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Cite this: *RSC Adv.*, 2014, 4, 51342

Influence of thermal treatment and Au-loading on the growth of versatile crystal phase composition and photocatalytic activity of sodium titanate nanotubes†

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A coalescence influence of Au-loading followed by calcination at 800 °C led to a notable change in crystal-structure, morphology, phase composition and photocatalytic activity of titanate-nanostructures. After calcination at 800 °C, bare sodium titanate nanotubes (TNT) having a BET surface area (S_{BET}) of 176 m² g⁻¹ is transformed into sodium titanate nanorods of $S_{\text{BET}} = 21 \text{ m}^2 \text{ g}^{-1}$, whereas calcination of Au-loaded (Au⁺³, Au⁰ and Au-nanoparticle (AuNP)) TNT at 800 °C led to a variety of fragmented particles having different crystal structures, S_{BET} (21–39 m² g⁻¹), shape and sizes (50–75 nm), attributed to strain induced thermal decomposition of TNT after Au-loading, and the oxidation state of Au is determined by XPS analysis. The comparative photocatalytic activity of these as-prepared catalysts to that of P25-TiO₂ under UV-light were evaluated for the photooxidation of the insecticide imidacloprid which gradually degraded to various intermediate photoproducts and finally decomposed to CO₂. The degradation of imidacloprid follows pseudo-first order kinetics, where 0.5 wt% Au⁰-deposited-TNT after calcination exhibits the highest photocatalytic activity (rate constant $k = 8.9 \times 10^{-3} \text{ min}^{-1}$), which is comparatively explained on the basis of their crystal phase, surface-area, morphology and the relaxation time of photoexcited electron–hole pairs, as measured by time resolved spectroscopy.

Received 3rd July 2014
Accepted 30th September 2014

DOI: 10.1039/c4ra06605g

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1 Introduction

Sodium titanate nanotubes having a layered structure, hollow-porous morphology and higher surface area, generally exhibit flexible photocatalytic activity (PCA) depending^{1–6} upon the sodium content, crystal phase, and calcination temperature. Systematic studies of TNT with moderate Na content on the thermal treatment at 200 to 900 °C revealed that it retains its tubular morphology when calcined at 200–450 °C, indicating its thermal stability in this temperature range and showing higher photocatalytic activity^{1,5} than the most active P25-TiO₂ (P25) photocatalyst. However, with further increase in calcination temperature to ~700–800 °C, the hollow interior of TNT collapses through the condensation of edge sharing TiO₆ corrugated layers resulting in rigid and solid sodium titanate nanorods (TNT(C)) showing almost similar photoactivity^{7,8} to the P25 catalyst.

The PCA of TNT was further enhanced^{9–13} by impregnation with transition metals (Fe, Ni, Pt, Au, Ru *etc.*) followed by calcination at 200–450 °C. It has been reported^{9,11,12,14} that

incorporation of metals (Fe, Au, Ni) into hollow interior of TNT facilitated the formation of core–shell structure with improvement in the lifetime of photoexcited e⁻/h⁺ pair, hence the photocatalytic activity. For instance, in comparison to bare TNT, Fe and Au incorporated TNT were reported^{11,12} to be 5.0 and 7.6 times more photoactive toward the photooxidation of CO and H₂ production, respectively, where no significant change in either morphology or crystal structure was observed. However, the effect of these impregnated metals in TNT after calcinations > 450 °C have been rarely reported, and is expected^{15,16} to cause deformations in crystal structure/morphology during calcination. The metal may induce a strain in the crystal structure¹⁵ or decrease the surface free energy¹⁶ of TNT that may interfere with its crystal growth during calcination. Very recently, a report by Potari *et al.*¹⁷ demonstrated that calcination of Rh deposited TNT at 600 °C led to the formation of nanoparticles of size ~10 nm, instead of any elongated morphology like solid nanorods^{1–6} *i.e.*, TNT(C) formed during calcination of bare TNT. In this context, present work demonstrates that calcination of Au photodeposited Au⁺³ and Au nanospheres (3–5 nm) impregnated TNT under atmospheric conditions at ~800 °C for 2 h resulted in the formation of a variety of geometrical morphologies *e.g.*, nanopolygons like heptagons, hexagons, pentagons, *etc.* These nanoparticles were found to possess different crystal structures (monoclinic, orthorhombic and rhombohedral) and

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra06605g

phase compositions in comparison to monoclinic TNT(C) particles that were obtained after calcination of monoclinic TNT without Au loading, under similar conditions. The formation of versatile crystal geometries, allowed exploring the crystal phase dependent photocatalytic activity relative to the mostly studied anatase, anatase–rutile, rutile and brookite TiO₂ phases. Hence, various physicochemical properties of as-prepared titania nanocomposites were briefly investigated for the photooxidation of neurotoxic^{18–21} insecticide imidacloprid (IMI) to plausible intermediate products that mineralize to CO₂ under different periods of UV-light irradiation.

2 Experimental

Sodium hydroxide (AR), methanol (AR), acetonitrile (HPLC), isopropyl alcohol (AR), auric chloride (HAuClO₄·xH₂O) and nitric acid were purchased from Loba Chemie, India. Commercially available P25–TiO₂ and imidacloprid were obtained from Degussa Corporation, Germany and Ravi Organics Pvt. Ltd. (Mumbai), India, respectively. Standard CO₂ gas (200 ppm) with N₂ gas was obtained from Centurion Scientific Pvt. Ltd, New Delhi, India. All the chemicals were used without further purification.

2.1 Synthesis, characterization and photoactivity of TNT and TNT(C) particles

In a typical experiment, an appropriate amount of P25 was mixed with NaOH (10 M) and autoclaved for 20 h as reported recently by our group.⁶ The Au nanospheres were prepared by method as described in our previous report.²² The Au loading was carried out by (i) the addition of 1.2 ml of 0.01 mM aqueous solution of HAuCl₄·xH₂O (0.5 wt% of Au) during the preparation of TNT, designated as TNT-Au⁺³, and was irradiated in de-aerated 5 ml of 50% v/v aqueous isopropyl alcohol under UV light (125 W Hg arc lamp) for 2 h, as a result Au⁺³ is reduced⁶ to Au⁰ and designated as TNT-Au⁰. (ii) Mixing of TNT (100 mg) with 500 μl spherical Au nanoparticles (NP, size 3–5 nm) in 3 ml of de-ionized water under stirring for 2 h followed by drying, named as TNT-AuNP sample. Bare and Au-loaded TNT were calcined in an alumina crucible at 800 °C (heating rate 5 °C min⁻¹) for 2 h using muffle furnace (Jupiter Scientific) and are abbreviated as TNT(C) and TNT-Au⁺³(C), TNT-Au⁰(C) and TNT-AuNP(C).

All the samples were characterized by absorption spectrophotometer (Ocean Optics 4000USB) and XRD (Panalytical X'Pert using Cu Kα, λ = 1.54178 Å). X'Pert HighScore Plus software was used for identification of various crystal structure(s) formed after calcination. Transmission electron microscopy (TEM) images were recorded on Hitachi 7500 electron microscope, using 120 kV accelerating voltage. Samples for TEM analysis were prepared by depositing them onto Cu grid by dropping a drop of methanolic suspension (5 mg ml⁻¹) on it which was then dried. The elemental detection analysis (EDS) was performed on JEOL JSM-6510LV by fixing them onto Cu grid having double sided adhesive carbon tape. The XPS spectra of as-prepared samples were recorded on Leybold Heraeus-

Shengyang SKL-12 electron spectrometer equipped with VG CLAM 4 MCD electron energy analyzer, using Al-Kα as excitation source, for the 4f electrons of Au-only in order to determine its oxidation state. The samples for XPS-analysis were prepared by fixing the fine powdered sample (~50 mg) on the stub having double side-adhesive carbon tape, and the unattached sample to this stub was removed before the XPS analysis. The BET surface area was measured with Smart Sorb 91/92 using 150 mg of sample preheated at 150 °C for 1 h. Time resolved luminescence decay curves of powder samples were recorded using Nitrogen laser (excitation at 390 nm) pulsed in operation (5–7 ns pulse width) coupled with Tektronix TDS-1012 oscilloscope, where 100 ml of 50 ppm aqueous solution of imidacloprid (IMI, substrate for degradation) and 50 mg of as-prepared TNT-Au⁰(C) and TNT-AuNP(C) catalysts were stirred for 30 min in dark. The mixture was centrifuged (Remi-3402, 4000 rpm for 4 min), dried (70–80 °C for 30 min) and denoted as IMI + TNT-Au⁰(C) and IMI + TNT-AuNP(C) and their time resolve luminescence decay curves were also recorded. Prior to this analysis the samples (10–20 mg) were placed onto quartz stub, 100 μl of methanol was added, dried (70–80 °C) for 20–30 min in-order to fix the samples on this stub. All physicochemical properties and description for as-prepared nanostructures are listed in Table 1.

The photooxidation of IMI was carried out in a test tube (sealed with rubber cap) containing 5 ml aqueous solution of imidacloprid (50 ppm) and 2.5 mg bare or Au loaded nanocrystals under UV (125 W Hg arc, 10.4 mW cm⁻²) irradiation for 3 h. A blank experiment without catalyst was also performed under above experimental conditions to study the photo-degradation behavior of IMI only under UV-light. The reaction solution was analyzed by high performance liquid chromatography (HPLC, Agilent 1120LC) using C-18 column (BDS, Qualigens) of dimensions 250 mm × 4.6 mm and particle size of 5 μm with 80 : 20: acetonitrile–water as mobile phase at a flow rate of 1 ml min⁻¹ and detection wavelength of 270 nm. The evolution of CO₂ was determined by injecting 1 ml of gaseous mixture from the reaction vessel (gas tight test tube) into gas chromatogram (NUCON-5765) using Porapak-Q column with nitrogen as carrier gas (30 ml min⁻¹) using Thermal Conductivity Detector (TCD). Column oven was maintained at 40 °C while the injector and detector were kept at 70 and 80 °C, respectively. Intermediates formed after 3 h of UV-light exposure were identified by injecting 20 μl of reaction sample in LC-MS (Bruker-300 PS) having single-quadrupole detector, equipped with C-18 column (Hypersil, 150 mm × 4.6 mm, 5 μm) using a mobile phase of 80 : 20: acetonitrile–water at a flow rate of 1 ml min⁻¹.

3 Results and discussion

The XRD pattern and TEM images for as-prepared TNT and TNT(C) are shown in Fig. 1. It was found that as-prepared TNT possess monoclinic crystal structure for Na₂Ti₃O₇ (tritanate) as evidenced (ICSD card no. 00-014-0085) by its characteristic peak at 2θ = 10.0015° for (101) plane. The presence of Na in TNT and TNT(C) is confirmed by EDS analysis (ESI, Fig. 1†) and is in agreement^{6,23} with our recent reports. The calcination of bare

Table 1 Description and physico-chemical properties of as-prepared nanostructures

Catalysts	Description	Chemical composition (crystal structure %)	Lattice parameters (Å)			EDX analysis				Compression Strain
			Calculated (reported)			Elements (wt%)				
			<i>a</i>	<i>b</i>	<i>c</i>	Na	Ti	O	Au	
TNT	Sodium titanate nanotubes	Na ₂ Ti ₃ O ₇ (monoclinic, 100%)	8.4 (8.5)	3.7 (3.8)	9.0 (9.1)	3.02	57	39	—	7.4 × 10 ⁻⁴
TNT(C)	Sodium titanate nanotubes calcined at 800 °C	Na ₂ Ti ₆ O ₁₃ (monoclinic, 100%)	15.2 (15.1)	3.7 (3.7)	9.1 (9.1)	2.61	58.9	38.4	—	1.5 × 10 ⁻⁴
TNT-Au ⁺	0.5 wt% Au ⁺ impregnated sodium titanate nanotubes	Na ₂ Ti ₃ O ₇ (monoclinic, 100%)	19.2 (19.3)	3.7 (3.7)	3.0 (3.0)	—	—	—	—	6.9 × 10 ⁻³
TNT-Au ⁺ (C)	0.5 wt% Au ⁺ impregnated sodium titanate nanotubes calcined at 800 °C	Na ₂ Ti ₉ O ₁₉ (monoclinic, 83%)	12.2 (12.2)	3.7 (3.7)	15.7 (15.6)	0.15	60.6	38.9	0.3	1.5 × 10 ⁻³
		NaTiO ₂ (rhombohedral, 5%)	2.9 (3.0)	3.0 (3.0)	16.2 (16.2)					1.1 × 10 ⁻³
		Na ₂ Ti ₆ O ₁₃ (monoclinic, 12%)	15.2 (15.0)	3.7 (3.6)	9.1 (8.9)					1.4 × 10 ⁻³
TNT-Au ⁰ (C)	0.5 wt% Au-photodeposited sodium titanate nanotubes calcined at 800 °C	TiO ₂ (anatase, 78%)	12.2 (12.2)	3.7 (3.5)	15.6 (15.6)	0.24	59.5	39.7	0.4	2.4 × 10 ⁻²
		TiO ₂ (rutile, 22%)	3.0(2.8)	3.0 (2.9)	16.2 (16.2)					2.8 × 10 ⁻²
TNT-AuNP(C)	0.05 wt% Au nanosphere impregnated sodium titanate nanotubes calcined at 800 °C	Na ₂ Ti ₆ O ₁₃ (monoclinic, 26%)	12.2 (12.2)	3.7 (3.7)	15.6 (15.6)	0.57	57.8	41.5	0.04	0.9 × 10 ⁻⁴
		NaTiO ₂ (rhombohedral, 46%)	3.0 (3.0)	3.0 (3.0)	16.1 (16.2)					0.1 × 10 ⁻⁴
		Na ₂ Ti ₃ O ₇ (orthorhombic, 28%)	19.3 (19.3)	3.7 (3.7)	3.0 (3.0)					0.2 × 10 ⁻⁴

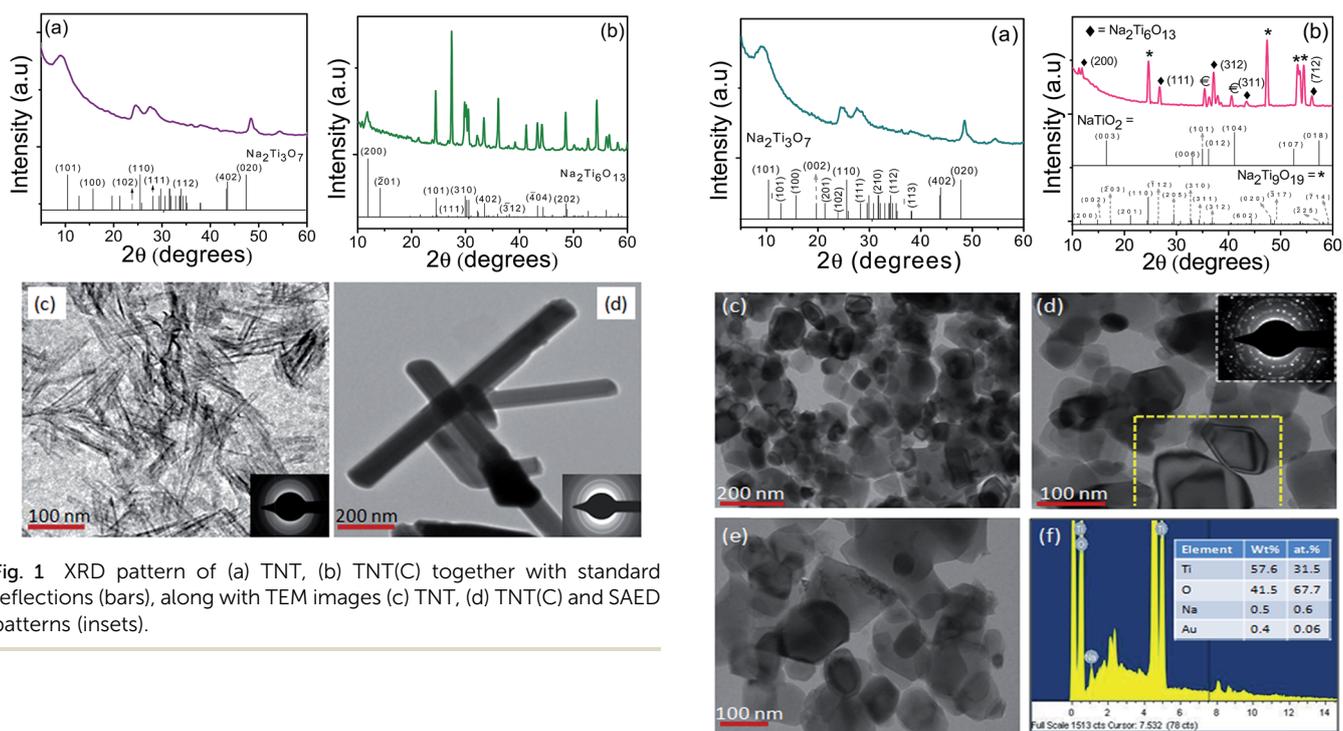


Fig. 1 XRD pattern of (a) TNT, (b) TNT(C) together with standard reflections (bars), along with TEM images (c) TNT, (d) TNT(C) and SAED patterns (insets).

TNT caused its transformation to nanorods (TNT(C)) particles of orthorhombic Na₂Ti₆O₁₃ (hexatitanate) crystal structure. The TEM images of TNT and TNT(C) showed tubular and rod like morphology and their corresponding SAED pattern indicates

Fig. 2 XRD pattern (a) TNT-Au⁺, (b) TNT-Au⁺(C) along with their standard reflections (bars), (c–e) TEM images of TNT-Au⁺(C), (f) its corresponding EDS pattern; inset: SAED pattern of TNT-Au⁺(C).

amorphous and crystalline nature, respectively, are in accordance with their respective XRD pattern.

The XRD pattern, TEM and EDS analysis of TNT-Au⁺³ and TNT-Au⁺³(C) samples are shown in Fig. 2. It was found that the XRD pattern of TNT-Au⁺³ is almost similar to TNT, whereas, TNT-Au⁺³(C) was found to be composed of a mixture of well crystalline, strained Na₂Ti₆O₁₃ (nonatitanate, ICSD card no. 01-073-2256), Na₂Ti₆O₁₃ (hexatitanate) and NaTiO₂ (monotitanate, ICSD card no. 00-016-0251) crystal structures. Interestingly, deviation in lattice parameters (Table 1) and shift in characteristic peaks for nonatitanate ($2\theta = 24.71^\circ$ to 24.81°), hexatitanate ($2\theta = 11.84^\circ$ to 11.92°), and monotitanate ($2\theta = 40.67^\circ$ to 40.72°) were found corresponding to (110), (200) and (104) planes, respectively which might be due to exchange of Na⁺ ions by Au⁺³ ions. For a 6-fold coordinated ion the radius of Na⁺ ions (1.12 Å) is more than radius of Au⁺³ (0.85 Å) ion, hence the exchange of the former with the later ion resulted in compression strain *ca.* 6.9×10^{-3} in crystal structure of TNT-Au⁺³, and subsequently causing these variations. The morphology of TNT-Au⁺³(C) was found to be of nanopolygons, with its SAED pattern exhibiting crystalline nature and is similar to XRD pattern. The presence of Au in TNT-Au⁺³(C) is further confirmed by EDS analysis (Fig. 2f) where 0.4 wt% of Au was found to be present along with Na (0.5 wt%), Ti (57.6 wt%) and O (41.5 wt%). The measured $S_{\text{BET}} = 160 \text{ m}^2 \text{ g}^{-1}$ of TNT-Au⁺³ was reduced to $28 \text{ m}^2 \text{ g}^{-1}$ after its calcinations (TNT-Au⁺³(C)) that can be ascribed to the formation of highly crystalline nanopolygons particles like morphology.

On the other hand, TNT-Au⁰ found to corresponds to H₂Ti₃O₇·H₂O (trinitanic acid), while, TNT-Au⁰(C) is found to be a mixture of anatase and rutile phases, as revealed by the characteristic peaks in their respective XRD patterns as seen in Fig. 3. The formation of trinitanic acid instead of trinitanate could be attributed to the exchange of Na⁺ ions by the photo-produced H⁺ ions during photodeposition of Au. This H⁺ ions could be replaced²⁴ easily by Na⁺ ions due to (i) weaker van der Waals forces of attraction between Na⁺ with Ti₃O₇⁻² layers, (ii) longer bond length (2 Å) of Na–O in Na₂Ti₃O₇·H₂O than 1 Å of H–O bond length in H₂Ti₃O₇·H₂O, and (iii) lower elution strength of the Na⁺ ions than H⁺ ions favoring their exchange. However, small deviations have been found in lattice parameters for TNT-Au⁰(C) having anatase (ICDS card number: 00-001-0562) and rutile (ICDS card number: 00-01-1292) phases in comparison to their standard values. This may be due to incorporation of Au⁺³ ions in-between octahedral layers of TiO₆ in TNT that got exchanged and subsequently deposited during UV-illumination resulting in a strain in the crystal structure and altering the lattice parameters.

The acquired TEM images for morphological analysis of TNT-Au⁰ and TNT-Au⁰(C) are shown in Fig. 3. The deposition of Au-nanoparticles of size 10–15 nm onto TNT can be clearly seen for TNT-Au⁰. However, the presence of Au (0.5 wt%) was confirmed by the EDS elemental analysis (Fig. 3d). The TNT-Au⁰(C) was found to be composed of fragmented nanocrystals of size 50–60 nm with more number of boat shaped nanoparticles than that found for TNT-Au⁺³(C). Moreover, the obtained SAED pattern for TNT-Au⁰(C) also indicates its high crystallinity and is

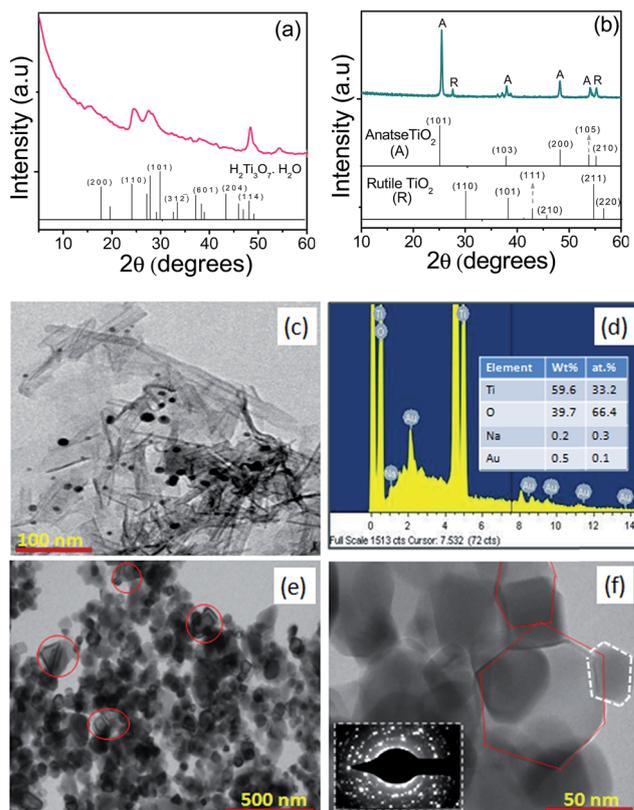


Fig. 3 XRD pattern of (a) TNT-Au⁰, (b) TNT-Au⁰(C) together with their standard reflections (bars), (c) TEM image of TNT-Au⁰, (d) its corresponding EDS pattern, (e–f) TEM images of TNT-Au⁰(C) and its subsequent SAED pattern (inset).

in conformity with its XRD pattern. The S_{BET} for TNT-Au⁰ ($156 \text{ m}^2 \text{ g}^{-1}$) was ~ 1.2 times less than TNT ($176 \text{ m}^2 \text{ g}^{-1}$) and is in accordance with our previous report,⁶ showing decrease in S_{BET} after photodeposition of Ag and Cu onto TiO₂ nanorods, P25 and TNT. However, $S_{\text{BET}} = 39 \text{ m}^2 \text{ g}^{-1}$ for TNT-Au⁰(C) was higher than $S_{\text{BET}} = 28 \text{ m}^2 \text{ g}^{-1}$ for TNT-Au⁺³(C) that could be rationalized to its small particle size.

The XRD pattern, TEM images of TNT-AuNP, TNT-AuNP(C) and SAED and EDS pattern of TNT-AuNP(C) are shown Fig. 4. The XRD pattern of TNT-AuNP reveals it be composed of monoclinic Na₂Ti₃O₇, while TNT-AuNP(C) was found to be a mixture of Na₂Ti₃O₇, Na₂Ti₆O₁₃ and NaTiO₂ crystal structures and well consistent to its *ca.* lattice parameters to that of reported values (ICSD card no. 01-072-0148 and 01-089-0802) indicating it to be almost strain free. It might be because of negligible probability of exchange of Na⁺ ions by AuNP with much larger diameter (3–5 nm). The absence of strain (Table 1) in the crystal structure of TNT-NP sample also supports the assumption that Na⁺ ions in TNT-Au⁺³ and TNT-Au⁰ samples were exchanged by Au⁺³ ions, resulting in a strain in the crystal structures of TNT-Au⁺³(C) and TNT-Au⁰(C). Moreover, the sample TNT-AuNP(C) was found to be a mixture of nanorods and broken distorted particles as can be seen in SAED pattern which is in agreement to its XRD profile. The presence of Au in TNT-AuNP(C) was also confirmed by the EDS analysis. The S_{BET}

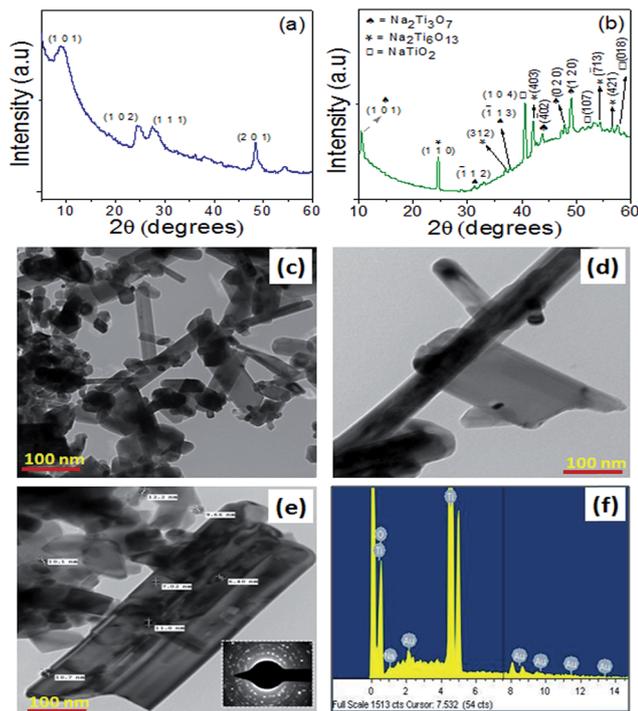


Fig. 4 XRD pattern of (a) TNT-AuNP (b) TNT-AuNP(C), (c–e) TEM images of TNT-AuNP(C) with its corresponding SAED pattern (inset) and (f) its EDS pattern.

of TNT-AuNP and TNT-AuNP(C) was found to significantly decrease from 165 to 32 m² g⁻¹ revealing AuNP loading may cause the growth of smaller fragmented particles during calcinations and possessing higher surface area to that of TNT(C).

The observed diverseness in the morphology of TNT-Au⁺³(C) and TNT-Au⁰(C) in comparison to TNT(C) is probably due to induced compression strain (C_{strain}) in their crystal structures. This C_{strain} produced in the crystal structure of TNT after the exchange of Na⁺ ions with Au⁺³ ions is believed to inhibit the nucleation growth of TNT during its calcination at 800 °C. The formation of smaller particles of size 50–60 nm for TNT-Au⁰(C) with more number of boat shaped particles than 65–75 nm of TNT-Au⁺³(C) can be ascribed to its higher C_{strain} (~25 times) that might have caused inhibition in the nucleation growth during thermal treatment resulting in small size and boat shaped particles. This fact was in-turn confirmed from negligible C_{strain} in the crystal structure of the TNT-AuNP(C), transforming most of TNT particles into nanorods. However, some broken particles of TNT-AuNP(C) are also formed, as the Au-loading at the surface of TNT decreases surface energy and interferes with the crystal growth during calcination, although not calculated here. This work is in agreement with the report of Potari *et al.*,¹⁷ showing the formation of smaller nanoparticles (~10 nm) after the post thermal treatment of Rh-impregnated TNT particles.

Although, elemental analysis confirmed the presence of Au but oxidation state of the deposited Au-species over titanate surface was not known. Hence, XPS analysis (Fig. 5) reveals the binding energy of 82.6 eV and 86.8 eV for elemental Au⁰ characteristic to Au⁰ (4f_{7/2} and 4f_{5/2}, respectively) electrons are

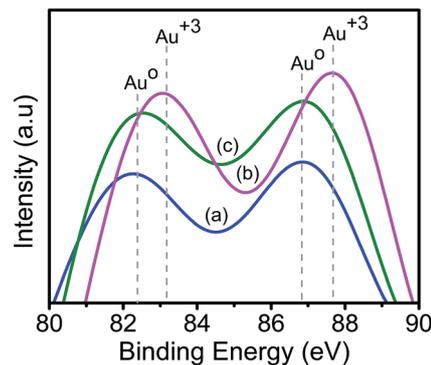


Fig. 5 XPS spectrum of Au 4f region of (a) TNT-AuNP(C), (b) TNT-Au⁺³(C) and (c) TNT-Au⁰(C).

present in both the Au-photodeposited (TNT-Au⁰(C)) and AuNS impregnated (TNT-AuNP(C)) samples as expected. Whereas, the binding energy (83.7 and 87.9 eV) characteristic to Au⁺³ ions are present in TNT-Au⁺³(C) sample, which are in agreement with the reported^{25–27} binding energy of Au⁺³ (4f_{7/2} = 83.7 eV and 4f_{5/2} = 87.3 eV) and Au⁰ (4f_{7/2} = 82.8 eV and 4f_{5/2} = 86.6 eV) oxidation state.

Since, Au loading onto TiO₂ is reported^{12,22} to affect the charge recombination process, therefore it was measured (ESI, Fig. 2†) before assessing the PCA of as-prepared catalysts. Fig. 6 showed the average charge recombination time τ_{av} = 68 μs for charge carriers of photoirradiated TNT(C) is ~1.8 times more than τ_{av} = 41 μs for TNT particles that was further increased to the highest τ_{av} = 81 μs after Au-loading and calcination for TNT-Au⁰(C) catalyst. This increase in τ_{av} is because of the deposits of Au as co-catalyst on the support, acting as a sink for the photogenerated electrons^{6,11,22} enhancing the life time of charged species and is in correlation with the results obtained for Au-loaded sodium titanate nanorods in our recent report.²³ However, τ_{av} = 67 μs for IMI + TNT-AuNP(C) and τ_{av} = 74 μs for IMI + TNT-Au⁰(C) was found to be relatively lower than their respective un-adsorbed bare catalyst samples, indicating that the presence of electron withdrawing groups (NO₂ and Cl) in IMI favoring the recombination of excited charge carriers. These results are in accordance to the recent work of

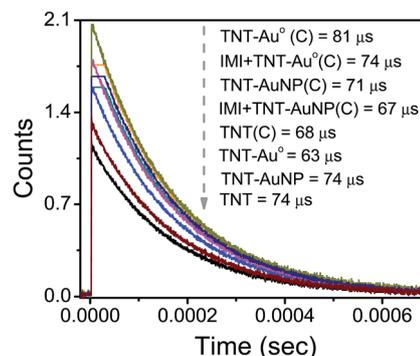


Fig. 6 Time resolve luminescence decay spectrum for as-prepared samples with average relaxation time.

Paramaguru *et al.*²⁸ where significant quenching in fluorescence intensity was found for pyrene adsorbed TiO₂ possessing substituted electron withdrawing groups in pyrene.

Time course of photocatalytic oxidation of IMI in presence of as-prepared catalysts relative to P25 and the *ca.* pseudo-first order apparent rate constants are shown in Fig. 7. It is found that no significant change in the amount of IMI was observed when it was irradiated under UV-light in absence of any catalyst, indicating its stability under these experimental conditions. Among the bare catalysts hollow and porous TNT exhibited the highest photocatalytic activity, whereas Au-loading onto TNT always increases the photocatalytic. The highest photocatalytic activity of TNT is attributed to the collective effect of (i) hollow interior and high specific surface area for better adsorption of the substrate, and (ii) small wall thickness (0.8–1.1 nm) favoring fast diffusion of charge carriers at its surface. The interfacial charge migration is a key factor in deciding the PCA of a catalyst. However, among the various as-prepared bare and Au-loaded catalysts, TNT-Au⁰(C) is found to be most photoactive ($k = 8.9 \times 10^{-3} \text{ min}^{-1}$) followed by TNT-Au⁰ ($k = 5.4 \times 10^{-3} \text{ min}^{-1}$) as compared to the mostly photoactive P25. The high activity (1.6 times) of TNT-Au⁰(C) having lower (4 times) S_{BET} than TNT-Au⁰ can be ascribed to its better crystallinity that may reduces the surface defects acting as recombination sites of excited charge carriers and thus exhibits high photoactivity. This fact is also supported by the time resolve measurements revealing high $\tau_{\text{av}} = 81 \mu\text{s}$ for TNT-Au⁰(C) than $\tau_{\text{av}} = 63 \mu\text{s}$ for TNT-Au⁰ sample. Moreover, lower Fermi level position of Au than the conduction band of TiO₂ also favours photo-excited electron transfer from the conduction band of TiO₂ to Au co-catalyst, thus can easily reduce the dissolve O₂ to oxidative superoxide radicals at the catalyst–solution interface. The photoproducted holes in the valance band of TiO₂ can directly

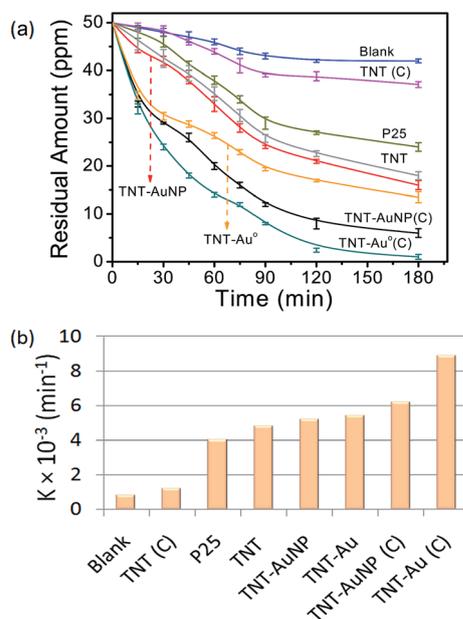


Fig. 7 (a) Photocatalytic degradation of imidacloprid with and without (blank) catalysts and (b) pseudo first order rate constants.

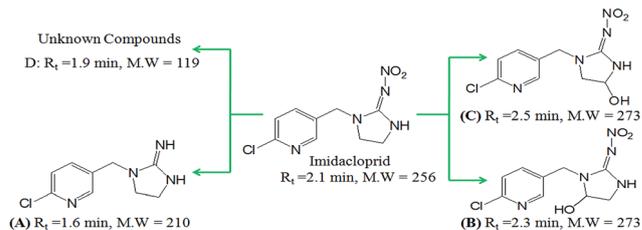


Fig. 8 Schematic representation for structural formulas corresponding to different retention time (R_t) and molecular weights (MW) of some identified/unidentified compounds.

oxidize the adsorbed molecule or can produce the oxidative hydroxyl radicals causing further improvement in photocatalytic oxidation of IMI.

The LC chromatographs (ESI, Fig. 3 and 4†) indicated decrease in peak height of the imidacloprid (retention time $R_t = 2.05 \text{ min}$) after 180 min of its photooxidation by TNT-Au⁰(C) under UV-light irradiation with simultaneous appearance of many new peaks at $R_t = 1.6, 1.9, 2.3$ and 2.5 min . The various intermediate products were identified by LC-MS analysis (Fig. 8) as compound A = 1-((6-chloropyridin-3-yl)methyl)imidazolidin-2-imine ($R_t = 1.6 \text{ min}$), compound B = (Z)-N-(1-((6-chloropyridin-3-yl)methyl)-5-hydroxyimidazolidin-2-ylidene)nitramide ($R_t = 2.3 \text{ min}$), and compound C = (Z)-N-(1-((6-chloropyridin-3-yl)methyl)-4-hydroxyimidazolidin-2-ylidene)nitramide ($R_t = 2.5 \text{ min}$) *etc.*, however the compound D corresponding to $R_t = 1.9$ in the chromatograph remained unidentified.

Time course graph in Fig. 9 for photomineralization of imidacloprid to CO₂ showed gradual increase in its amount with UV-light irradiation and became the highest (25.7 ppm = 3.1 μmol) in case of TNT-Au⁰(C) photocatalyst, showing 34.4% complete mineralization from 97.2% (48.6 ppm) of its photo-degradation, in contrast, only 15.3% (11.5 ppm = 1.38 μmol) of CO₂ of mineralization was found from 31.5 ppm (0.71 μmol) of IMI by bare TNT catalyst. This trend indicates incomplete mineralization of IMI due to the formation of heteroatom containing intermediates as identified LC-MS analysis. Thus, it is evident that among all the prepared catalysts and mostly

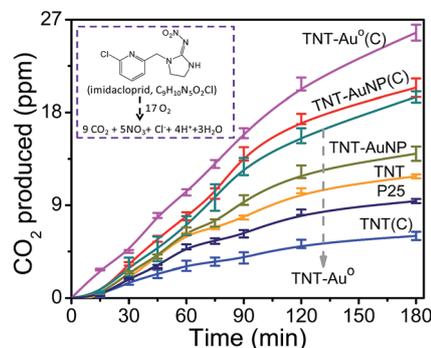


Fig. 9 Amount of CO₂ produced by photodegradation of imidacloprid at various time intervals with P25 in-comparison to bare and various Au-loaded TNT (before and after calcinations), inset; balanced chemical equation for complete mineralization of imidacloprid.

photoactive P25-TiO₂, TNT-Au⁰(C) exhibited the highest photocatalytic activity for the complete photomineralization of IMI to CO₂ depending on UV-light irradiation time.

4 Conclusions

In summary, present work revealed that depending upon thermal treatment, oxidation state and method of Au-loading, sodium titanate nanotubes could be converted to a variety of nanostructures having diverse surface morphology, particles size and shape, crystal structure and composition, which in turn affects their photocatalytic activity. Thus, it found that sodium titanates after heat treatment at suitable temperature may be useful for preparing more photoactive catalyst than conventional P25-TiO₂ used in many practical applications.

Acknowledgements

The authors acknowledge University Grants Commission and Department of Science and Technology, New Delhi, Government of India for providing financial support. Degussa Corporation, Germany is gratefully acknowledged for the gift of TiO₂ sample.

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