes can be accompanied by both radical induction and radical neutralization near the surface of the crystal.

On the other hand, the absorption of UV photons by water molecules is accompanied by formation of the same radicals as the ones formed on the surface of semiconductor NPs ($HO^{\bullet}$, $H^{\bullet}$, $O_2^{\bullet -}$ and $HO_2^{\bullet}$).

So, an irradiation of hydrosols of photoactive NPs is accompanied by the formation of free radicals with participation of free charge carriers as on the surface of the nanocrystals, so within the water. On the other hand, opposite process also takes place i.e. the recombination and neutralization of radicals as in the water, so on the surface of NPs.

$$\sum M_i \sum R_i^{\bullet}{}_{ads} + \sum R_i^{\bullet}{}_{vol}$$

where M_i denotes molecules or ions (for instance, H_2O, O_2, H^+), $R_i^{\bullet}{}_{ads}$, $R_i^{\bullet}{}_{vol}$ are radicals on the surface of nanocrystals or in the water.

Shift of the equilibrium to the one or another side depends on the ability of nanocrystals to generate or inactivate free radicals in the system.

For determination of the intensity of radical formation in the system, the organic compounds able to interaction with radicals with formation of the products of destruction were used. Usually, for these purposes dyes easily destructing under an action of free radicals are chosen. During interaction with the free radicals decrease of an optical density of characteristic dye bands in the absorption spectra is observed.

The task of this paper was an estimation of the degree of photoinduction and inhibition of free radical generation at UV irradiation in the water solutions of NPs with different nature and form-factor. In the work NPs of rare earth based orthovanadates and orthophosphates, cerium dioxide and C_{60} fullerenes perspective for biological and medical applications [14–17] were used.

2. Experimental

2.1. Materials

Lanthanide chlorides 99.9% and anhydrous sodium metavanadate ($NaVO_3$, 96%) (Acros Organics company) were used without further purification. Sodium tripolyphosphate ($Na_5P_3O_{10}$, 98%), sodium citrate ($Na_3C_6H_5O_7$, 99%), hexamethylenetetramine ($(CH_2)_6N_4$, 99 %), H_2O_2, 35%, NH_4OH, 25%, from Macrochem Co., Ltd. were used. The inorganic salts, toluene and isopropanol were commercial products of reagent grade. The fullerene C_{60} (>99.9% pure) supplied by Aldrich was used. Na_3VO_4 solution with pH value of 13 was obtained by adding solution NaOH (1 mol/L) to $NaVO_3$ water solution. Anionic dye (1,1′-di(3-sulfopropyl)-3,3,3′,3′-tetramethylindodicarbocyanine sodium salt (DiD-C3S)) was synthesized in the Institute for Scintillation Materials NAS of Ukraine.

2.2. Methods

$ReVO_4$:Eu (Re = La, Gd, Y), CeO_2 and $CePO_4$:Tb hydrosols were synthesized according to the methods described earlier [18–20]. NPs in hydrosols were stabilized by sodium citrate and had negative values of ζ potential. Colloidal solutions of NPs were purified from impurities by the means of dialysis during 72 h. For dialysis of solution Cellu Sep H1 3.5 KDa dialysis membranes were used. The solid phase concentration was equal to 1 mg/ml. C_{60} fullerene water colloidal solution with the concentration of 0.042 mg/ml (58×10^{-5} M) was prepared by transfer of C_{60} molecules from toluene to water using ultrasound sonication [21].

All colloidal solutions are transparent in transmitted light and opalescent in lateral light (Tyndall cone). Colloidal particles pass easily through nitrocellulose ultrafilters with pore diameter of 100 nm. pH was equal to 7.2–7.6. The solutions were stored in sealed ampules without changing their properties for more than 2 months at normal conditions.

All types of NPs had a negative surface charge, so, to exclude an electrostatic interaction with NPs and localization of the dye on the surface of NPs, as an indicator of free radicals DiD-C3S anionic dye was used (Fig. 1). At DiD-C3S cationic dye addition to colloidal solutions of NPs of all types no changes in dye absorption spectrum was observed. Any changes of ζ-potential of NPs, increase of hydrodynamic diameter of NPs or coagulation also were not registered confirming an absence of interaction of the anionic dye with the surface of negatively charged NPs. So it is supposed that the effects relating to photodegradation of the dye take place not on the surface of NPs, but instead within the solution. It must be noted that cationic dyes usually interact with the surface of negatively charged particles by coulomb forces with subsequent

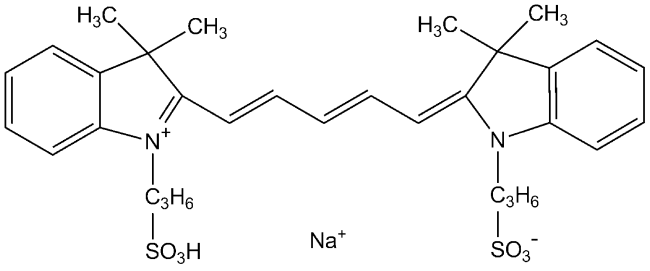

Fig. 1. Structural formula of 1,1′-di(3-sulfopropyl)-3,3,3′,3′-tetramethylindodicarbocyanine sodium salt (DiD-C3S).