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# Photocatalytic removal of airborne indoor pollutants by IR illuminated silver coated $TiO_2$ catalyst: Advantage of one-dimensional $TiO_2$ nanostructures in IR active photocatalysis



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# GRAPHICAL ABSTRACT

The degradation of common airborne pollutants in indoor conditions was successfully demonstrated with silver coated 1-D TiO<sub>2</sub> nanotubes under IR irradiation.



#### ARTICLEINFO

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## ABSTRACT

The development of IR sensitive photocatalysts is indispensable for the abatement of indoor pollutants as most of the photocatalysts mainly absorb radiation in the UV region and weakly in the visible region and not responding to indoor conditions. On the other hand, IR photons initiated photochemical reaction needs a highly efficient excited charge separation step as it is a multi-excitation process. In order to enhance the charge separation process in multi-step excitation photocatalytic systems, in this investigation the photocatalytic activities of silver coated 1-D TiO<sub>2</sub> nanotubes were employed and the photocatalytic activity of 1-D TiO<sub>2</sub>nanotubes was compared with the photocatalytic activity of TiO<sub>2</sub> nanoparticles. A superior photocatalytic activity was noted with the silver coated 1-D TiO<sub>2</sub> nanotubes under IR irradiations than that of silver coated TiO<sub>2</sub> nanoparticles. The impedance measurements were conducted by electrochemical impedance spectroscopy to differentiate the transport resistances, electron-hole recombination and electron lifetime of the silver coated 1-D TiO<sub>2</sub>nanotubes and nanoparticles. The possibility of the use of silver coated 1-D TiO<sub>2</sub> nanotubes for the degradation of common airborne pollutants with near IR photons (similar to indoor conditions) was successfully demonstrated.

#### 1. Introduction

The TiO<sub>2</sub> catalyst has been the most investigated photocatalyst

among the heterogeneous semiconductor photocatalytic materials in clean energy and environmental remediation due to its excellent photocatalytic activity, high chemical and physical stability, good thermal

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https://doi.org/10.1016/j.colsurfa.2020.124509 Received 6 January 2020; Received in revised form 23 January 2020; Accepted 24 January 2020 Available online 25 January 2020 0927-7757/ © 2020 Elsevier B.V. All rights reserved. and electrical property, low cost, non-toxicity and high availability [1,2]. Different TiO<sub>2</sub> structures such as nanoparticle, nanotubes, nanorods, nanowire, nanofiber and nanoflower possess significant various physical, electrical and chemical properties [3-5]. The significant different photocatalytic activities reported for different TiO<sub>2</sub> structures were correlated to differences in their size, shape, surface area, morphology and dimensionality [6]. Several studies claimed that the three dimensional hierarchical nanostructures assembly of one dimensional nanotube, nanorods, nanowires, are excellent candidates for photodegradation of organic pollutant because they possess an excellent ability to adsorb organic pollutants, high surface to volume ratio and improved light scattering within the structure [7,8]. Despite different 1-D structures of TiO<sub>2</sub> exhibit enhanced photocatalytic activities, they are active only in the UV region of the solar spectrum owing to their high bandgap energy ( $\sim 3.2 \text{ eV}$ ) and hence the overall photocatalytic efficiency does not warrant for pragmatic applications especially in indoor conditions where the available light is mostly Vis-near IR radiations.

In the recent past, several strategies have been employed to improve the photocatalytic response of TiO<sub>2</sub> materials in the visible region, i.e. non-metal doping of N, F,C,S and co-doping of non-metals [9], doping of noble metal nanoparticle, such as Au, Ag, Pt, Pd [10-12] and transition metal deposition, oxygen rich/vacant TiO<sub>2</sub> modification [13-15], coupling with another semiconductor such as ZnO, CdS, BiVO<sub>3</sub>, Ag<sub>2</sub>O, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub> [16–18], dye-sensitization [19] and introducing of defects in the TiO<sub>2</sub> lattice [20]. Among those TiO<sub>2</sub> modification methods, doping of Ag and Ag based compounds on TiO<sub>2</sub> nanostructures is a simple way to improve the Vis-IR photocatalytic activity of semiconductor based photocatalysts owing to silver exhibits a facile tunability of the band gap allowing wide solar response as well as being a relatively cheap [21,22]. Extensive research has been carried out on Ag and Ag<sub>2</sub>O modified TiO<sub>2</sub> for photodegradation and hydrogen production under UV and visible light radiation. Some research has pointed out that composite of Ag<sub>x</sub>O and TiO<sub>2</sub> could be able to produce hydrogen from water and methanol mixture with the aid of UV radiation [23]. Ag2Oand Ag coated titania nanoparticles have been applied to degradation of methylene blue undervisible radiation [24], and in an another study, Ag<sub>2</sub>O nanoparticle decorated TiO<sub>2</sub> nanorod composite has been reported as an advanced candidate to degrade methylene blue under visible light [25].

In all these past investigations, the major goal was to enhance the catalytic activities of TiO<sub>2</sub> in the visible regions of the solar spectrum. However, few efforts have been reported in activation of TiO2 under infrared light, i.e. IR active Ag/Ag<sub>2</sub>O/TiO<sub>2</sub>and Au/TiO<sub>2</sub> nanocomposites for water reduction reaction have been successfully demonstrated [26]. Liang et al. demonstrated the IR driven CO<sub>2</sub> reduction with ultrathin oxygen-deficient cubic WO<sub>3</sub> layers in which IR light harvesting is due to formation of an intermediate band (due to oxygen deficiency) within the forbidden gap [27]. The visible to near-infrared photocatalysis have been reported with black phosphorus/graphitic carbon nitride catalyst [28] and Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst using graphene oxide as the electron mediator [29]. In a recent investigation, Visible and near infrared light active photocatalysis based on conjugated polymers has been reported [30]. However, photocatalytic degradation of pollutants with IR active TiO<sub>2</sub> photocatalysts has not adequately been investigated. In a recent study we reported the IR active silver coated TiO<sub>2</sub>nanoparticles for the photodegradation of phenol [10]. As the IR radiation initiated photochemical reactions are multiphoton process, enhanced charge separation is an important prerequisite and hence in this report, to improve the charge separation and consequently photocatalytic activity in the IR region, silver coated 1-D TiO<sub>2</sub>nanostubes were employed. Our study clearly demonstrates that the nanotubes based Ag/Ag<sub>2</sub>O/TiO<sub>2</sub>(NT) shows enhanced photocatalytic activity under IR radiation than in the case of nanoparticle based composite catalyst, Ag/Ag<sub>2</sub>O/TiO<sub>2</sub>(NP). The analysis of physical as well as electronic properties of both TiO2 nanoparticles and nanotubes provides strong support for the observed enhanced catalytic activity of Ag/

 $Ag_2O/TiO_2(NT)$ . The IR response of the catalyst suggested the stepwise promotion of electrons within the sub-bands by absorbing IR photon and therefore, electronic up-conversion mechanism is proposed for the catalytic effect under IR radiation [18,31].

#### 2. Experimental

#### 2.1. Catalyst preparation

All chemicals were analytical grade, AgNO<sub>3</sub> (99.8 %-100.5 %, Sigma-Aldrich and BDH), NH<sub>3</sub> (25 %, Thomas Baker), TiO<sub>2</sub> (P25, Degussa), NaOH (99 %, VWR), HCl (37 %, Sigma-Aldrich), phenol (99 %. ACS reagent, Sigma-Aldrich) were used and the chemical reagents were prepared in distilled deionized water. All glassware was cleaned by soaking overnight in HNO3 (10 %) and rinsed several time with distilled water. For the synthesis of TiO<sub>2</sub> nanotube, 2.00 g of TiO<sub>2</sub> was mixed well with 35 ml of 10 M NaOH solution for 5 h and homogenized by applying ultrasonic waves by ultrasonic horn sonicator (Bandelinsonopuls, TT 19 probe, titanium alloy (Ti-AI6-V4), cycle 2, power 40) for 5 min and then the solution was transferred to a Teflon lined autoclave until three forth of its volume and heated at 150°C for 48 h. [32] Consequently, it was allowed to natural cooling. The paste prepared by solvothermal synthesis was collected and washed thoroughly with distilled water until the pH of the sample is 3.5-3.6 and then it was freeze-dried. The sample was stored in a desiccator until used in preparation of catalyst. For the deposition of silver on TiO<sub>2</sub> NP and TiO<sub>2</sub> NT, a stoichiometric amount of 1.0 M NH<sub>4</sub>OH was added to a solution containing TiO<sub>2</sub> (100.00 mg of TP or TN) and AgNO<sub>3</sub> (x mg, x = 25.0, 30.0, 40.0, 45.0 mg) in a 5 ml distilled water. The mixture was stirred for 30 min and heating was continued at 120°C while stirring until a dry powder is obtained. The resulting dry powder was calcined at 180°C for one hour with a temperature gradient of 8°C min<sup>-1</sup>, and subsequently allowed to natural cooling. Finally, the resulting sample was ground to obtain fine and uniform sized particles and the catalyst was stored in the complete dark, ambient temperature in a desiccator to avoid moisturizing until further use.

#### 2.2. Characterization of materials

Diffuse reflectance spectrum of finely ground Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP), Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT), TiO<sub>2</sub>(P25), TiO<sub>2</sub> nanotubes and Ag<sub>2</sub>O particles were taken using Shimadzu UV-2450 UV-vis spectrophotometer in reflectance mode. X-ray diffraction (XRD) pattern were obtained by a powder X-ray diffractometer PANalyticalX'Pert diffractometer (X'Pert PRO MPD, PW3040/60) within the  $2\theta$  ranging from 5° to 90° by a speed of 2° minute<sup>-1</sup> with Cu-K $\alpha$  ( $\lambda$  = 0.154060 nm) radiation (40 kV, 40 mA). The X-ray diffractions were carried out for the catalysts, TiO<sub>2</sub> (P25), TiO<sub>2</sub> nanotubes and Ag<sub>2</sub>O and powder XRD patterns were analysed and compared with the standard data, available in the JCPD (Joint Committee on Powder Diffraction Standards) files, for the identification of crystalline phases of the catalysts. The chemical states of the each element in the catalyst was determined qualitatively and the quantitatively by X-ray photoelectron spectroscopy from hemispherical electron energy analyser (ESCALAB-250XI) multifunctional imaging electron spectrometer (Thermo Fisher Scientific Inc.) with an Al Ka Xray tube (1486.6 eV). For the comparison purpose, XPS analyses of TiO<sub>2</sub>(P25) and TiO<sub>2</sub> nanotube were also conducted. Scanning electron microscopy was probed to analyse the surface morphology of the catalysts. In order to obtain the microscopic image of the powdered catalyst were spread over a conductive carbon tape pasted on a sample stand and then gold was sputtered on the sample with a mini sputter coater (Quorum sc 7620) by applying 10 mA time at  $3 \times 10^{-6}$  bar pressure and the samples were loaded into scanning electron microscope (Hitachi SU6000 FESEM) to probe the microscopic image of the catalyst. The element and the ratio of the element present in the catalytic sample were analysed by Energy dispersive X-ray analysis. The

EDX spectrum of finely ground catalysts were lorded into scanning electron microscope recorded (Hitachi SU6000 FESEM) and then examine the elemental distribution of the catalyst by using EDX equipment associated with the SEM Instrument. TEM micrograph of finely ground catalysts and  $TiO_2(P25)$ , $TiO_2$  nanotubes were taken by using JEM-2100 transmission electron microscope operating at 200 kV and particle size and the fringe patterns of the each crystalline lattice and crystal lattice phases of the catalyst were identified. The specific surface area, average pore diameter, total pore volume, and pore size distribution of the samples were determined from the adsorption and desorption isotherms of nitrogen at 77 K after outgassing procedure under vacuum at 250°C for 10 h, using a Quantachrome Autosorb-1 instrument (QUDRASORB SI-MP-10). RAMAN, Horiba JY, Lab RAM HR800, FTIRBruker Tensor27).

#### 2.3. Photocatalytic measurement

The phenol degradation was carried out in a glass vacutainer with 10 ml internal volume. Under dark condition, Xmg of (5, 10, 15 or 20) catalyst was spread over 5 cm<sup>2</sup> area and the system was sealed by a rubber septum and evacuated by a 10 ml syringe and 10 ml of 200 ppm phenol gas was injected into the vacutainer in the vicinity of the catalyst. Finally, the infrared (IR) radiation was directed onto the catalyst in order to perform the catalytic reaction. The IR radiation source was confined with eight light emitting diodes (880 nm, Ø 5 mm,  $3.2 \text{ mWcm}^{-2}$ ). The detail description of the IR light illumination source is given in the SI. The reaction products in phenol degradation were analysed quantitatively and qualitatively by Gas Chromatography (GC-789011) coupled with thermal conductivity detector.

#### 2.4. Electrochemical impedance spectroscopy (EIS) analysis

The electron transfer kinetics and ionic process in the catalyst was measured by the electrochemical impedance spectroscopy (EIS). For EIS measurements, the catalyst was deposited on the FTO glass by spin coating of the catalyst prepared by mixing 10 % methanol and sintered at 190 °C for 30 min and allowed natural cooing. After sandwiching the catalyst coated electrode with Pt counter electrode, an electrolyte solution (10 % methanol) was added in between the two electrodes. Finally, the impedance measurement was performed with Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) at10 mV amplitude ac signal and in the frequency range from 0.1 Hz to 1 MHz under dark and light conditions at open circuit voltage.

#### 3. Results and discussion

The photodegradation of gaseous phenol with silver coated TiO<sub>2</sub> nanoparticles under indoor conditions has been successfully demonstrated [10]. In this investigation, the  $\rm TiO_2(NP)$  in the Ag\_O/Ag/ TiO<sub>2</sub>(NP) catalyst was replaced with the TiO<sub>2</sub> nanotube (NT) with the aim of enhancing the charge separation and the photocatalytic activities of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) for the degradation of airborne pollutants with IR radiations were investigated. To understand the compositions and structures of the silver coated [Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT)] and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP)] catalysts, XRD was carried out and the XRD patterns of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) are shown in Fig. 1a and b respectively. In both TiO<sub>2</sub>(NP) and TiO<sub>2</sub>(NT) structures, appearance of diffraction peaks at 25.43°, 37.92°, 48.03°, 53.97°, 55.05°, 62.70°, 68.80°, 70.39° and 75.05 can be attributed to the tetragonal phase of anatase TiO<sub>2</sub> and whereas the peak at 27.80°, 36.80° and 41.80° that corresponds to the tetragonal phase of rutile TiO<sub>2</sub>, indicates the structural similarity between TiO<sub>2</sub>(NT) and TiO<sub>2</sub>(NP) [33,34]. As shown in Fig. 1a, the diffraction peaks of Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) at 24.3°, 32.6°, 38.1°, and 65.4° perfectly correlate to the (110), (111), (200), (220) and (311) crystal planes of cubic Ag<sub>2</sub>O



Fig. 1. X-ray diffraction patterns of silver coated (a)  $Ag_2O/Ag/TiO_2(NP)$  and (b)  $Ag_2O/Ag/TiO_2(NT)$ .

(JCPDS 41–1104)(JCPDS No.76–1393) [35–37]. Additionally, the diffraction peaks appeared at 31.3°, 39.6° and 64.3° match with AgO (200), (111) and (311) planes respectively (JCPDS No.89–3081). The three peaks at 44.3°, 46.2°, and 64.6° can be indexed to the (200), (231), and (220) crystal planes of cubic Ag(0) respectively (JCPDS 04-0783) [33,34]. The strongest peak of Ag(111) might likely be masked by the TiO<sub>2</sub> peak at  $2\theta = 38^{\circ}$ .On the other hand, as shown in Fig. 1b, the intensity of diffraction peaks that correspond to the crystalline phases of Ag<sub>2</sub>O, AgO and Ag in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) are weak compared to that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). Furthermore, the sharp and enhancement of the intensity of diffraction peaks of Ag<sub>2</sub>O, AgO and Ag in the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) hetero-structure indicates the high degree of crystallinity of Ag<sub>2</sub>O, AgO and Ag in the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst compared to that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst.

The micro-structural details of silver coated TiO<sub>2</sub> nanoparticles and nanotubes were investigated by the HRTEM images. The TEM image and the lattice fringes of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst are shown in Fig. 2a and b respectively while Fig. 2c and d respectively show the TEM image and the lattice fringes of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). As shown in Fig. 2a and b, the average size of the spherical shape TiO<sub>2</sub> particles is 25 - 30 nm and the resolved inter-planar distances is ca. 0.35 nm corresponding to the (101) plane of anatase TiO<sub>2</sub> [38]. These TiO<sub>2</sub>(NP) are uniformly covered by 2 - 5 nm size silver/silver oxides particles and the observation of particles with fringe widths of 0.335 nm in Fig. 2b confirms the presence of cubic Ag<sub>2</sub>O[110] [39,40]. Furthermore, in



Fig. 2. The TEM image (a) and the lattice fringes (b) of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst and the TEM image (c) and the lattice fringes (d) of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst.

Fig. 2b, particles with inter-planer distances of ca. 0.226 and 0.234 nm, corresponding to the AgO(101) and the Ag(111) respectively. The fringe width 0.208 nm could be due to AgO (200) or Ag. These TEM results further confirm the X-ray diffraction results in which the presence of Ag<sub>2</sub>O, AgO and Ag crystalline structures were noted on the TiO<sub>2</sub>(NP). Similarly, the TEM image and the lattice fringes of the Ag<sub>2</sub>O/ Ag/TiO<sub>2</sub>(NT) shown in Fig. 2c and d demonstrate the uniformly covered by 2-5 nm size silver/silver oxides particles on the TiO<sub>2</sub>(NT) and these silver nanoparticles with fringe widths of 0.335, 226 and 0.234 nm can be assigned to the crystal planes of Ag<sub>2</sub>O [111], AgO(101) and the Ag(111) respectively. In the TEM image of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) (Fig. 2c), in addition to 1-D TiO<sub>2</sub>(NT), few irregular shape TiO<sub>2</sub>(NT) were also observed and these TiO<sub>2</sub> structures appear as two-dimensional TiO<sub>2</sub> crystalline sheets due to partially formed TiO<sub>2</sub>(NT) during the hydrothermal synthesis of TiO<sub>2</sub>(NT). It is well known that the formation of two-dimensional TiO<sub>2</sub> crystalline sheets due to lateral growth of TiO<sub>2</sub>(NT) in the [001] direction [41]. The XRD and TEM results confirms the crystalline structure similarity of the TiO<sub>2</sub> and the silver/ silver oxides in both Ag2O/Ag/TiO2(NP) and Ag2O/Ag/TiO2(NT) and hence warrants the direct comparison of the catalytic activities of silver coated TiO<sub>2</sub>(NP) and TiO<sub>2</sub>(NT).

As the oxidation states and hence the surface composition and electronic structure of silver coated  $TiO_2$  is a crucial factor in controlling the photocatalytic activity of  $Ag_2O/Ag/TiO_2(NT)$  and  $Ag_2O/Ag/TiO_2(NP)$ , oxidation states of Ag and Ti in silver coated  $TiO_2(NP)$  and  $TiO_2(NT)$  were analysed by XPS. In the Ti 2p spectra of pure  $TiO_2(NP)$  shown in Fig. 3a, the main peak at 457.80 (Ti 2p3/2) and 463.58 (Ti 2p1/2) eV can be assigned to  $Ti^{4+}$  state in the  $TiO_2(NP)$ . The Ti 2p spectra and Ag 4d spectra of the  $Ag_2O/Ag/TiO_2(NP)$  are shown in Fig. 3b and c respectively. As shown in Fig. 3b, peaks at BEs of 458.56 eV and 464.28 eV could be assigned to the  $Ti^{4+}$  state while minor peaks at BEs of 457.52 eV and 462.71 eV could be attributed to

the  $Ti^{3+}$  state [42,43]. The appearance of a small shoulder peak that corresponds to Ti<sup>3+</sup> states is due to the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> (457.7 eV), suggesting charge transfer from the Ag to the  $TiO_2$  surface. As shown in Fig. 3c, Ag 3d<sub>5/2</sub> peaks of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) at 367.94, 367.42 and 368.32 eV are due to  $Ag^{+2}$ ,  $Ag^{+}$  and  $Ag^{\circ}$  states respectively [44,45]. However, Ag 3d<sub>3/2</sub> peaks are slightly shifted to higher binding energies with respect to that of authentic Ag 3d which could be due to charging effect. The dominance peak at BE of 367.94 indicate that the silver is mostly present in its AgO crystalline structure. Similarly, the Ti 2p spectra of pure TiO<sub>2</sub>(NT) is shown in Fig. 3d, while and the Ti 2p spectra and Ag 4d spectra of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) are shown in Fig. 3e and f respectively. The XPS spectrum of the bare  $\rm TiO_2(NT)$  indicates that the  $\rm Ti^{4+}$  peak at 457.82 (Ti 2p3/2) and 463.55 (Ti 2p1/2) eV are similar to that of TiO<sub>2</sub>(NP) indicating that both  $TiO_2(NP)$  and  $TiO_2(NT)$  have similar oxidation state. The  $Ti^{4+}$  and Ti<sup>3+</sup> peaks in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) (Fig. 3e) appear at BEs of 458.15, 463.88 eV and 457.37, 460.00 eV respectively. Meanwhile, the relative higher peak intensity of the Ti<sup>3+</sup> state in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) than that in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) suggests the enhance charge transfer from the Ag to the TiO<sub>2</sub>(NT) surface. As shown in Fig. 3f, Ag 3d<sub>5/2</sub> peaks of Ag<sub>2</sub>O/ Ag/TiO<sub>2</sub>(NT) appear at BEs 367.66, 367.37 and 368.12 eV are due to  $Ag^{+2}$ ,  $Ag^{+}$  and  $Ag^{\circ}$  states respectively [44,45].

In the XPS results of both  $Ag_2O/Ag/TiO_2(NP)$  and  $Ag_2O/Ag/TiO_2(NT)$ , the main Ti 2p3/2 peak has been positively shifted after silver coating which could be attributed to interaction between the Ag clusters and the titania surface [46]. The positive shift in Ti 2p3/2 peak is higher in silver coated TiO<sub>2</sub>(NT) than that of TiO<sub>2</sub>(NP) indicating enhanced Ag-TiO<sub>2</sub> interaction in the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). On the other hand, in the Ag 3d spectrum, a small downward shift in BE of the Ag 3d peak is observed in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) compared to Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) suggest the formation of increased Ag<sub>2</sub>O/Ag clusters size on the TiO<sub>2</sub>(NP) catalyst. Quantitative analysis of the relative intensities of



Fig. 3. XPS spectra of (a) Ti 2p of the bare TiO<sub>2</sub>(NP), (b) Ti 2p and (c) Ag 4d of theAg<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst, (d) Ti 2p of the bare TiO<sub>2</sub>(NT), (e) Ti 2p and (f) Ag 4d of theAg<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst.

 $Ti^{4+}/Ti^{3+}$  indicated the generation of more reduced  $Ti^{3+}$  states in the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst than the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst. Presence of reduced Ti<sup>3+</sup> states leads to color changes where the white color TiO<sub>2</sub> turns into blue due to the presence of Ti<sup>3+</sup> or/and oxygen vacancies and these vacancy states localize at 0.75-1.18 eV below the conduction band minimum of the rutile phase of TiO<sub>2</sub> [47,48]. The XPS results confirm the presence of  $Ti^{4+}$ ,  $Ti^{3+}$ ,  $Ag^0$ ,  $Ag^+$  and  $Ag^{+2}$  oxidation states in both Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalysts. Especially, the presence of reduced states significantly enhance the photocatalytic activity by enhancing the light absorption as well as charge carrier transport and hence the photocatalytic activity of Ag<sub>2</sub>O/ Ag/TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) could be differed greatly. On the other hand, formation of aggregated silver clusters on TiO<sub>2</sub>(NP) may contribute to enhance charge recombination and hence lower photocatalytic activity in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) than that of Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT)

The light harvesting properties of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/ Ag/TiO<sub>2</sub>(NP) were investigated by the diffuse reflectance absorption spectroscopy. As shown in Fig. 4, bare TiO<sub>2</sub>(NP) and TiO<sub>2</sub>(NT) absorb mainly in the UV region while both Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NP) catalysts absorb light from UV-to far IR regions. The origin of a slight absorption of TiO<sub>2</sub>(NT) could be attributed to the improved light scattering within the structure. The origin of the visible-NIR absorption of silver coated TiO<sub>2</sub>(NT) and TiO<sub>2</sub>(NP) can be explained as follows; it is known that oxygen vacancies are consequently generated in the TiO<sub>2</sub> lattice with the formation of  $Ti^{3+}$  states in the Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) to main the charge balance and these mid-gap oxygen vacancy energy levels are located at 0.75-1.18 eV below the conduction band of TiO<sub>2</sub>. (while the neighboring Ti atoms with the oxygen vacancy site form shallow donor states below the conduction band originated from Ti 3d states [49,50]). The electrons in these mid-gap states/ shallow donor states get excited to the conduction band (CB) by the absorption of visible-NIR light, yielding a blue color in the reduced TiO<sub>2</sub> [27]. Especially, the absorption observed at 450-900 nm region corresponds to 1.37–2.75 eV and such a shoulder absorption is characteristic



**Fig. 4.** The diffuse reflectance absorption spectra of (a) bare  $TiO_2(NP)$ , (b) bare  $TiO_2(NT)$ , (c)  $Ag_2O/Ag/TiO_2(NP)$  and (d)  $Ag_2O/Ag/TiO_2(NT)$  catalysts.

of TiO<sub>2</sub> with mid-gap impurity states. [51,52] As shown in Fig. 4, the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst harvest light efficiently than that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst despite the silver content in both samples is the same. Hence, higher light adsorption by Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) could be due to presence of more reduced oxidation states of TiO<sub>2</sub>(Ti<sup>3+</sup>) and Ag<sub>2</sub>O(Ag<sup>°/+1</sup>) which could contribute to enhance the photocatalytic activity.

The presence of Ag<sub>2</sub>O, AgO and Ag in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst was confirmed by the combined analyses of XRD, TEM and XPS suggesting that the formation of AgO, Ag<sub>2</sub>O and Ag nanoparticles on TiO<sub>2</sub>(NT) and TiO<sub>2</sub>(NP) according to the reactions described in reactions 1–5. [53–55]

$$Ag_{(aq)}^{+} + TiO_{2} _{(S) \rightarrow} TiO_{2} / Ag_{(ads)}^{+}$$
(1)

$$TiO_2/Ag^+_{(ads)} + NH_4OH_{(aq)} \rightarrow TiO_2/AgOH_{(ads)}$$
(2)

$$TiO_2/AgOH_{(ads)} \rightarrow TiO_2/Ag_2O_{(ads)} + H_2O_{(l)}$$
(3)

$$TiO_2/Ag_2O_{(ads)} \rightarrow TiO_2/AgO/Ag^o_{(ads)}$$
(4)

$$TiO_2/AgO_{(ads)} \rightarrow TiO_2/Ag^o_{(ads)} + 1/2 O_{2(g)}$$
(5)

In the first step, aqueous  $Ag^+$  ions get impregnated onto the  $TiO_2$  surface and followed by the conversion the embedded  $Ag^+$  ions to AgOH on the  $TiO_2$  surface by the gentle addition of dilute ammonia solution to the solution containing  $Ag^+/TiO_2$  mixture in solution. The addition of dilute ammonia resulted in the formation of fine AgOH particles on  $TiO_2$  surface by the slow conversion of  $Ag^+$  in its hydroxide form. Finally, the excess of ammonia and solvent were removed by controlling heating to 150 °C. The resulting powder was calcined at 190 °C for 30 min in a furnace under air.In the preparation steps of  $Ag_2O$  coated  $TiO_2$  catalyst, some of the  $Ag_2O$  product may get converted to AgO and metallic silver in the presence of light and once AgO is formed, it readily converted to metallic silver due to instability of AgO as shown in reactions 4 and 5.

#### 4. Phenol degradation under IR illumination

In an earlier publication, the photocatalytic degradation of gaseous phenol was demonstrated by the use of  $Ag_2O/Ag/TiO_2(NP)$  catalyst and IR photons in which it was clearly demonstrated the IR photon initiated photocatalytic activity of the catalyst [10]. The reported inferior photocatalytic activity of  $Ag_2O/Ag/TiO_2(NP)$  catalyst under IR photons (IR source, 850 or 950 nm,  $3.2 \text{ mWcm}^{-2}$ ) was mainly due to insufficient charge separation. As it is known that the enhanced and highly efficient charge separation is a prerequisite especially for IR initiated photocatalysis, the photocatalytic activities of silver coated 1-D TiO<sub>2</sub> nanotubes were employed and the photocatalytic activity of 1-D TiO<sub>2</sub> nanotubes was compared with the TiO<sub>2</sub> nanoparticles.

As expected, the degradation of gaseous phenol was noted with both Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) under IR irradiation and the control experiments carried out under dark conditions revealed that the phenol does not undergo degradation and hence IR initiated photodegradation of phenol with both Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) is confirmed. The natural logarithmic plots of phenol degradation variation with the variation of theAg2O/Ag/TiO2(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst amount were shown in Fig. 5a and b respectively while insets in Fig. 5a and b show the calculated phenol degradation rate constants respectively. When plotting the concentration against the catalyst amount, the CO<sub>2</sub> yield which is the phenol mineralization product was taken as the measure of the final phenol concentration. As shown in Fig. 5a and b, the linear increase of phenol degradation rates with the catalyst amounts indicates the degradation of phenol with Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) under IR irradiation is a first order reaction. Furthermore, as shown in insets in Fig. 5a and b, the plot of rate constants vs. catalyst amount also indicates a first order rate dependence of phenol degradation rate on the catalyst amount and the calculated phenol degradation rate constants of  $Ag_2O/Ag/TiO_2(NT)$  are roughly three times higher than that of  $Ag_2O/$ Ag/TiO<sub>2</sub>(NP).

The effect of phenol concentration on the phenol degradation kinetics was also studied by performing a series of experiments by varying the initial phenol concentration while keeping the catalyst concentration at a constant value. Fig. 6a shows the natural logarithmic plot of phenol concentration against the initial phenol concentration and the inset in Fig. 6a shows the rate constant vs. the initial phenol concentration variation for the catalyst Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) while in Fig. 6b and the inset in Fig. 6b show the same plots for the catalyst Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). The variation of phenol concentration and rate constant with the initial phenol concentrations as presented in Fig. 6a and b suggest a pseudo-first order behavior with the initial phenol



**Fig. 5.** The natural logarithmic plots of phenol degradation under IR source,  $3.2 \text{ mW cm}^{-2}$ , 850 nm with the variation of the catalyst amounts for (a) Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and (b) Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT)catalyst. The insets in Fig. 5a and b show the calculated phenol degradation rate constants with the variation of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT)catalyst amounts respectively. During the experiment, the phenol concentration was kept at constant and the X mg of (5, 10, 15 or 20) catalyst was spread over 5 cm<sup>2</sup> area of the reactor.

concentration. According to Fig. 6, the calculated phenol degradation rate constants for the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) are  $1.89 \times 10^{-3}$  and  $6.81 \times 10^{-4}$  min<sup>-1</sup> respectively indicates the enhanced catalytic activity of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) due to 1-D nature of the TiO<sub>2</sub>(NT) enabling enhanced charge separation. Furthermore, the kinetics results of the degradation of phenol with the time for the catalyst Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) shown in Fig. 7 indicate first-order reaction rate constants of  $1.49 \times 10^{-3}$  and  $4.24 \times 10^{-3}$ s<sup>-1</sup> respectively substantiate the beneficial effect of 1-D nature of TiO<sub>2</sub> in IR initiated photocatalytic activity.

One could argue that the enhanced IR initiated photocatalytic activity of  $Ag_2O/Ag/TiO_2(NT)$  than that of  $Ag_2O/Ag/TiO_2(NP)$  could be due to difference in BET surface area as the measured BET surface areas of TiO\_2(NP), TiO\_2(NT),  $Ag_2O/Ag/TiO_2(NP)$  and  $Ag_2O/Ag/TiO_2(NT)$  were found to be 37.89, 113.96, 36.39 and 53.23 m<sup>2</sup>/g respectively. However, higher phenol degradation rates were observed with  $Ag_2O/Ag/TiO_2(NT)$  than that of  $Ag_2O/Ag/TiO_2(NP)$  even for the normalized surface areas or the number of catalytic sites indicated that the enhance catalytic activity of  $Ag_2O/Ag/TiO_2(NT)$  catalyst could not be assigned solely to the differences in the active sites of the catalysts. Nevertheless



**Fig. 6.** The natural logarithmic plot of phenol concentration under IR source,  $3.2 \text{ mW cm}^{-2}$ , 850 nm against the initial phenol concentration for (a) Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and (b) Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT)catalyst and the insets in Fig. 6a and b shows the rate constant vs. the initial phenol concentration variation for the catalyst Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) respectively. For the experiment, 20 mg of catalyst was spread over 5 cm<sup>2</sup> area of the reactor.



Fig. 7. The degradation kinetics of phenol with the time under IR source,  $3.2 \text{ mW} \text{ cm}^{-2}$ , 850 nm and 20 mg of catalyst (spread over 5 cm<sup>2</sup> area) for the catalyst (a) Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and (b) Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT).

it could be due to the possible enhancement of electron-hole separation in 1-D  $TiO_2(NT)$  in the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) than the TiO<sub>2</sub>(NP) in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP).

The degradation results presented indicated the enhanced gaseous phenol degradation kinetics with the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) catalyst than that of the Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) under IR illumination. The enhanced phenol degradation with the silver coated TiO<sub>2</sub>(NT) can be elucidated based on the IR initiated photochemical reactions. i.e. photochemical water splitting reaction has been reported for the silver coated TiO<sub>2</sub>(NP) and considering the excitation wavelengths of IR source  $(\sim 850 \text{ nm}-1.45 \text{ eV})$  and 950 nm-1.30 eV) and the bandgap energies of TiO<sub>2</sub> (3.2 eV) and Ag<sub>2</sub>O (1.58 eV)/Ag, multiphoton excitation process where optical near field (ONF) and phonon assisted reaction mechanism has been proposed and discussed in detail for the observed water splitting reaction [18,31]. As the direct electron excitation from the VB to the CB is not possible by the absorption of IR photons by the TiO<sub>2</sub> or silver nanoparticles due to insufficient energy of IR photons, the IR initiated photocatalytic activity of silver coated TiO<sub>2</sub>(NP) has been assigned to the stepwise promotion of electrons within the sub-bands by adsorbing IR photon and therefore, an electronic up-conversion reaction mechanism has been elucidated. Since IR photons initiated photochemical reaction is a multi-excitation process, highly efficient excited charge separation is a prerequisite and thus it was suggested that the inferior photocatalytic activity of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalyst under IR photons was mainly due to insufficient charge separation.

Hence, the 1-D nature of TiO<sub>2</sub>(NT) is more favourable for a multistep electron excitation process owing to their better charge separation property and hence EIS technique was employed to distinguish the different charge transfer processes at the interfaces of Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) catalysts. The EIS is a useful technique to understand the phenomena occurring at the semiconductor/ electrolyte interface where it allows discriminating the transport resistances, electron-hole recombination and electron lifetime of the photocatalytic systems. The impedance measurements of Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) were carried out under one sun conditions with a frequency range between 100 mHz and 100 kHz and the magnitude of the modulation signal was 10 mV and at 0.5 V potential in room temperature. The Nyquest plots for the Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) at 1.00 V<sub>RHE</sub> under one sun condition are shown in Fig. 8. In the Nyquest plot, the imaginary part of the impedance  $(-Z_{Imag})$  is shown as a function of the real part of the impedance (Z<sub>Re</sub>) for different values of frequency in which the activationcontrolled processes with distinct time-constants show up as unique impedance arcs and the shape of the curve provides insight into possible mechanism or governing phenomena [56,57]. In this



Fig. 8. The Nyquest plots for the (a) Ag\_2O/Ag/TiO\_2(NP) and (b) Ag\_2O/Ag/TiO\_2(NT) at 1.00  $V_{\rm RHE}$  under one sun condition.

#### Table 1

The estimated Rct, Csc and  $\tau$  values by fitting of EIS results of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT).

	Ag <sub>2</sub> O/Ag/TiO <sub>2</sub> (NT)	Ag2O/Ag/TiO2(NP)
Rct (ohm)	237	717
Csc (F)	$3.35 \times 10^{-5}$	7.95 × 10 <sup>-5</sup>
$\tau$ (ms <sup>-1</sup> )	9.14	56

investigation, Randles circuit (inset in Fig. 8) was used to rationalize the charge-transfer and transport phenomena that take place in photoelectrochemical systems as Randles electrical equivalent circuits was considered the most suitable for modelling the photocatalysts. In the Randles equivalent circuit, Rs stands for the series resistance,  $C_{SC}$  is the space-charge capacitance corresponding to the ability of storing charge in the double layer of the semiconductor/electrolyte interface and  $R_{CT}$ is the charge-transfer represented as a series combination of the chargetransfer resistance at the same interface and a Warburg impedance (W) related to mass transfer (diffusion) resistance [58]. As shown in Fig. 8, the EIS results of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) reflects the smaller arc radius compared to that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) suggesting the smaller electron transfer resistance, faster interfacial charge transfer at the interface leading to the effective separation of photogenerated electron-hole pairs in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT).

The estimated Rct, Rs, Csc and  $\tau$  values by fitting of EIS results of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) shown in Fig. 8 are given in Table 1. The shorter semicircle obtained in the higher frequency range in the Nyquest plot and the estimated Rct, Csc values indicate a lower space charge capacitance as well as charge transfer resistance for Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). On the other hand, space charge capacitance and charge transfer resistance of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) are higher than that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). The observed lower charge transfer resistance Rct and space charge capacitance Csc values for Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) than that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) indicated that photoexcited electrons in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) are likely to promote the fast conduction of electron/hole pairs until the surface resulting in efficient charge separation and that would enhance photocatalytic activity in Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT). Contrary, the higher Rct and Csc values for Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP) indicated that photoexcited electrons are likely to get rapidly recombined before they reach the semiconductor/electrolyte interface where the photocatalytic reactions take place. The calculated electron lifetimes  $(\tau)$  $\tau = 9.14 \, \text{ms}^{-1}$  $[Ag_2O/Ag/TiO_2(NP),$ and Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT),  $\tau = 56.6 \text{ ms}^{-1}$ ] at the depletion layer of the semiconductor by the relationship where  $\tau = R_{CT}C_{SC}$ , indicate the shorter  $\tau$  for Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) than that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP). As the  $\tau$  of Ag<sub>2</sub>O/Ag/  $TiO_2(NT)$  is short, consequently the time that an electron spends in the depletion layer of the semiconductor is low leading to the lower e-h charge recombination probability. Hence fast charge transfer process of the electron to the semiconductor surface can be expected in the case of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NT) than that of Ag<sub>2</sub>O/Ag/TiO<sub>2</sub>(NP). The EIS results firmly confirmed the 1-D nature of TiO<sub>2</sub>(NT) is more favourable for a multistep electron excitation process under IR illumination and enhanced gaseous phenol degradation kinetics with the Ag<sub>2</sub>O/Ag/ TiO<sub>2</sub>(NT) catalyst can be justified.

As explained earlier, IR initiated photocatalytic activity of  $Ag_2O/Ag/TiO_2$  involves a multi-excitation process and can be explained by reactions (6)–(10).

$$Ag_2O/TiO_2 + h\nu(IR) \rightarrow Ag_2O/TiO_2(e^- + h^+)$$
(6)

$$Ag_2O/TiO_2(e) + O_2 \rightarrow Ag_2O/TiO_2 + O_2$$
(7)

$$Ag_2O/TiO_2(h^+) + H_2O \rightarrow Ag_2O/TiO_2 + OH + H^+$$
(8)

 $C_6H_5OH_{(g)} + OH + O_2 \rightarrow CO_2 + H_20$  (9)

$$O_2 - + C_6 H_5 O H_{(g)} \rightarrow CO_2 + H^+$$
(10)

#### 5. Conclusions

Phenol undergoes partial mineralization to produce CO<sub>2</sub> when both  $Ag_2O/Ag/TiO_2(NT)$  and  $Ag_2O/Ag/TiO_2(NP)$  catalysts were irradiated with low energy IR photons. The IR initiated photodegradation of gaseous phenol on  $Ag_2O/Ag/TiO_2(NT)$  catalyst is superior to that of  $Ag_2O/Ag/TiO_2(NP)$ . The enhanced photocatalytic degradation of phenol by IR photons on  $Ag_2O/Ag/TiO_2(NT)$  catalyst can be attributed to the 1-D nature of  $TiO_2(NT)$  which promotes the fast conduction of electron/hole pairs resulting in efficient charge separation in multiphoton excitation process of  $Ag_2O/Ag/TiO_2(NT)$  catalyst. The better silver-TiO<sub>2</sub> interaction and formation of smaller silver clusters on  $TiO_2(NT)$  may also contribute to enhance the photocatalytic activity of  $Ag_2O/Ag/TiO_2(NT)$  in the IR region of the solar spectrum. More importantly, the  $Ag_2O/Ag/TiO_2(NT)$  photocatalyst can be used to abate airborne pollutant in indoor conditions.

#### Credit author statement

K.M.S.D.B. Kulathunga: carried out the experiment and assisted in writing the manuscript.

Chang-Feng Yan: reviewed and edited the original and final draft. Jayasundera Bandara: Original idea and Planned the experiment and methodology, writing and editing of the original and final draft.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2020.124509.

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