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KINETICS OF J-AGGREGATION OF TC-COATED AU COLLOIDAL NANOPARTICLES IN AQUEOUS SOLUTION

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Abstract

The kinetics of J-aggregation of thiacyanine dye (TC, 5,5'–disulfopropyl 3,3'–dichlorothiacyanine sodium salt) was studied in the presence of gold colloid. The synthesized Au colloidal dispersions were characterized by UV-Vis spectrophotometry. Kinetic measurements were carried out using a stopped-flow method to study the mechanism of J-aggregation, capturing both the slow and the fast phases of J-aggregate formation.

Introduction

The motivation for this work stems from a need to further understand the mechanism of the J-aggregate formation in aqueous solution consisting of thiacyanine dye (TC) and gold colloid. Hybrid nanoparticles consisting of noble metal cores functionalized with an organic dye shell are known for their unusual optical properties [1-3]. The modulation and enhancement of the dye's optical characteristics are due to the electronic coupling of the dye to the polarizations of the metallic nanoparticles [3]. Phenomena associated with these hybrid structures, such as dye-fluorescence quenching [4], interactions with enhanced optical fields [3], and non-linear behavior [5] render them potentially useful for future design of light energy conversion systems, molecular optoelectronic applications and sensory devices.

Since there is the lack of literature data considering kinetics of J-aggregate formation, the elucidation of the detailed reaction mechanism could provide the basis for obtaining further insights into this area of research. Therefore, the aim of this work was to investigate the kinetics of J-aggregation of the Au nanoparticles prepared using a $NaBH_4$ as a reducing agent and coated with TC dye.

Material and methods

Au colloidal nanoparticles were prepared by the reduction of 1 mM $KAuCl_4$ in aqueous solution with freshly prepared 0.1 M $NaHB_4$ solution under icy conditions (4° C) [6]. 30 mL milli-Q water was cooled with ice and then 330 µL freshly prepeared $NaHB_4$ solution and 10 mL $KAuCl_4$ solution were added to it under vigorous stirring, resulting in the vine – red Au colloidal solution. The colloid dispersions were stored at room temperature up to seven days. The concentration of stock dispersion of gold nanoparticles (7.4×10^{-8} M) was determined from the absorbance at 520 nm and molar absorptivity for the Au colloidal dispersion with average size of the particles 5-6 nm.

50 μM aqueous TC stock solution containing 1mM KCl was prepared by dissolving the solid TC. The dye working solutions (concentrations 1.6 – 16.0 μM) were prepared by appropriate dilution of 50 μM TC stock solution, immediately before measurements. Water purified with a Millipore Milli-Q water system was used for preparing all solutions. The mixing ratio by volume of TC dye with Au colloid was 1:2. The rate of reaction was evaluated from the change of absorbance at 475 nm using a stopped flow accessory with thermostated quartz cuvette.

Results and discussion

The absorption spectrum of TC dye in aqueous solution shows a short-wavelength maximum at 409 nm assigned to the dye dimmer and a long-wavelength maximum at 429 nm assigned to the dye monomer [1]. The absorption spectra of 7.4×10^{-8} M Au colloidal dispersion before and after adsorbing TC dye in the concentration range from 0.167×10^{-5} M − 1.67×10^{-5} M, were recorded in the presence of 0.1 M KCl and are shown in Fig. 1a. Inset in Fig. 1a shows the change of absorbance at 475 nm of 7.4×10^{-8} M dispersion of Au colloid, as the dependence on TC concentration. Upon addition of TC dye to the solution, a plasmon peak at ≈520 nm red-shifted to $\lambda\approx550$ nm accompanied by the emergence of the sharp absorption dip at 475 nm, which coincides in the position with the J-band of the TC J-aggregate [1]. A clear isobestic points were observed at 464 nm and 524 nm indicating the reactivity involving two species, reactant (equilibrated mixture of monomers and dimmers) and and product (J-aggregate). Kinetic measurements were carried out using a stopped-flow method to allow capturing phases of J-aggregate formation by following the change of absorbance at 475 nm. Typical kinetic curve obtained from spectrophotometric measurements of reaction rate in the dispersion containing 1.4×10^{-5} M TC and 7.4×10^{-8} M Au colloid is presented in Fig. 1b (line 3). The values for the first order rate constants for faster and slower process, $k_{1obs} = (4.514 \pm 0.445)$ s^{-1}, $k_{2obs} = (1.81 \pm 0.45)\times10^{-1}$ s^{-1}, as well as constants $A_1 = (2.4 \pm 0.2)\times10^{-2}$, $A_2 = (5.6 \pm 0.2)\times10^{-2}$ and $A_0 = (1.56 \pm 0.33)\times10^{-3}$ were obtained by fitting the experimental data in Fig. 3 to Eq.: $A = A_0 + A_1\exp(-x/t_1) + A_2\exp(-x/t_2)$, which describes two parallel first-order reactions. As the results indicate, the kinetic curve can be divided into two separated curves, which present the fast (curve 1, Fig. 1b) and the slow reaction process (curve 2, Fig. 1b).

Conclusion

Based on the results presented here we propose a 2-step mechanism for J-aggregate interaction. The kinetic curve indicates two processes, a fast one ($t_1^{1/2} = 0.221 \pm 0.022$) and a slow one ($t_2^{1/2} = 5.524 \pm 0.136$). The kinetic curve was derived from the formation of absorption minimum at 475 nm, which is indicative of J-aggregate formation on the surface of nanoparticles. A relatively fast drop in A^{475} suggests that J-aggregate formation is the fast process, with the dye possibly interacting with negatively charged Au nanoparticles via its sulfur from tiazole ring [7]. The slow process could be displacement of borate counterions from the surface of nanoparticles by the J-aggregate assemblies, but this assumtion needs to be further investigated.

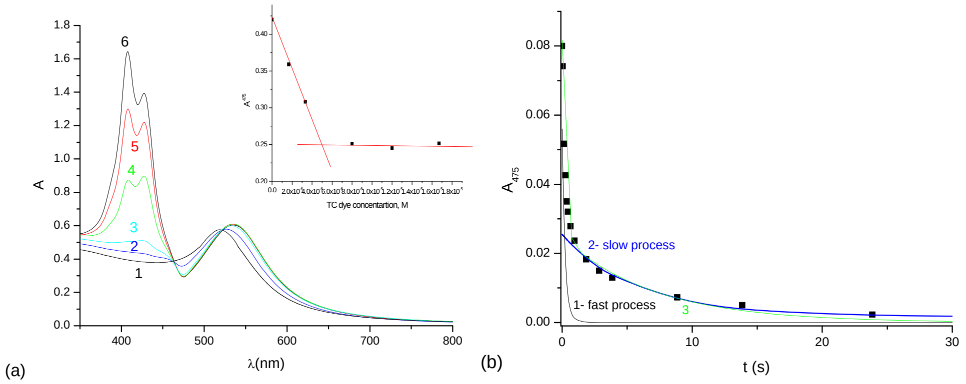

Fig. 1. (a) Absorption spectra of Au colloidal dispersion with TC dye. C_{Au} : 7.4×10^{-8} M, C_{TC} : without TC (1), 0.167×10^{-5} M (2), 0.33×10^{-5} M (3), 0.83×10^{-5} M (4), 1.33×10^{-5} M (5), 1.67×10^{-5} M (6). Inset: dependence of absorbance at 475 nm (A^{475}) on TC concentration; (b) Plot of absorbance (A_{475}) *vs* time for the dispersion containing 1.4×10^{-5} M TC and 7.4×10^{-8} M Au colloid at 16° C. Squares - experimental points; curve (1) - fast process; curve (2) - slow process and curve (3) – fit of experimental results to Eq.: $A = A_0 + A_1\exp(-x/t_1) + A_2\exp(-x/t_2)$.

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