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Review

A comparative study of the photochromic compounds incorporated on the surface of nanoparticles

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ABSTRACT

Among several interesting applications of the noble-metal nanoparticles, the photochemical applications have gained considerable attention. This review presents an overview on the incorporation of covalently bound photochromic molecules on the surface of nanoparticles as photo-responsive systems, whose properties can be manipulated by light and can find application as materials for surface-enhanced spectroscopy, optical filters, waveguides and sensors.

Contents

1. Introduction

The self-assembly of photo-responsive molecules on metal nanoparticle (MNP) surfaces has received considerable attention in recent years because it provides the opportunity of using switching devices as photo-responsive components in applications of optical storage, molecular recognition, photo-switchable surface wettability and drug delivery [1–14]. Photochromic dyes undergoing a reversible color change upon irradiation by UV light have been used as smart colorants in a wide range of areas [15–20]. A well-known method to attach organic molecules to MNP surfaces is through the formation of self assembled monolayers (SAMs) [21,22]. Photochemical properties of photochromic dyes attached on the surface of MNPs are also affected by the metal. Generally, metals readily quench the electronic exited states of the molecules placed on their surfaces. Energy transfer and electron transfer to the metal surfaces are the main causes of the quenching [23,24]. These quenching processes are faster than fluorescence process; the time constant of energy transfer and electron transfer on the metal surfaces is normally around several picoseconds (ps) and fluorescence lifetime is normally around several nanoseconds. On the other hand, the time constant of the photocyclization reaction is normally around several picoseconds. Therefore, the cyclization reaction can compete with the quenching process. Here, we review the photochromic behavior of NPs capped with the photochromic compounds.

2. Azobenzene derivatives on the surface of nanoparticles

Among photo-responsive molecules, azobenzene derivatives are the most studied due to their higher quantum yields for the photoisomerization in solution, simple molecular structures and

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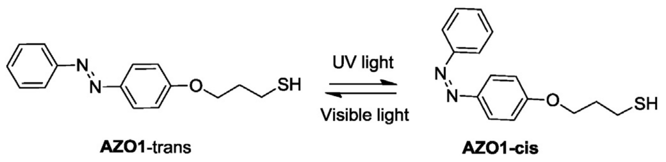

Fig. 1. Photoisomerization reaction of an azobenzene-derivatized thiol (**AZO1**).

relatively good stability of both isomers. These derivatives could be photoisomerized repeatedly between the *cis* and *trans* conformations with 366 and 436 nm light, respectively. The *trans* isomer displays a larger absorbance than the *cis* conformer at 338 nm due to the π → π* transition and a lower absorbance at 438 nm due to the n → π* transition. When the azobenzene group was isomerized upon irradiation with UV light to the *cis* conformer, the absorbance band at 348 nm decreased, and absorption band intensity at 436 nm increased. These spectral changes were reversible. Recently, photoisomerization of azobenzene molecules (**AzO1**) attached to silver nanoparticles (AgNPs) via thiol bonding was studied by P. Ahonen et al. (Fig. 1) [25].

Spectra of the *trans* and *cis* isomers of the azobenzene thiol **AZO1** in toluene solution and silver nanoparticles (AgNPs) functionalized with **AZO1** were recorded and a comparison was made (Fig. 2). A difference in the spectral changes during the photoisomerization was observed close to the plasmon absorption wavelength (~460 nm) of AgNPs capped with thiol, which was considered as an evidence for the interaction between the azobenzene chromophore and the nanoparticle. The intensity of the plasmon band of the functionalized nanoparticles decreased as the azobenzene ligand was photoisomerized from *trans* to *cis* state, whereas for the free azobenzene molecule the intensity of absorption wavelength near 440 nm increased as the photoisomerization occurred. This enhancement of the absorbance of *trans* azobenzene-functionalized nanoparticles is likely due to the change in the conductance of the azobenzene ligands through the conformational change [26]. This means that the free electrons of the nanoparticles are spread further from the core when the ligand is in *trans* conformer. Thus, it seems that the *trans* **AZO1** can be considered as an antenna when attached to the surface of AgNPs and by changing the state of **AZO1**, the dielectric properties of the nanoparticle can be tuned by light.

Azobenzene- and stilbene-terminated alkanethiolate molecules [27] as well as unsymmetrical azobenzene disulfide were used for functionalization of AuNPs (Fig. 3) [28]. The *trans-cis* photoisomerization of the appended compounds was observed in solutions and in the composite clusters. The photoisomerization quantum yields of the composite clusters were affected by the length of the linker because of distance-dependent through-bond quenching by the metal core. In fact, quenching of the excited composite clusters by the metal core became weaker as the chromophore was positioned further from the metal core upon increasing the linker length. The photo-induced reaction rates follow first-order kinetics and are identical to those of free azobenzene molecules. This suggests that no steric effects are involved in the reactions. A Raman spectroscopy study of the *cis-trans* photoconversion of 4-dimethylamino-azobenzene carboxylate on the surface of AuNPs indicated that both the *cis*- and *trans*- conformations coexist after adsorption [29]. Irradiation of functionalized AuNPs by 440 nm light decreased the concentration of molecules in the *cis*-form.

AuNPs modified with photo-responsive azobenzene-alkanethiol molecules **Az-B-SH** has been prepared as shown in Fig. 4, by K. Shin et al. and its photoisomerization behavior has been studied [30]. Azobenzene-modified AuNPs (**Az-B-Au**) carried out very efficient *trans* → *cis* photoisomerization upon irradiation with 350 nm light similar to azobenzene and reached to the photostationary state within 180 s. After the dark incubation, slow thermal back reversion to *trans* form is completed within 5 days. Both *trans* → *cis* photochemical isomerization rate and *cis-trans* thermal isomerization rate become faster when azobenzene is anchored on the surface of AuNPs.

M. Suda et al. have designed azobenzene-thiol-passivated AuNPs with different sizes and the differences between two kinds of AuNPs in the magnetic and photo-magnetic properties (Fig. 5) [31]. In these systems, they examined that when the particle size was reduced to 1.7 nm, ferromagnetism even at room temperature was observed while diamagnetism was dominating with the particle size of 5.0 nm. The ferromagnetism could be controlled by alternating photo-illumination with UV and visible light in the solid state even at room temperature. The changes in the magnetization values were significant, and were estimated to be around 27%. Furthermore, reducing the particles size to 1.7 nm also gave rise to photo-magnetic properties because the decrease in particle size provided free volume between each of the azobenzene ligands. This photo-magnetic effect could be attributed to photo-induced changes in the values of d-charge losses due to the photoisomerization of azo ligands, which were accompanied by the inversion of surface dipole values to the opposite sign.

G. L. Hallett-Tapley et al. demonstrated that pseudo-naked, ~12 nm spherical, ablated AuNPs, catalyzed the *cis-trans* isomerization of azobenzenes [32]. However, *cis-trans* isomerization has been suggested to be largely environment dependent, dictated by both solvent polarity and molecular substituents [33,34]. AuNPs have long been shown to act favorably as electron sinks and participate in redox reactions [35]. In this study, they proposed that effective electron transfer (eT) from the catalyst surface plays a key role in the isomerization mechanism (Fig. 6), though the exact role of the AuNPs with in the azobenzene activation has yet to be defined. As such, Fig. 6 is used to simply illustrate the participation of eT in the isomerization mechanism. These results suggest an electron transfer from azobenzene to the AuNP, resulting in the formation of an azobenzene radical cation intermediate and supporting a rotational mechanism about the N=N bond, confirmed

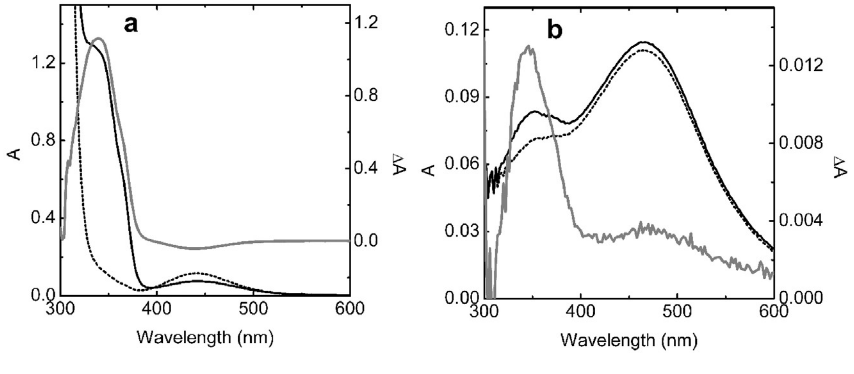

Fig. 2. (a) Spectra of the *trans* conformer (solid line), and the *cis* conformer (dashed line) of the free **AZO1** in toluene and the difference in the spectrum of the conformers (gray line). (b) Spectra of silver nanoparticles functionalized with the *trans* (solid line), and the *cis* conformers (dashed line) of **AZO1**. The gray line is the difference between these spectra.