Photochromic behavior of silver nanoparticle incorporated titanosilicate ETS-10 films

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**A R T I C L E   I N F O**

Article history:  
Received 28 November 2013  
Received in revised form 25 April 2014  
Accepted 6 May 2014  
Available online 14 May 2014

Keywords:  
Photochromism  
ETS-10  
Titanosilicates  
Silver nanoparticles  
Host-Guest systems

**A B S T R A C T**

The partially reversible photochromic behavior of Ag\textsuperscript{0} nanoparticle incorporated titanosilicate ETS-10 films was achieved for the first time. Ag\textsuperscript{+} ions were incorporated into ETS-10 matrix by ion-exchange of extra framework cations (i.e., Na\textsuperscript{+} and K\textsuperscript{+}) to form Ag\textsuperscript{+} ion-exchanged ETS-10. The colored (i.e., activated state) and colorless (i.e., bleached state) forms of the photochromic system of Ag\textsuperscript{0} nanoparticle incorporated ETS-10 films were achieved through thermal reduction and exposure to visible laser at 532 nm wavelength, respectively. The resulting Ag\textsuperscript{0}-ETS-10 films and also Ag\textsuperscript{+}-ETS-10 crystals have been characterized by ICP-OES, XRD, XPS, FE-SEM, HR-TEM, UV–vis spectroscopies. Partial restoration of color was achieved after second thermal treatment, which implies reversibility of the photochromic process. Furthermore, Density Functional Theory (DFT) results showed that ETS-10 had robust geometry and incorporation of the silver nanoparticles had minimal effect on the structure. The relationship of ETS-10’s unique structural formation along with the integration of Ag\textsuperscript{0} nanoparticles within its matrix and its subsequent photochromic property was shown for the first time.

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1. Introduction

Photochromism is defined as a light-induced reversible change of color [1]. General applications of photochromism can be divided into two categories: (i) those directly related to changes in absorption spectra such as optical information storage [2–4], variable transmission optical materials, and (ii) those related to changes in other physical or chemical properties such as refractive index etc. The most famous applications are smart windows [5] and sunglasses. Up to now, photochromic properties of organic materials such as spirooxazine, chromene derivatives [6], and azobenzene [7] have been most systematically examined. However, the number of inorganic materials known to display photochromism is limited. The most explored thin-film inorganic photochromic materials are the transition metal oxides WO\textsubscript{3}, NiO, and MoO\textsubscript{3} [8,9], which have also been investigated for applications in electrochromic devices [10] that show a reversible color change when a small DC voltage is applied.

Recently, silver doped titania has been studied extensively by the group of Prof. Tatsuma as a promising photochromic inorganic material [11–14], where electrons at the valence band of TiO\textsubscript{2} are excited upon UV irradiation, chemical or thermal means to the conduction band and then are used to reduce Ag\textsuperscript{+} ions into Ag\textsuperscript{0} nanoparticles. The formed Ag\textsuperscript{0} nanoparticles interact with visible light through their surface plasmon resonance and their electrons move towards the conduction band of TiO\textsubscript{2}, which results in the oxidation of Ag\textsuperscript{0} nanoparticles into Ag\textsuperscript{+} ions. The design of new hierarchical composite materials, such as silver nanoparticle incorporated TiO\textsubscript{2} matrixes that are used as porous templates for silver nanoparticle growth were investigated for photochromic applications. In such systems, the interest has usually been into mesoporous TiO\textsubscript{2} films with high surface area and controlled porosity [15].

In such porous matrixes, although TiO\textsubscript{2} films are used as templates for the reduction of silver nanoparticles, the role of TiO\textsubscript{2} has been discussed to particularly identify the necessity of these units in the visible light-induced oxidation process of silver
nanoparticles [11]. Afterwards, the requirement of TiO₂ with its semiconducting property was indeed shown to facilitate photo-oxidation of Ag⁺ into Ag⁰. The Ag⁰ nanoparticles in an insulating silica matrix were found not to exhibit photochromism, showing the ultimate evidence of the electron transport path via TiO₂ [11].

Engelhard titanosilicate ETS-10 is a relatively new class of microporous crystalline material (pore dimensions: 4.9 Å and 7.6 Å) where its Ti substituted silica matrix is composed of Si in tetrahedral and Ti in octahedral coordination [16]. The building units of ETS-10 are uniquely arranged to form 1-D TiO₂⁻ quantum wires (i.e., –Ti–O–Ti–O–Ti–) that are effectively separated from each other by the silica matrix [17] and have band gap energy, which was shown to be related to the length of the crystals along [110] direction [18]. ETS-10 is a unique nanoporous material in the sense that there are no molecular nanowires or nanorods that are embedded in a chemically inert large-band-gap medium identical to ETS-10.

Each TiO₂⁻ quantum wire incorporates two negative charges, which are compensated by extra framework charge-balancing cations Na⁺ and K⁺. Existence of extra framework cations creates an opportunity to incorporate any desired cation (i.e., Ag⁺) into the ETS-10 matrix by ion-exchange. It was previously shown that it is possible to create Ag⁰ nanoparticles by the reduction of Ag⁺ ions within the ETS-10 matrix opening the possibility to use this unique material in different applications [19]. Although ETS-10 has been stated to be an alternative inorganic material for different optical applications with its above mentioned unique properties [20], there is still a lot of room to examine this material in different applications. Accordingly, photochromic behavior of silver nanoparticle loaded ETS-10 can be considered due to 1-D quantum-confined form of titanias (i.e., TiO₂⁻ quantum wires) that run in the crystal in a and b directions and exchangeable extra framework charge-balancing cations (i.e., Na⁺ and K⁺) in the as-synthesized materials as indicated by the ETS-10 stoichiometry (NaₓK₁₋ₓTiSi₅O₁₃) [16].

Herein, we report the partially reversible photochromic behavior of Ag⁰-ETS-10 films for the first time. The unique combination of TiO₂⁻ quantum wires within the silica matrix forming ETS-10 structure raised the possibility to investigate the possible photochromic behavior of Ag⁰ nanoparticle incorporated ETS-10 films and the possible role of these quantum wires in the photochromic mechanism. This is the first study in which the relationship of this unique structural formation in ETS-10 along with the integration of Ag⁰ nanoparticles within its matrix is accompanied by its subsequent photochromic property.

2. Materials and methods

2.1. General

TiO₂ (P25, 76 wt.% anatase and 24 wt.% rutile, Degussa), Na₂SiO₃ were obtained from Sigma-Aldrich. AgNO₃, NaCl (99.0%), KCl (99.0%), and H₂SO₄ (96.5%) were received from J.T. Baker. Deionized water was distilled by water purification system (Milli-Q system). All glassware and Teflon coated magnetic stirring bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 373 K.

2.2. Analytical procedures and equipment

Morphological properties of the all ETS-10 films were examined by field emission scanning electron microscope (FE-SEM, FEI Quanta 400) SEM at an accelerating voltage of 30 kV. Phase identification of all samples was done by X-ray powder diffraction (XRD) using Rigaku-Ultima IV XRD by using thin-film attachment. The diffraction peaks were scanned between 5° and 50° with grazing angle of 0.3° with scan speed of 1°/min. Inductively coupled plasma optical emission spectrometry (ICP-OES – Perkin Elmer Optima 4300DV) was used for the elemental analysis. For the relative crystallinity measurements, peak height method was used by using the pure ETS-10 films as a reference. In the literature the peak heights of 2θ degrees in between 24.65° and 27.5° were used for the relative crystallinity measurements of pure ETS-10 crystals [21]. However, in our previous literature report [19] it was shown that when the powder XRD patterns of ETS-10 was compared with XRD pattern of Ag⁺-ETS-10 samples, systematic variations in the relative intensities at certain 2θ values were observed. As silver loading increased, relative intensities of (200), (204), and (224) reflections increased for Ag⁺-ETS-10 (5, 10 and 15 wt.%). Therefore, the relative crystallinity of the samples was calculated according to main Bragg peak, i.e. 2θ is equal to 24.7°. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 5000 VersaProbe spectrometer with an Al-Kα radiation source. The binding energies were referenced to the internal standard C ls binding energy at 284.5 eV. The sub-peaks under the high resolution silver and titanium spectra were identified by using PeakFit v4.12. The high resolution spectra of silver and titanium were fitted by Gaussian–Lorentzian functions after removal of the background by choosing two point linear background function. The fitting percentages were adjusted to be 98.99% and 99.99% for high resolution spectra of the titanium and silver, respectively. Specimens for high resolution-transmission electron microscopy (HR-TEM) analysis were prepared through solution-drop method. ETS-10 films were scratched through razor blade and a small amount of ETS-10 powder was added to ethanol solution and sonicated for 5 min. A small droplet of solution was dropped onto a standard holey carbon coated copper grid. HR-TEM investigations were performed using a JEOL JEM2100F field emission scanning/transmission electron microscope at an accelerating voltage of 200 kV. The HR-TEM images (i.e., two different images of the same film) of I-Ag⁺-ETS-10 and 5h-II–Ag⁺-ETS-10 films were examined to estimate size of the silver nanoparticles by using PhotoRuler Manual Version 1.0.0. Around 80 particles were counted for each film from two different areas taken from the same sample. UV–vis spectra were recorded using a Varian Cary EL08083100 UV–Visible spectrophotometer. The analysis range was 290–800 nm, before analysis of the samples, baseline subtraction was performed. The computations employed in Density Functional Theory (DFT) study were done using plane-wave pseudopotential DFT with the generalized gradient approximation (GGA) and ultra soft pseudopotentials. XCrysDen was used as a visualizer tool. Force threshold for geometric optimization calculations were 0.0025 eV/A per atom. Kinetic energy cut off was 35 Ryd and charge density cutoff was 350 Ryd for plane-wave basis set.

2.3. Synthesis of titanosilicate (ETS-10) as host matrix

ETS-10 crystals were synthesized by using the molar composition of 3.4 Na₂O:1.5 K₂O:TiO₂:5.5 SiO₂:150 H₂O [22]. In this preparation, NaCl and KCl were dissolved in deionized water in a bottle. After dissolving these components, sodium silicate solution was added and hand-shaken for 5 min, forming the Si precursor solution. For preparation of the Ti precursor solution, H₂SO₄ was added to deionized water in another bottle. To this, P₂5 TiO₂ was added and hand-shaken for 5 min. After both precursor solutions were hand-mixed, the Ti precursor solution was poured into the Si precursor solution. The resulting mixture was hand-shaken for 5 min. The mixture was transferred into Teflon-lined stainless steel autoclaves. The static synthesis was carried out for 3 days at 503 K; the products were cooled to room temperature, centrifuged, washed with deionized water, and dried overnight in ambient air at ~343 K.
2.4. Preparation of Ag⁺-ETS-10 matrix and Ag₀-ETS-10 films

Ag⁺ ion-exchanged ETS-10 samples (denoted as Ag⁺-ETS-10) were obtained by adding 500 mg of as-synthesized ETS-10 crystals to a 100 mL aqueous AgNO₃ solution with a concentration of 5.15 mM (5.15 mM corresponding to a maximum theoretical loading of 10 wt.% Ag⁺). The solution was stirred vigorously for 24 h at room temperature. In order to prevent auto-reduction of silver ions, the beaker was covered with parafilm and then with aluminum foil to prevent the solution from sunlight during stirring.

After ion exchange, the samples were washed several times with deionized water, collected by centrifugation and dried at 323 K under ambient air. After ion-exchange, drying temperature was chosen to be low (i.e., 323 K) to prevent auto-reduction of silver ions. The silver content of samples was determined by ICP-OES to be 8.18 ± 0.05 wt.% corresponding to 81.8% efficiency of ion-exchange. The Si/Ti molar ratios were 4.57 and 4.40 for as-synthesized ETS-10 and Ag⁺-ETS-10, respectively, which were found to be in correlation with what was reported before [19,22]. Glass substrates used for film preparation (20 mm × 25 mm × 1 mm) were cleaned by successive ultrasonication in acetone, ethanol, and 2-propanol. Each sonication step was carried out for 15 min and followed by 20 min drying in ambient air at 353 K. White colored Ag⁺-ETS-10 films were produced through spin-coating on pre-cleaned glass using an acetone suspension containing 5 wt.% of Ag⁺-ETS-10 crystals. The acetone suspension was sonicated for 30 min before spin-coating to prevent agglomeration of Ag⁺-ETS-10 crystals. Spin-coating of the films with silver ion-exchanged ETS-10 was done in clean room environment under yellow light to prevent samples from UV light. The colors of the silver ion-exchanged samples (i.e., powder and films) were white, which indicates that there was no auto-reduction after treatments. Average film thicknesses were determined to be 1.25 μm from cross sectional FE-SEM analysis (SI-1). Thermal reduction of Ag⁺ ions to Ag₀ nanoparticles within the ETS-10 films was carried out through calcination at 473 K for 3 h in ambient air (i.e., heating from 303 K to 473 K at 5 K/min, isothermal heating at 473 K for 3 h, and convective cooling to 303 K). These films with Ag₀ nanoparticles were denoted as I-Ag₀-ETS-10.

2.5. Testing the photochromic activity of Ag₀-ETS-10 films

A laser was used to convert metallic silver nanoparticles to their oxidized state in ambient air by exciting the nanoparticles at 532 nm wavelength. These ETS-10 films that were exposed to laser light and oxidized are denoted as LT-ETS-10. The laser source used throughout the study was HIPPO Spectra Physics laser, which is a diode-pumped solid state (DPSS) Q-switched laser. A focused laser beam with beam diameter 80 μm was used to scan an area of 10 mm × 25 mm on the I-Ag₀-ETS-10 film by moving the laser beam at a constant speed of 600 mm/s. The parameters of the laser (i.e., output power, repetition rate) were tuned to change the incident power on the sample. Different laser powers were applied to determine the effect of power on the photochromic behavior of the films. Selected intensities which were used in the experiment were 90 W/mm², 100 W/mm², 116 W/mm², and these films were denoted as 90-LT-ETS-10, 100-LT-ETS-10, 116-LT-ETS-10, respectively. In order to investigate the reversible behavior of ETS-10 films after visible laser treatment, thermal treatment was applied for the second time, where LT-ETS-10 samples were gradually calcined in a conventional oven at 473 K. During the second thermal treatment, LT-ETS-10 films were kept at 473 K for 3 h and 5 h to see if any changes during Ag₀ formation was going to take place. These samples were denoted as 3h-II-Ag₀-ETS-10 and 5h-II-Ag₀-ETS-10, respectively.
color was not fully attained, it was clearly observed that the color of 5h-II-Ag⁰-ETS-10 films was slightly darkened with respect to the initially treated 116-LT-ETS-10 films. Accordingly, partial reversibility was observed in 5h-II-Ag⁰-ETS-10 films (i.e., color darkening) after second thermal treatment (Fig. 1d). The films were placed on the logo of Middle East Technical University to distinguish transparency of the films after each treatment (i.e., Fig. 1a–d, left). The color of the films was shown more distinctly in Fig. 1a–d, right.

It is known that the duration, the spectral width and the irradiance of the visible light exposure have an influence on the final color of the obtained films [23]. Upon achieving a controlled and reversible change in the color of the originally obtained I-Ag⁰-ETS-10 films, it was of interest to investigate the effect of power of the visible laser to see whether a consistent change in the brownish color was going to be attained or not. Accordingly, three different laser powers were applied to I-Ag⁰-ETS-10 films. It was seen that the color of the films bleached more significantly as the power of visible laser increased (SI-2). Consistently, gradient bleaching and color change of the films were also observed in the literature for silver nanoparticle incorporated TiO₂ under visible laser illuminations with different irradiances [23].

3.1. FE-SEM and HR-TEM

Microporous ETS-10 crystals contain exchangeable extra framework charge-balancing cations (i.e., Na⁺ and K⁺) in the as-synthesized materials. Existence of extra framework cations creates an opportunity of incorporation of desired cations (i.e., Ag⁺) into ETS-10 matrix by ion-exchange and their reduction to nanoparticles within ETS-10 matrix through several reduction techniques [24,25], which leads to the formation of small narrow-sized silver nanoparticles in the inner surface of the crystals. Morphologies of I-Ag⁰-ETS-10, 116-LT-ETS-10, 5h-II-Ag⁰-ETS-10 films were investigated by FE-SEM and HR-TEM analyses. The formation of Ag⁰ nanoparticles with sizes in the range of 10–20 nm and some 30 nm was observed on the outer surface of ETS-10 crystals as can be seen in Fig. 2a and c. The detailed investigation on the formation of silver nanoparticles at the inner and outer surface of the ETS-10 crystals was discussed in a more detailed way in our previous publication [19]. Silver nanoparticles incorporated into the framework of ETS-10 crystals was more interesting for the current discussion since there should be interaction in between silver nanoparticles and TiO₂⁻ quantum wires within the ETS-10 framework to observe photochromism. Accordingly, HR-TEM analysis was carried out to examine silver nanoparticles incorporated into the ETS-10 crystals. HR-TEM images revealed that silver nanoparticles were formed upon thermal treatment as well with a mean size of 2.5 nm (Fig. 2d). The formation of silver nanoparticles which are smaller than 2 nm was observed inside the channels of ETS-10 by tilting specimen to [1 1 0] zone axis where the largest pores within the ETS-10 become parallel to the beam direction in the literature [19]. The observation of the fringes of the pores of zeolitic materials on the incorporated metal nanoparticles is generally accepted as an indicator of formation of metal nanoparticles within the crystals [26,27]. As a result, it is of high possibility that the observed silver nanoparticles in Fig. 2d with a mean size of 2.5 nm was within the pores of ETS-10.

Although the calculated crystallinity of the I-Ag⁰-ETS-10, 116-LT-ETS-10, 5h-II-Ag⁰-ETS-10 films was decreased to 87%, 70% and 77% for each treatment, respectively (vide infra), FE-SEM and HR-TEM images of the samples revealed that there was no observable structural change (i.e., melting) after any treatment (i.e., reduction, visible laser treatment, or second thermal treatment). The distinction of each treatment was more observable in HR-TEM images (Fig. 2e and f). Within the limitations of bright-field (BF) imaging conditions the mean size of nanoparticles formed within the pores of ETS-10 through thermal treatment was found to be 2.5 nm (Fig. 2d). It was shown that almost all nanoparticles in the pores of ETS-10 crystals have disappeared after exposure to visible laser at 532 nm through the excitation of the SPR of Ag⁰ nanoparticles (Fig. 2e). It is known that at specific size and morphology of Ag⁰ nanoparticles, surface electrons resonate with the incident light at certain wavelength [23,28]. Accordingly, some of the electrons were excited and transferred to ambient oxygen or to the conduction band of ETS-10 [11–14]. Consequently, the Ag⁰ nanoparticles transformed into Ag⁺ ions and the size of the nanoparticles shrank with respect to initial Ag⁰ nanoparticles. After second reductive treatment, the Ag⁺ nanoparticles reappeared at a mean size of 4 nm, which is slightly larger than the nanoparticles formed by
the thermal reduction method as seen in Fig. 2f. Such an occurrence was also noted in the literature where it was said that lower thermodynamic energy is needed to reduce ions on the already formed nanoparticles. Therefore, during the second reduction process, nanoparticles could have preferred to contribute to the growth of a negligible number of existing nanoparticles (or nuclei) instead of producing separate independent nanoparticles, leading to larger nanoparticle formation [29, 30].

3.2. XRD

The HR-TEM results were consistent with XRD results (Fig. 3, inset). An increase in the intensity of the Bragg peak at 38.2° was observed in the XRD patterns of I-Ag0-ETS-10 films (Fig. 3b), which is representative of the Ag0 nanoparticles attributable to the metallic silver in (111) plane [24,25]. Although as-synthesized ETS-10 crystals also have a peak at 2θ degree of 38.4°, a comparison of the relative change in the intensity of Bragg peak at 38.2° clearly gives some insight to the effect of all treatments as can be seen Fig. 3, inset. The highest intensity was observed for the I-Ag0-ETS-10 films; while, 2θ degree of 38.2° noticeably diminished in 116-LT-ETS-10 films with respect to I-Ag0-ETS-10 films. After second thermal treatment of the 116-LT-ETS-10 film, although the original peak intensity was not attained, the peak intensity of 38.2° increased again for 5h-II-Ag0-ETS-10 films with respect to 116-LT-ETS-10 films.

Furthermore, as seen from the comparison of the XRD patterns for the ETS-10 films given in Fig. 3, there was no noticeable change in the positions of the Bragg peaks. No significant peak broadening was detected for the samples with respect to the as-synthesized ETS-10 sample as well. The relative crystallinity of the films was calculated to be 87% for I-Ag0-ETS-10 films, while 2θ degree of 38.2° noticeably diminished in 116-LT-ETS-10 films with respect to I-Ag0-ETS-10 films. After second thermal treatment of the 116-LT-ETS-10 film, although the original peak intensity was not attained, the peak intensity of 38.2° increased again for 5h-II-Ag0-ETS-10 films with respect to 116-LT-ETS-10 films.

3.3. UV–vis spectroscopy

UV–vis spectra of the ETS-10, I-Ag0-ETS-10, 116-LT-ETS-10, and 5h-II-Ag0-ETS-10 films are shown in Fig. 4. ETS-10 shows an absorption band only in the UV range due to the presence of Ti4+ in octahedral coordination [32]. Therefore, the spectrum of

![Fig. 3. X-ray diffraction (XRD) patterns of (a) ETS-10 (black), (b) I-Ag0-ETS-10 films (red), (c) 116-LT-ETS-10 films (blue), and (d) 5h-II-Ag0-ETS-10 films (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 4. UV–vis spectra of (a) ETS-10 (black), I-Ag0-ETS-10 films (red), 116-LT-ETS-10 films (blue), 5h-II-Ag0-ETS-10 films (green), (b) I-Ag0-ETS-10 films (black), 90-LT-ETS-10 films (red), 100-LT-ETS-10 films (blue), 116-LT-ETS-10 films (green) and (c) I-Ag0-ETS-10 films (black), 116-LT-ETS-10 films (red), 3h-II-Ag0-ETS-10 films (blue), 5h-II-Ag0-ETS-10 films (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)
ETS-10 has no absorption band in the visible region, while UV–vis spectra of I-Ag$^0$-ETS-10 films show a broad absorption in the visible range. The broad absorption observed could be due to the large Ag$^0$ nanoparticles (i.e., ~15–20 nm) on the outer surface of ETS-10 crystals and/or dielectric medium of the surrounding matrix [15]. It seems that the absorption spectrum in the current study is governed by ~450 nm peaks, which shows that the generated silver nanoparticles were mostly in the smaller size regime. This is consistent with the HR-TEM results in Fig. 2d (Mean size of Ag$^0$ nanoparticles = 2.5 nm). Accordingly, the absorption around 450 nm can be attributed to small Ag$^0$ nanoparticles. In order to show the reversibility of the observed photochromism process in ETS-10, a second thermal treatment was performed after the visible laser treatment. After the second thermal treatment of 116-LT-ETS-10 films, the dark yellowish brown color reappeared (Fig. 1d). UV–vis spectroscopy showed that second thermal treatment lead to partial restoration (i.e., increase) of the absorption band at around wavelength of 450 nm (Fig. 4a), with a slightly more pronounced increase observed upon an increase in the duration of thermal treatment (Fig. 4c). Accordingly, it seems that, although full restoration of the SPR band at 450 nm was not achieved upon thermal treatment, the redox parameters chosen for photochromism process are indeed affecting the state of Ag$^+$ ions/Ag$^0$ nanoparticles within ETS-10.

To elucidate the effect of power on the oxidation (i.e., bleaching state), the power of the visible laser was altered through attenuation filter (i.e., 90 W mm$^{-2}$, 100 W mm$^{-2}$ and 116 W mm$^{-2}$). It was clear that the original yellowish brown color became consistently lighter as the power of visible laser increased in the oxidation process from 90 W mm$^{-2}$ to 116 W mm$^{-2}$ (SI-2). The UV–vis spectra of the films upon changing power of visible laser are shown in Fig. 4b. The SPR activity of the 116-LT-ETS-10 films also noticeably decreased with respect to the 90-LT-ETS-10 films and 100-LT-ETS-10 films. It must be also noted that the film colors were quite stable over time. The color of the 116-LT-ETS-10 film was slightly darkened after few months at room temperature in darkness.

3.4. XPS

In XPS analysis, high resolution Ag 3d spectra for the I-Ag$^0$-ETS-10 films (Fig. 5a) show doublet for Ag$^0$ nanoparticles at 368.1 eV for 3d$5/2$ and 374.1 eV for 3d$3/2$ with a binding energy (BE) separation of 6.0 eV, which is indicative of Ag$^0$ nanoparticles [33]. Compared to the binding energy values of silver metal (i.e., 368.0 eV and 374.0 eV), 0.1 eV shift toward higher values could be attributed to both the quantum size effect and peculiar electronic properties of the ETS-10 matrix [34]. The BEs of Ag 3d$5/2$ (i.e., 368.1 eV) for the I-Ag$^0$-ETS-10 films shifted to the BEs of 368.3 eV for both 116-LT-ETS-10 and 5h-II-Ag$^0$-ETS-10 films. The shift to metallic form (i.e., shift to BEs of 368.1 eV for Ag 3d$5/2$) was not observed for 5h-II-Ag$^0$-ETS-10 films. Therefore, the high resolution Ag 3d$5/2$ spectrum was deconvoluted into two doublets at 368.1 and 368.5 eV for 5h-II-Ag$^0$-ETS-10 film to determine the binding energies accurately. Details of the curve fitting results of the Ag 3d$5/2$ spectra for I-Ag$^0$-ETS-10 and 116-LT-ETS-10 films and the corresponding relative sub-peak area ratios (i.e., Ag$^+$/Ag$^0$) were shown in Table 1. According to Table 1, the ratio of the deconvoluted peak area at 368.5 eV (i.e., Ag$^+$) to total area revealed that the ratio of the silver increased from 10.96% to 38.69% for the cycle of I-Ag$^0$-ETS-10 → 116-LT-ETS-10 and decreased from 38.69% to 29.67% for the cycle of 116-LT-ETS-10 → 5h-II-Ag$^0$-ETS-10, which was expected from the photochromic cycles. When the main Ag 3d$5/2$ peak was considered, the shift to metallic form (i.e., shift to BEs of 368.1 eV for Ag 3d$5/2$) was not observed for 5h-II-Ag$^0$-ETS-10 films. However, detailed identification of the deconvoluted peaks revealed that ionic form of the silver was increased for 116-LT-ETS-10 with respect to I-Ag$^0$-ETS-10 and decreased for 5h-II-Ag$^0$-ETS-10 with respect to 116-LT-ETS-10, which was in correlation with XRD and UV–vis spectroscopy analyses.

High resolution Ti 2p spectra were fitted by Gaussian–Lorentzian functions after removal of the background. Ti 2p spectra of I-Ag$^0$-ETS-10, 116-LT-ETS-10 and 5h-II-Ag$^0$-ETS-10 films were depicted in Fig. 6. Details of the curve fitting results of the Ti 2p spectra for the films and the corresponding relative sub-peak area ratios were presented in Table 1. The peak in 458.7 eV, related to octahedral Ti species, was observed to shift to 459.1, 458.9, and 459.1 eV for the I-Ag$^0$-ETS-10, 116-LT-ETS-10, and 5h-II-Ag$^0$-ETS-10, respectively. Similar shifts in the octahedral coordination of Ti species were also observed upon acid treatment in ETS-10 as well [35].

The oxidation state of the titanium is expected to shift from Ti$^{4+}$ to Ti$^{3+}$ for the cycle of I-Ag$^0$-ETS-10 → 116-LT-ETS-10 and return back from Ti$^{3+}$ to Ti$^{4+}$ for the cycle of 116-LT-ETS-10 → 5h-II-Ag$^0$, ETS-10 as also shown in the equations below,

$$\text{Ag}^0 \rightarrow \text{Ag}^+ + e^- \quad (1)$$
$$\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+} \quad (2)$$

![Fig. 5. X-ray photoelectron spectroscopy (XPS) high resolution Ag 3d spectra of (a) I-Ag$^0$-ETS-10 films, (b) 116-LT-ETS-10 films and (c) 5h-II-Ag$^0$-ETS-10 films.](image-url)
Table 1: Binding energy of the deconvoluted peaks of the Ti 2p and Ag 3d spectra and the corresponding relative sub-peak area ratios of the films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE of Ti 2p_(1/2) (eV)</th>
<th>BE of Ti 2p_(3/2) (eV)</th>
<th>BE of Ag 3d_(5/2) (eV)</th>
<th>Area of Ti(^{3+})/(\text{Ti}^{3+} + \text{Ti}^{4+}) (%)</th>
<th>Area of Ag(^{+})/(\text{Ag}^{+} + \text{Ag}^{0}) (%)</th>
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<tbody>
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<td>I-Ag(^0)-ETS-10</td>
<td>462.9</td>
<td>464.9</td>
<td>457.7</td>
<td>368.1</td>
<td>368.6</td>
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<td>3.69</td>
<td>10.96</td>
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<tr>
<td>116-LT-ETS-10</td>
<td>462.7</td>
<td>464.6</td>
<td>457.7</td>
<td>368.1</td>
<td>368.5</td>
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<td>5.44</td>
<td>38.69</td>
</tr>
<tr>
<td>5h-II-Ag(^0)-ETS-10</td>
<td>462.8</td>
<td>464.8</td>
<td>457.9</td>
<td>368.1</td>
<td>368.5</td>
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<td>5.44</td>
<td>38.69</td>
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\(^a\) The percentage was calculated according to the ratio of the deconvoluted peak area at 462.9 eV (i.e., \(\text{Ti}^{3+}\)) to total area.

\(^b\) The percentage was calculated according to the ratio of the deconvoluted peak area at 368.5 eV (i.e., \(\text{Ag}^{+}\)) to total area.

3.5. Mechanism of photochromic process at titanosilicate ETS-10 films

For reversible photochromic reactions, electron–hole (e\(^−\)-h\(^+\)) pairs generated by electronic transition must react with each reactant in every cycle. For instance, in the structure of Ag\(^0\) nanoparticle incorporated TiO\(_2\), electronic transition is generated through UV radiation and the created e\(^−\)-h\(^+\) pairs initiate several reactions for reversible photochromic process [11–14,37,38]. In the case of ETS-10, silica matrix should not contribute to electronic transition. Instead, TiO\(_2\) quantum wires (i.e., Ti–O–Ti–O–Ti) are considered to be responsible for the electronic transition, which was also discussed in detail in the literature [39,40]. It was shown that the oxygen atoms along the TiO\(_2\) quantum wires are confined in narrow range of energies, which suggests that electrons are confined in the TiO\(_2\) octahedral [40]. Using DFT modeling of ETS-10 with 132 atoms where two Ti atoms were surrounded by Si and O atoms in one unit cell, band gap energy of ETS-10 was calculated as 3.37 eV [41].

Ag nanoparticles were modeled in a range of 0.9–2.0 nm, which varies in a range of about 20–300 atoms. Relaxation computations were completed for the eligible models (i.e., up to 150 atoms) under vacuum condition. Density Functional Theory (DFT) calculations within the gradient-corrected approximation (GGA) have been carried out on ETS-10 and silver nanoparticles with the aim to elucidate the effect of geometric optimization of particles and ETS-10 together. All interactions between atoms (i.e., the interaction between Ag and Si, O or Ti) were included in these calculations. 20-atom sized (i.e., 0.9 nm) silver nanoparticle was used for the DFT calculations instead of 300-atom sized (i.e., 2.0 nm) silver nanoparticle, since calculations did not converge due to quiet high number of atoms in one unit cell for a DFT input (i.e., total 432 atoms for 2.0 nm-sized silver nanoparticle). Relaxation calculations were completed under absolute temperature at vacuum level. The results suggest that ETS-10 had robust geometry and incorporation of the silver nanoparticles had minimal effect on the structure. However, in order to investigate the interactions in more detail, Molecular Dynamics (MD) simulations should be performed with temperature parameters. The Fermi level of the silver nanoparticles consisting of 20 Ag atoms in one unit cell (at size of ~0.9 nm) and conduction band edge of ETS-10 were calculated to be ~3.19 eV and ~0.8 eV, respectively (Fig. 7a). Within the limitation of DFT study to find Fermi level accurately, it could be speculated that the Fermi level of the silver nanoparticles consisting of 20 Ag atoms matches with the band gap energy of ETS-10, which could enable transfer in redox reactions.

Size of the silver nanoparticles formed affects the photochromic process due to the size dependent redox potential (or Fermi level) of silver nanoparticles. This is known to influence both thermodynamics and kinetics of the photoinduced dissolution of Ag\(^0\) nanoparticles [42]. Han et al., calculated that Ag\(^0\) nanoparticles of a few nanometer sizes are subject to easier oxidation than those of over 20 nm in the viewpoint of thermodynamics [42]. In the case...
of zeolites, the cages and channels of zeolites provide a novel environment for molecular and nanoparticle assembly for photochemical reactions [43]. Dutta et al. showed that, zeolites can be active participants in reactions with photoexcited entrapped molecules as electron donors and acceptors [43]. As a result, the porous structure of the zeolites prevents recombination of the charge-separated species. Accordingly, since the created Ag nanoparticles are smaller due to the confining effect of the pores of ETS-10 matrix, they can be oxidized easily (Fig. 5).

The proposed mechanism of photochromic process for ETS-10 films is given as following. The reduced metallic state is formed through thermal treatment. In the absence of thermal treatment (or after visible light radiation), the metallic Ag nanoparticles gradually transform into oxidized state. The visible light accelerates oxidation process through photo-excitation of electrons of Ag nanoparticles. The suggested reactions for the reversible photochromic process for Ag nanoparticles incorporated ETS-10 is shown in the equations below.

The main reaction;
\[
\text{Ag}^{0} \rightleftharpoons \text{Ag}^{+} \quad (3)
\]
In the presence of thermal energy;
\[
\text{TiO}_{2}^{-} + h^{+} + e^{-} \quad (4)
\]
\[
\text{Ag}^{+} + e^{-} \rightarrow \text{Ag}^{0} \quad (5)
\]
In the absence of thermal energy (or visible light radiation);
\[
\text{Ag}^{0} \xrightarrow{\text{Vis}} \text{Ag}^{+} + e^{-} \quad (6)
\]

4. Conclusions

The photochromic behavior of Ag nanoparticles incorporated ETS-10 and the possible role of the unique TiO$_2$ quantum wires in the photochromic mechanism were comprehensively investigated for the first time. For that purpose, Ag$^+$ ions were incorporated into ETS-10 matrix by ion-exchange of extra framework cations (i.e., Na$^+$ and K$^+$) to form Ag$^+$ ion-exchanged ETS-10. The redox process, which contains colored form (i.e., activated state) of the photochromic system/colorless form (i.e., bleached state) of the photochromic system of Ag nanoparticles incorporated ETS-10 films, was achieved through thermal reduction of the films and exposure of them to visible laser at wavelength of 532 nm, respectively. XRD, HR-TEM and UV–vis spectroscopy results showed that photochromic cycle was obtained for Ag nanoparticles incorporated ETS-10 films. According to XPS results, the ratio of the deconvoluted peak area at 368.5 eV (i.e., Ag$^+$) to total area revealed that the ratio of the silver increased from 10.96% to 38.69% for the cycle of I-Ag$^0$-ETS-10 → 116-LET-ETS-10 and decreased from 38.69% to 29.67% for the cycle of 116-LET-ETS-10 → 5h-II-Ag$^0$-ETS-10, which was expected from the photochromic cycles. Furthermore, the XPS results proved that the valance state of the titanium shifted from Ti$^{4+}$ to Ti$^{3+}$ and vice versa for the films, which support the photochromic mechanism of the silver incorporated ETS-10 films indisputably in addition to the other results.

Acknowledgments

The support provided by METU-Central Laboratory is greatly acknowledged. The support provided by European Union project with the project number FP7-PEOPLE-2012-IRSES, 318524 is acknowledged. The authors would like to thank Dr. Caner Durucan, Özlem Altıntaş Yıldırım, Gözde Alkan for their valuable support in UV–vis spectroscopy. The French National Research Agency (ANR) is acknowledged for financial support in the framework project UPCOLOR No. JCJC 2010 10021. The support provided by the NATO CBP. NUKR. SFPP. 984173 is also acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014.05.009.

References