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Synthesis and photochromic properties of thiolated *N*-salicylidene-anilines on silver nanoparticles

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ABSTRACT

Here, we synthesized the salicylidene-aniline (anil) photochromes with thiol group (thiolated Schiff base) to modify silver nanoparticles (AgNPs) surface and their photochromic properties were described. A photochromic response related to the light induced tautomerization of the anils functionality along with bathochromic shift in the absorption band is observed in AgNPs surfaces. We have also examined that enol→keto photoisomerization rate by UV light for functionalized AgNPs are clearly faster than free anils.

1. Introduction

A great deal of attention has been focused on functionalized nanoparticles (NPs) due to the broad range of applications for which they are potentially useful [1–10]. As such, the searches for new functional and responsive conjugated NPs continue to be a subject of interest. Specifically, optically responsive NPs exhibiting photochromism properties are particularly sought after for use in such applications as display technology, data storage, molecular recognition applications and photo-switchable surface wettability [11–17]. Recently, azobenzenes, diarylethenes, and spiropyrans are representative classes of photochromes that have been successfully incorporated into NPs surfaces [18–25]. In our research group, we developed 1,3-diazabicyclo[3.1.0]hex-3-ene, as a class of photochromic compound that is somewhat less well known, with thiol, disulfide and azobenzene-thiol groups on AgNPs surfaces [26–28]. The modified AgNPs showed a pronounced bathochromic shift in the absorption band of the open ring photoisomers and in the surface plasmon resonance absorption (SPRA) of AgNPs. Furthermore, we have also observed that trans/cis and cis/trans photoisomerization rate by UV light and thermally induced condition for functionalized azobenzene AgNPs are noticeably faster than free ligands.

Based on these developments, we have synthesized another interesting class of photochromic compounds including *N*-salicylidene-anilines (anils, Schiff bases) with thiol group that used to form self-assembled monolayers on AgNPs surface, as shown in Scheme 1.

Photochromic properties of *N*-salicylidene-anilines, including colorability and thermal bleaching, are highly dependent on the molecular conformation and crystalline environment around the molecule. Until now, different methods such as chemical modification [29–34], mixing with polymers [35–37], zeolites [38–40], mesoporous silica [41–43], cyclodextrins [44], cationic host matrix [45,46], clathrates [47,48] and bile acids [49], confining in a metal organic frame work (MOF) [50,51] and co-crystal formation through acid-base interactions [52,53] have been reported to modify the *N*-salicylidene-anilines with an aim to change photochromic reactivity. Therefore, here, for the first time, the photochromic behaviors of thiolated *N*-salicylidene-anilines on AgNPs surface were studied. Modifying the surroundings of thiolated Schiff bases (**TSB**) is indeed expected to impact the optical properties of the molecular switch. The photochromic property for **TSB** is based on a tautomerization reaction between the enol-imine and keto-enamine forms upon UV light irradiation [54–56]. As a result of this, the proton transfer tautomer possesses significant differences in structure and electronic configuration from its related

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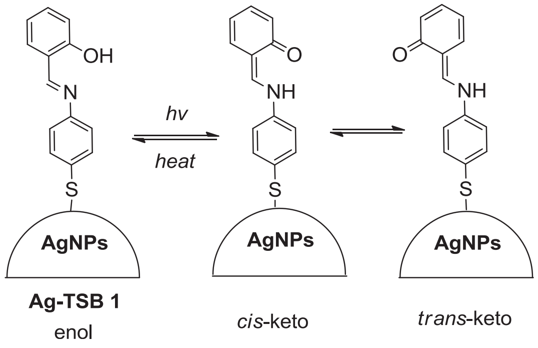

Scheme 1. Photochromic behavior of **Ag-TSB 1.**

normal species. Many important applications of these phenomena such as probes for solvation dynamics and biological environments, the development of laser dyes, ultraviolet stabilizers, metal ion sensors and scintillator counters are attributed to this rare photophysical property [57]. The incorporation of **TSB** molecules on the AgNPs surface (**Ag-TSB**), leads to photo-responsive systems, which their properties can be manipulated by light and can be applied as materials for surface enhanced spectroscopy [58], optical filters [59], plasmonic devices [60], and sensitive optical chemical and biological nanosensors [61].

2. Experimental

2.1. Materials and apparatus

The following reagents were purchased from Merck and used without further modification: $AgNO_3$ (99.9%), polyvinylpyrrolidone (PVP, K30, MW 40000), 4-aminothiophenol and $NaBH_4$ (99%). The ^1H NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. Chemical shifts (δ) are reported in ppm and the coupling constants (J) are given in Hertz (Hz). The UV–Vis absorption spectra in the range of 200–500 nm (EtOH or $CHCl_3$, $c = 1.0 \times 10^{-4}$ M) were measured with a Shimadzu UV-2100 spectrometer. The photoinduced (trans-keto photoisomer) was formed upon UV irradiation (Hg lamp DRSh-260+UV-transmitting glass filters). Spectral data were obtained using quartz cuvettes with 1 cm optical path length before and after UV irradiation for various times. The FT-IR spectra for the samples were obtained using Shimadzu FT-IR-8900 spectrophotometer by using KBr pellets. The X-ray diffraction (XRD) patterns were recorded in air at ambient temperature by Phillips (pw-1840) X-ray diffractometer with Cu-Kα radiation source ($\lambda = 1.54056$ Å) at 40 KV voltage and 25 mA current in a wide angle range ($2\theta = 10$–70). The morphology and particle sizes of synthesized powder were characterized by transmission electron microscope (TEM) images. The TEM samples were prepared by suspending the nanoparticles in EtOH followed by sonication for several minutes. One drop of the dilute nanoparticles/EtOH suspension was placed on a carbon-coated holey TEM copper grid and was dried in air. The dried grid was then loaded into a double tilt sample holder. The sample was then examined with a Philips CM-20 STEM equipped with a Gatan UltraScan 1000 CCD camera and an energy dispersive X-ray spectrometer: INCA Energy TEM 200. TEM images were taken at 200 KV.

2.2. General procedure for synthesis of thiolated Schiff bases (*TSB 1–4*)

4-Aminothiophenol (0.29 g, 1 mmol) and 2-hydroxybenzaldehyde (0.11 mL, 1 mmol) were added to absolute EtOH (3 mL) and the mixture was refluxed at 80 °C for 3–6 h. The precipitate obtained was filtered, washed with cool water and recrystallized in EtOH to afford pure desired product.

2.3. 2-(((4-Mercaptophenyl)imino)methyl)phenol (*TSB 1*)

Yield (92%), M.P. 138–139 °C, red solid; IR (KBr, υ/cm^{-1}): 3400 (O–H stretch), 1617 (imine C=N stretch), 2689 (S–H stretch), 1560 (aromatic C=C stretch), 1258 (C–O stretch), 838, 757 (aromatic out of plane bend). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 13.50 (s, 1H, OH), 8.63 (s, 1H, CH=N), 7.37 (m, 2H, Ar–H), 7.25 (d, J = 8.8 Hz, 2H, Ar–H), 7.04 (d, J = 8.0 Hz, 1H, Ar–H), 6.98 (t, J = 8.8 Hz, 1H, Ar–H), 6.93 (d, J = 8.8 Hz, 2H, Ar–H), 5.18 (s, 1H, SH). UV–Vis (EtOH) λ_{max}/nm: 275 ($n \rightarrow \pi^*$) and 348 ($\pi \rightarrow \pi^*$) nm before irradiation and 275 ($n \rightarrow \pi^*$), 348 ($\pi \rightarrow \pi^*$) and 425 (SPRAB) nm after irradiation. Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.09; H, 4.84; N, 6.11; Found: C, 68.41; H, 4.52; N, 6.16.

2.4. 2-(((2-Mercaptophenyl)imino)methyl)-6-methoxyphenol (*TSB 2*)

Yield 84%, M.P. 165–166 °C, yellow solid; IR (KBr, υ/cm^{-1}): 3428 (O–H stretch), 2570 (S–H stretch), 1609 (imine C=N stretch), 1564 (aromatic C=C stretch), 1247 (C–O stretch), 855, 727 (aromatic out of plane bend). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.35 (s, 1H, OH), 8.62 (s, 1H, CH=N), 7.44 (t, J = 8.0 Hz, 1H, Ar–H), 7.39 (d, J = 8.4 Hz, 1H, Ar–H), 7.36 (t, J = 8.0 Hz, 1H, Ar–H), 7.26 (d, J = 8.3 Hz, 1H, Ar–H), 7.08 (d, J = 8.6 Hz, 1H, Ar–H), 7.03 (d, J = 8.8 Hz, 1H, Ar–H), 6.99 (t, J = 8.4 Hz, 1H, Ar–H), 5.71 (s, 1H, SH), 3.94 (s, 3H, OCH_3). UV–Vis (EtOH) λ_{max}/nm: 268 ($n \rightarrow \pi^*$) and 346 ($\pi \rightarrow \pi^*$) nm before irradiation and 268 ($n \rightarrow \pi^*$), 360 ($\pi \rightarrow \pi^*$) and 400 (SPRAB) nm after irradiation. Anal. Calcd for $C_{14}H_{13}BrNO_2S$: C, 64.84; H, 5.05; N, 5.40; Found: C, 64.41; H, 5.27; N, 5.44.

2.5. 2-(((4-Mercaptophenyl)imino)methyl)-6-methoxyphenol (*TSB 3*)

Yield 86%, M.P. 135–136 °C, red solid; IR (KBr, υ/cm^{-1}): 3420 (O–H stretch), 2588 (S–H stretch), 1615 (imine C=N stretch), 1506 (aromatic C=C stretch), 1258 (C–O stretch), 836, 729 (aromatic out of plane bend). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 13.91 (s, 1H, OH), 11.16 (s, 1H, SH), 8.64 (s, 1H, CH=N), 7.27 (m, 3H, Ar–H), 7.06 (m, 2H, Ar–H), 6.93 (d, J = 8.4 Hz, 2H, Ar–H), 3.96 (s, 3H, OCH_3). UV–Vis (EtOH) λ_{max}/nm: 275 ($n \rightarrow \pi^*$) and 362 ($\pi \rightarrow \pi^*$) nm before irradiation and 275 ($n \rightarrow \pi^*$), 362 ($\pi \rightarrow \pi^*$) and 425 (SPRAB) nm after irradiation. Anal. Calcd for $C_{14}H_{13}BrNO_2S$: C, 64.84; H, 5.05; N, 5.40; Found: C, 64.53; H, 5.14; N, 5.32.

2.6. 2-(((2-Mercaptophenyl)imino)methyl)phenol (*TSB 4*)

Yield 85%, M.P. 173–174 °C, red solid; IR (KBr, υ/cm^{-1}): 3425 (O–H stretch), 2357 (S–H stretch), 1611 (imine C=N stretch), 1560 (aromatic C=C stretch), 1275 (C–O stretch), 845, 748 (aromatic out of plane bend). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.30 (s, 1H, OH), 8.53 (s, 1H, CH=N), 7.48 (t, J = 8.1 Hz, 1H, Ar–H), 7.42 (d, J = 8.4 Hz, 1H, Ar–H), 7.37–7.40 (m, J = 8.4 Hz, 3H, Ar–H), 7.05–7.07 (m, 2H, Ar–H), 6.92 (t, J = 8.3 Hz, 1H, Ar–H), 3.61 (s, 1H, SH). UV–Vis (EtOH) λ_{max}/nm: 278 ($n \rightarrow \pi^*$) and 370 ($\pi \rightarrow \pi^*$) nm before irradiation and 278 ($n \rightarrow \pi^*$), 374 ($\pi \rightarrow \pi^*$) and 400 (SPRAB) nm after irradiation. Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.09; H, 4.84; N, 6.11; Found: C, 68.33; H, 4.64; N, 6.20.