Electronic Supplementary Information

Room temperature synthesis of protonated layered titanate sheets using peroxo titanium carbonate complex solution

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Experimental section

Materials:

Titanium isopropoxide was purchased from Sigma Aldrich, USA. Ethanol, ammonium hydroxide, ammonium carbonate, lead nitrate, methylene blue were purchased from S. D. Fine-Chem. Limited, India. All the chemicals were used without further purification. For all applications water with a resistivity of 18 MΩ cm was used, obtained from a Millipore water purifier.

Preparations of aqueous titanium peroxo carbonate complex solution:

0.01 mole titanium iso-propoxide was dissolved in 10 ml ethanol. To the ethanol solution 40 ml ammoniacal water was added slowly with constant stirring (500 rpm). Immediately after the addition of water a white precipitate appeared and stirring was continued for another 15min. the resultant precipitate was collected by centrifuge and washed for 4 times using de-ionized water. Then, 25 ml 1.6 molar aqueous ammonium carbonate solutions was added to the resultant precipitate with constant stirring. To this milky white reaction mixture, 3 ml 30% H_2O_2 was added which resulted a light yellow colored clear precursor solution. The final volume of the solution was made to 40ml.

Synthesis of Layered titanate:

The resultant clear aqueous titanium peroxo carbonate complex solution was stirred for overnight. Initially after 2 h of stirring the clear solution became turbid and after over night the yellow color of the solution turned to color less and precipitate appeared. Precipitate was filtered, washed properly with de-ionized water and dried at ambient condition over night. The dried powdered was calcined at 450°C for 6h.

Separately, the clear aqueous titanium peroxo carbonate complex solution was refluxed at 100°C for 1, and also hydrothermally treated in a Teflon-lined stainless steel autoclave at 130°C. In both the cases, the resultant precipitate was filtered, washed properly with de-ionized water and dried at ambient condition over night.

Characterizations:

A scanning electron microscope (SEM) (Leo series 1430 VP) equipped with INCA was used to determine the morphology of samples. The sample powder was supported on aluminum stubs and then coated with gold by plasma prior to measurement.

Transmission electronic microscope (TEM) images were collected using a JEOL JEM 2100 microscope and samples were prepared by mounting an ethanol dispersed samples on lacey carbon formvar coated Cu grid.

Powder X-ray diffraction patterns were recorded in the 2θ range of 2-80° on a Philips X'pert X-ray powder diffractometer using Cu Kα (λ= 1.54178 Å) radiation.

The nitrogen adsorption - desorption measurements at 77 K were performed by using an ASAP 2010 Micromeritics, USA, after degassing samples under vacuum (10^{-2} torr) at 250 °C for 4 h. The surface area was determined by Brunauer-Emmett-Teller (BET) equation. Pore size distributions were determined using BJH model of cylindrical pore approximation.

Ion-exchange experiment:

Experiment for heavy metal ion exchange and organic dye sorption capacity was carried out using aqueous solution of Pb (NO)$_3$ and Methylene blue (MB) at room temperature under stirring condition throughout the reaction. Ion exchange isotherm of Pb^{2+} exchange was determined by equilibrating 10 mg of layered titanate in 25 ml of aqueous Pb (NO)$_3$ with concentrations between $0.2 - 3.00 \times 10^{-3}$ molL^{-1} at pH ~ 5.5. In order to investigate the sorption kinetics, amount of Pb^{2+} adsorbed after equilibrating the adsorbent in solution for 5, 10, 20, 30, 60 and 120 min was measured for all the concentrations. During the reaction the pH of the solution was adjusted to ~5.5 by adding dilute HNO$_3$. This precaution is needed to avoid the formation of PbCO$_3$ or Pb (OH)$_2$ on the adsorbent surface. After equilibration solid adsorbent was separated through centrifugation and filtration, and the concentration of Pb^{2+} was measured by ICP-OES. For dye adsorption 25 ml of 20 ppm solution of Methylene blue was stirred with

10 mg of the adsorbent separately for 5, 10, 20, 30, 60, and 120 minute respectively. During the experiment pH value was adjusted within 9.5 – 10 by adding dilute ammonia for each case. The MB concentration in the solution at different time interval was determined quantitatively by the change of a specific absorption peak of the sample measured with a Shimadzu UV-2550 UV-VIS spectrophotometer.

Supplementary Results

1. TEM
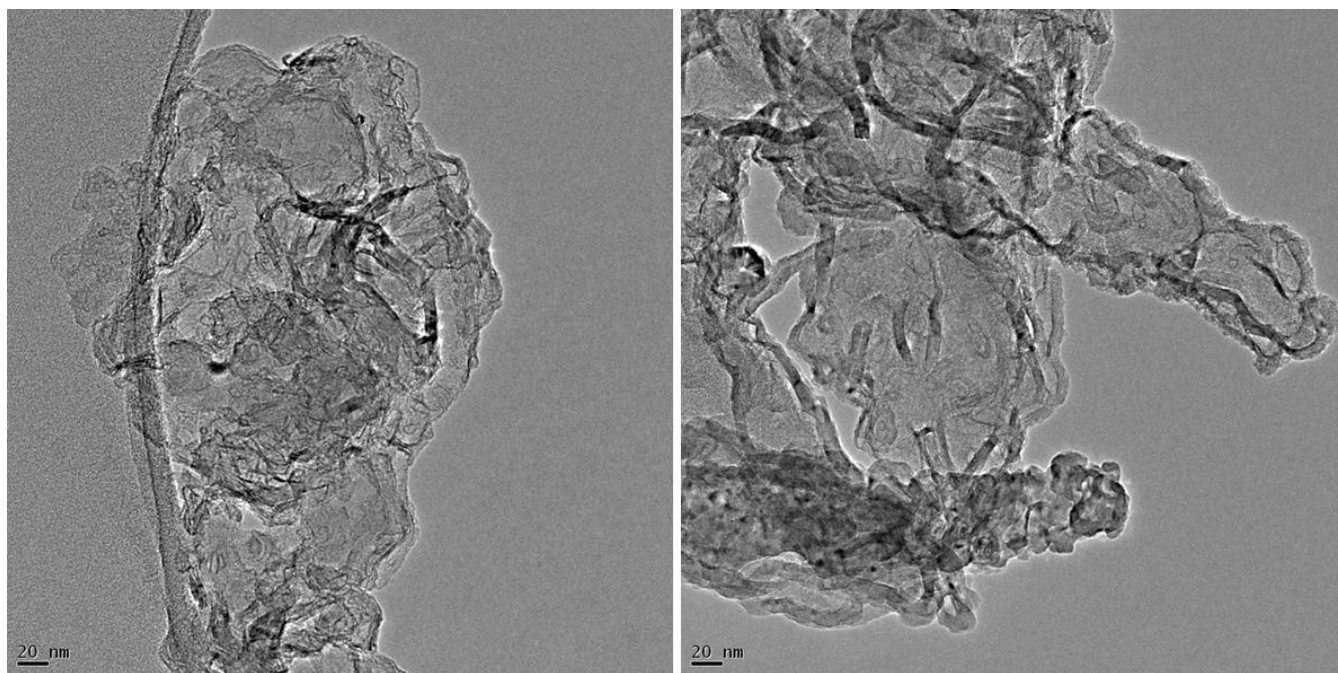
Fig. S1   Additional TEM micrograph of the layered titanate synthesized at room temperature.

2. N$_2$ sorption

Fig. S2 represents the nitrogen adsorption-desorption isotherms of the layered titanate synthesized at room temperature. The isotherm is similar to type II and the hysteresis loops are almost H3 type, (according to the IUPAC classification) generally observed for the adsorbent with slit like structures.[1] The total surface area was $96 m^2 g^{-1}$.
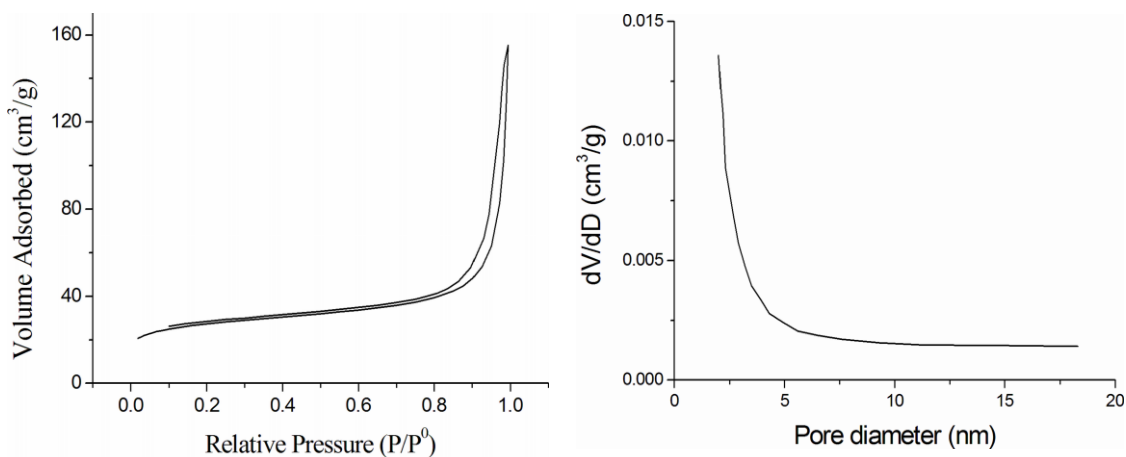

Fig. S2　　N$_2$ sorption-isotherm and pore size distribution of layered titanate synthesized at room temperature.

3. NMR

In the ^{13}C-NMR spectra of mixed solution of ammonium carbonate and H$_2$O$_2$, peaks at 165.16 ppm with 162.34 ppm can be assigned to carbonate (CO$_3^{2-}$) and peroxy carbonate (CO$_4^{2-}$) respectively.[2] Where as in the ^{13}C-NMR spectra of precursor solution, mixed solution of titanium hydroxide, ammonium carbonate and H$_2$O$_2$, the peaks at -165.16 ppm (responsible for free CO$_3^{2-}$) remained same but the peak at 162.34 ppm (responsible for free CO$_4^{2-}$) shifted to 161.5 ppm and sometimes an additional peak at 158.42 ppm was also observed. This peak shifting is most probably due to the formation of titanium peroxy carbonate complex (Ti-O-O-C).

S5
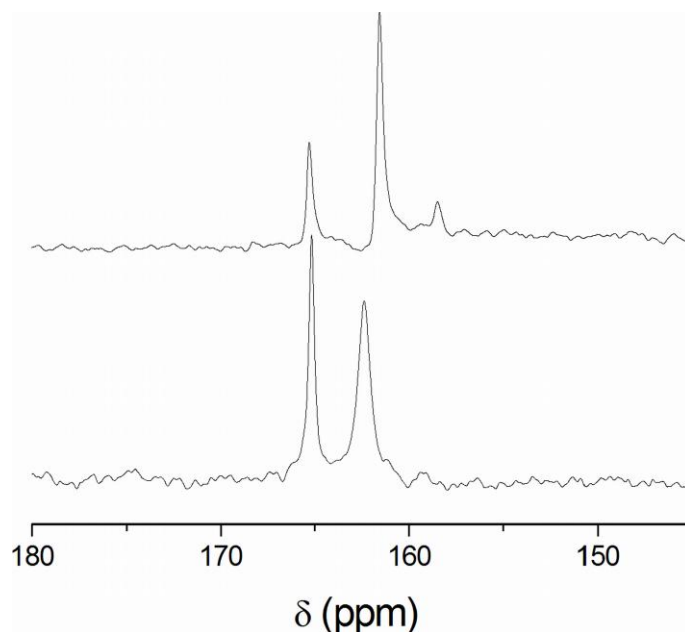
Fig. S3 ^{13}C-NMR spectra of (a) aqueous solution of ammonium carbonate and H_2O_2 and (b) precursor solution (clear aqueous complex solution of ammonium carbonate, H_2O_2 and titanium hydroxide).

4. FTIR

It is very complicated to analyze the FTIR bands in the presence of water and H_2O_2. However, the FTIR spectra obtained for different solution mixture of constituent reactant confirmed the presence of different functional group. Band at ~3500 cm^{-1}, responsible for –OH stretching of the aqueous solution of the constituent reactant, was broad in nature, but after addition of H_2O_2 in titanium containing solution became sharper, i.e., after the addition of H_2O_2 the environment of OH changed. In addition, after the addition of H_2O_2 to the titanium containing solution, band at 2400 cm^{-1} due to OH of chelated complex, band in the range of 940-980 cm^{-1} due to free –O-O- group was observed. The bands for Ti-O-C and Ti-O-O were also observed in the range of 1000-1200 and 700 cm^{-1} respectively.[3]
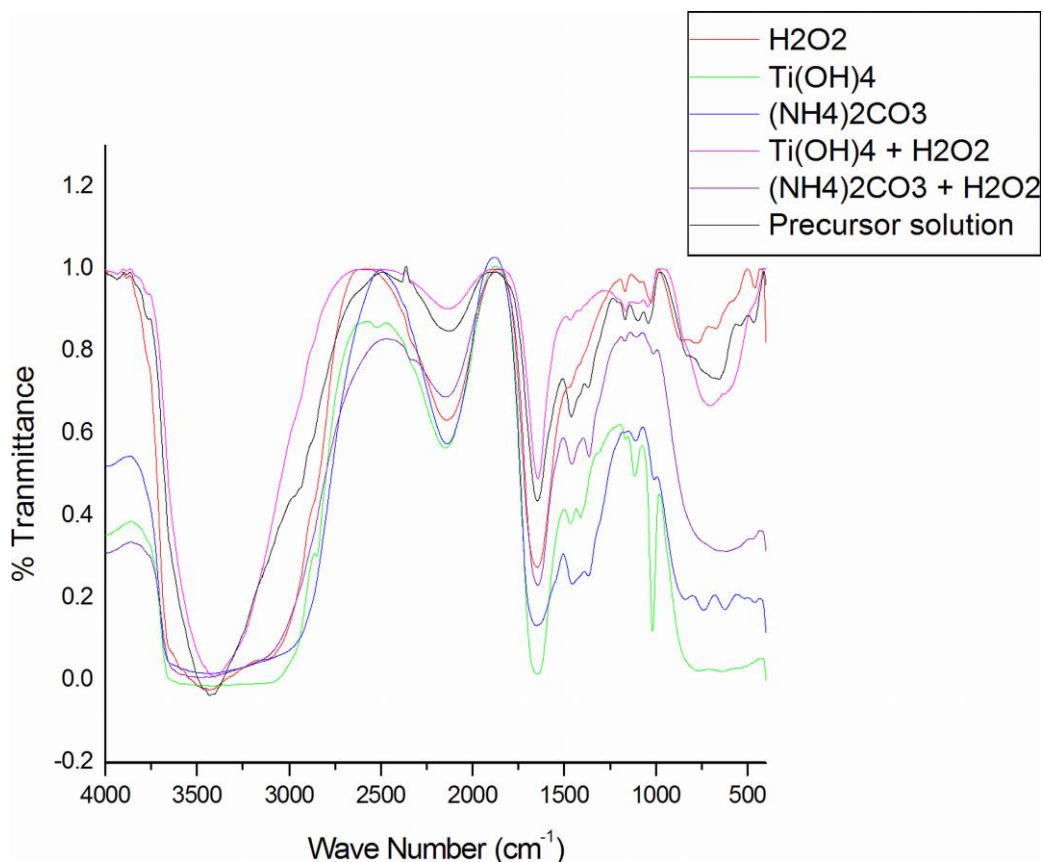
Fig. S4.   Stacked plot of FTIR spectra of different aqueous solution mixtures of reactants.

5. Stability of the precursor titanium peroxy carbonate solution.

From the Fig. S5, it is evident that the stability of the precursor solution increases with incerasing amount of carbonate in the initial solution. The solution having titanium to ammonium carbonate molar ratio of 1:2 (a) did not resulted any clear solution in the initial stage, most probably that amount of carbonate was not sufficient, where as solution having titanium to ammonium carbonate molar ratios of 1:4 (b) gave clear solution and stable up to 3 h, after that starts to form turbid producing layered titanate, so we did all the further experiment using this solution. Here, it should be mentioned that solution having titanium to ammonium carbonate molar ratios of 1:15 (f) and 1:18 (g) was stable for minimum 7 days.
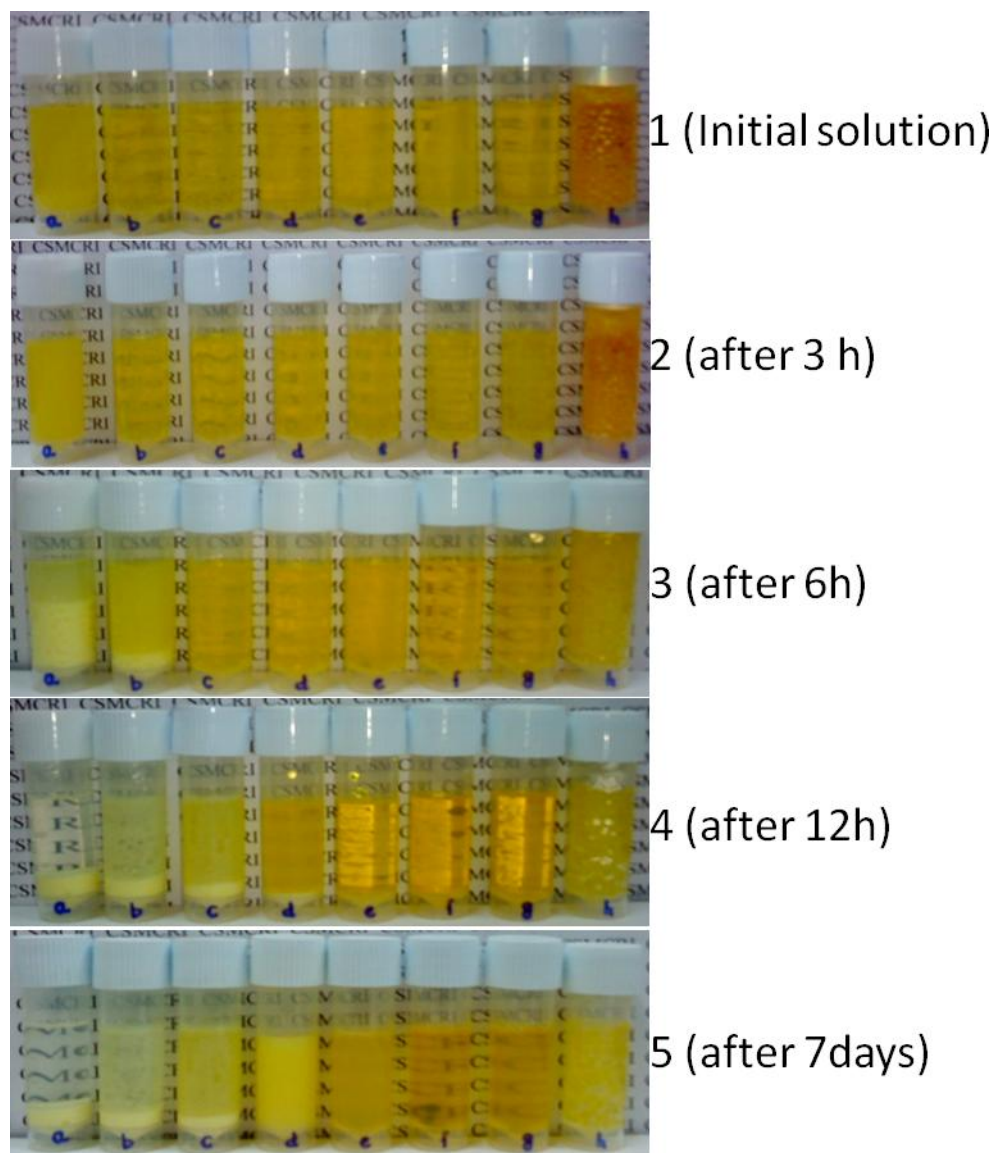
Fig. S5   Photogtaphs of the titanium peroxy carbonate precursor solution in varying times with different amount of titanium to ammonium carbonate molar ratios(a) 1:2, (b) 1:4, (c) 1:6, (d) 1:9, (e) 1:12, (f) 1:15, (g) 1:18 and h) 1:0.

Fig. S6 represents the photographs of 3 different solutions with same amount of H_2O_2 but varying ammonium carbonate and pH after 1 h of the preparation of solution. In the presence of ammonium carbonate (titanium to ammonium carbonate molar ratio of 1:4, pH~9.2) initially it gave a clear solution and remained unchanged after 1h (Fig. S6a). The solution prepared without ammonium carbonate or aqueous ammonium hydroxide, initially gave a turbid solution. After 1h it also turned to a turbid gel

(Fig. S6c). From the experiment, it is evident that the carbonate ion has a crutial role in the stabilization

of titanium ion. It forms chilate with titania and restricts self condensation towards gel formation.
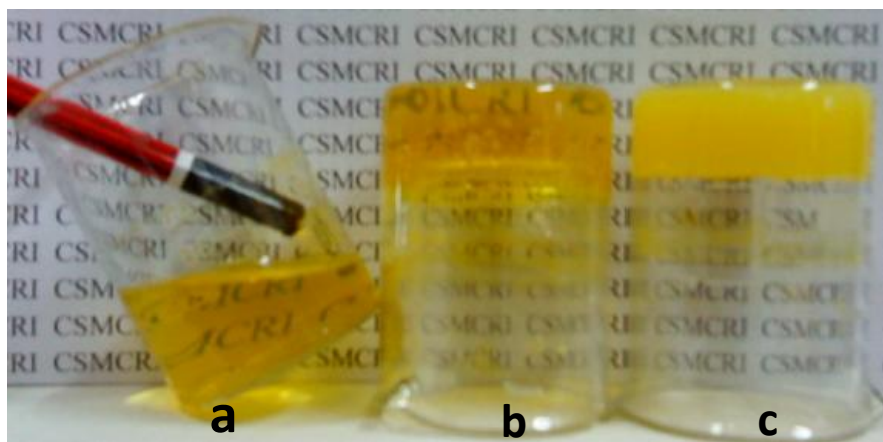
Fig. S6 Photogtaphs of the solutions after 1 h prepared by asme amount of H_2O_2 and (a) titanium hydroxide, ammonium carbonate, (b) titanium hydroxide, aqueous ammonium and c) only titanium hydroxide.

6. Results of layered titanates synthesized by refluxing the developed titanium peroxo carbonate solutions for 1 h.

SEM images showed the synthesized materials are granular in nature (Fig. S7a). TEM image depicted

the existence of 2D nano-sheets (Fig. S7b). The sheets are overlapped to each other. Fig. S7c represents

the typical XRD pattern of the synthesized layer titanate. Diffraction patterns indicates that the product

has an orthorhombic $H_2Ti_2O_5.H_2O$ (JCPDS 47-0124) layered crystal structure.
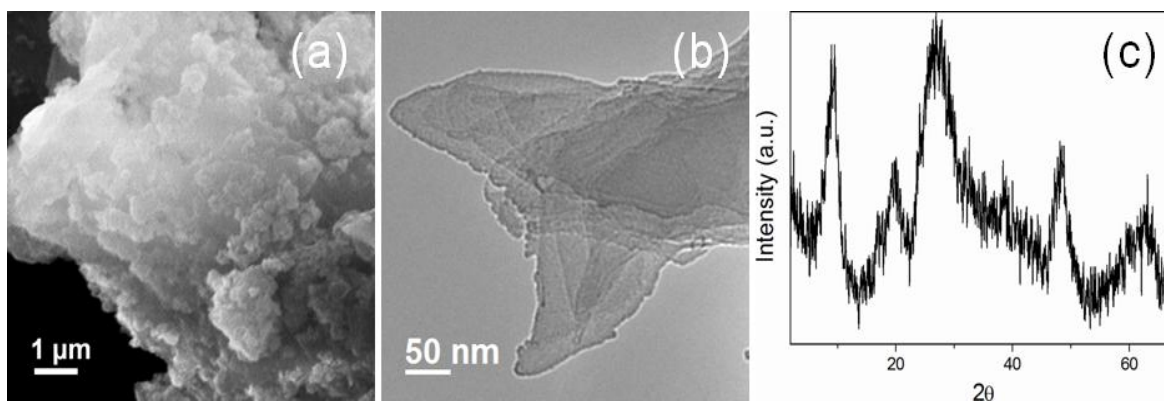
Fig. S7 (a) SEM image, (b) TEM image and (c) XRD pattern of the synthesized layered titanate $H_2Ti_2O_5.H_2O$ at reflux condition.

7.   After calcination at 450°C of room temperature synthesized layered titanate.

TEM image of the room temperature synthesized layered titanate after calcination at 450°C shows the existence of nano-sheet like morphology (Fig. S8a), i.e., after calcination overlapped sheets are merged together and gave the plate like structure. The distinct lattice planes in the HRTEM micrographs confirm the presence of high degree of crystallinity (Fig. S8b). Fig. S8c represents the typical XRD pattern of calcined material. Diffraction pattern indicates that the product has an anatase TiO_2 layered crystal structure.
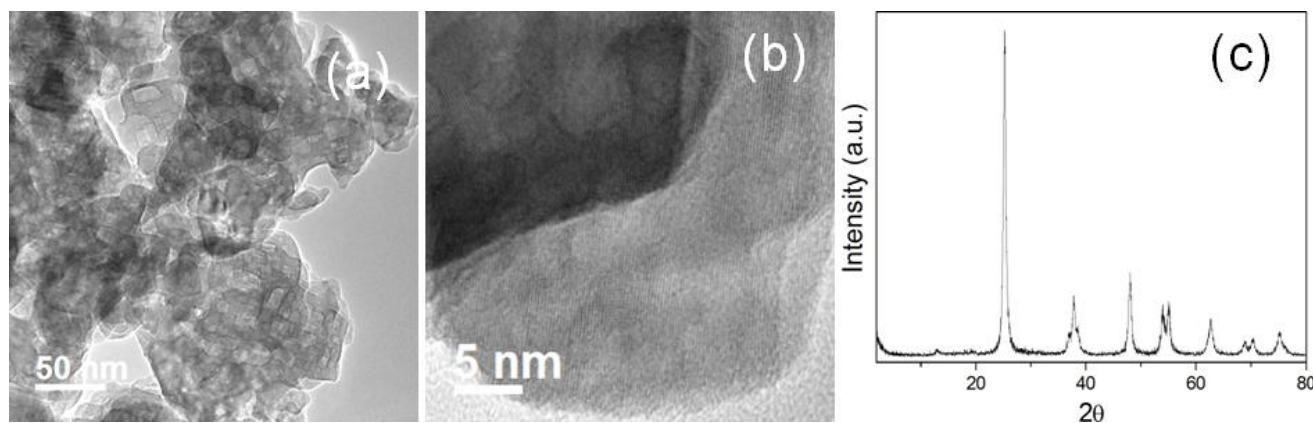

Fig. S8(a) TEM image (b) HR-TEM image and (c) XRD pattern of the calcined layered titanate at 450°C.

8.   Ion exchange:

The theoretical cation exchange capacity (CECs) of the layered dititanate reported as 9.05 mmol g^{-1}. Such CECs is much higher compared to other inorganic ion exchangers, e.g. layered clays, zeolites, and γ-ZrP (zirconium phosphate) having CECs in the range of 0.25-0.6 mmol g^{-1}. This indicates that the synthesized layered titanate can act as a potential sorbent for heavy metal ions uptake via ion exchange. In case of heavy metal ion removal, our material removes Pb^{2+} almost completely in less than 10 min, as evidenced by the concentration decrease of 0.6 mmolL^{-1} Pb^{2+} solution from 124.2 mgL^{-1} (C_0) to less than 0.3 mgL^{-1} at room temperature (Fig. S9). However the saturation capacity (Q_m) of the layered titanate for Pb^{2+} is 2.54 mmol g^{-1} (Fig. S10), which is considerably lower than it's theoretically, calculated exchange capacity. Our material also has a very high removal rate and excellent removal

capacity of MB dye. Almost 98.5% of dye was removed in 120 min of which 89% was removed in the

first 5 minute (Fig. S11).
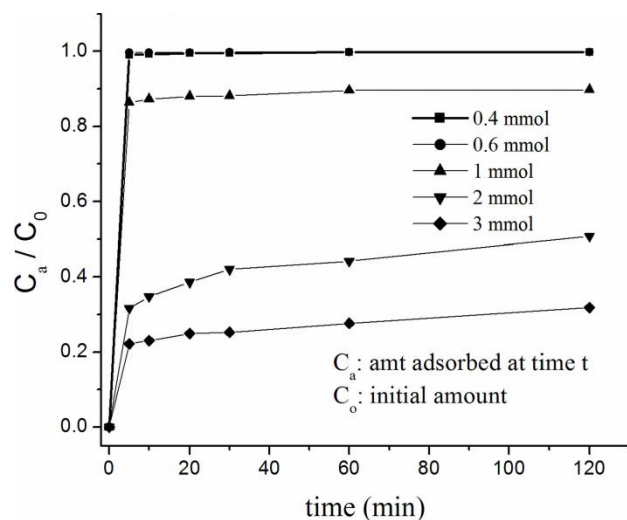
Fig. S9 Removal rate of Pb(II) on layered titanate. C_0 = initial con, C_a amount of Pb (II) exchanged after time t (5, 10, 20, 30, 60, and 120 min)
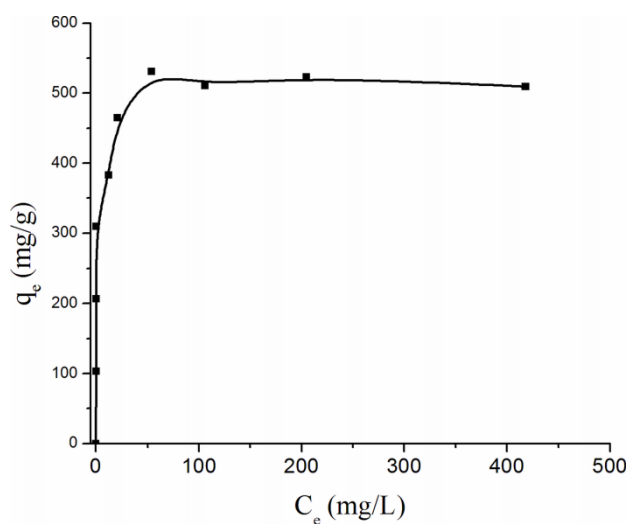
Fig. S10   Isotherm of equilibrium concentration for lead uptake in different concentrations of Pb(II) solution (0.2, 0.4, 0.6, 0.8, 1, 2, and 3 mmol g⁻1) showing the saturation capacity above 500 mg/g (2.54 mmol g^{-1}) layered titanate sheets.
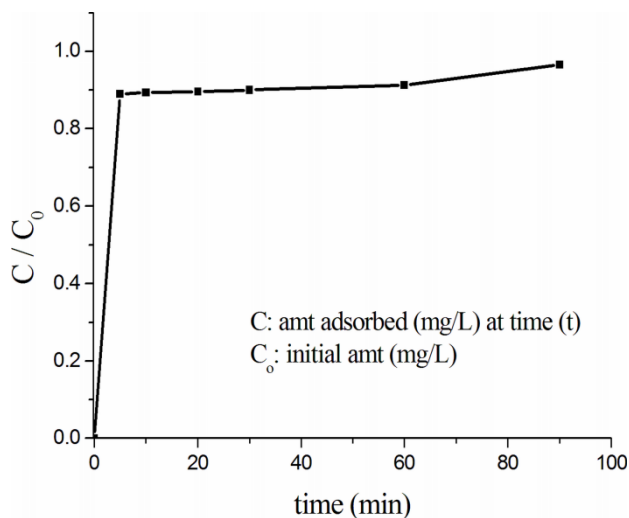
Fig. S11 Adsorption rate of Methylene blue ($C_o = 20$ mg L^{-1}) on layered titanate sheets.

Kinetics:

Kinetic nature of the ion exchange property of synthesized layered titanate was verified for pseudo-second-order kinetic models. The pseudo-second-order expression is given as

$$\frac{t}{q} = \frac{1}{h} + \frac{1}{q_e}t$$

(1)

Where, qe is the amount adsorbed (mg g^{-1}) at equilibrium, and q is the amount adsorbed after time t (min), h = Kq_e^2, K is the rate constant for pseudo-second-order adsorption (g mg^{-1} min^{-1}). Values of h are estimated from the intercept of t/q versus t plots using equation 1(Fig. S12). Feasibility of the kinetic path was examined from the values of rate constants (K) and correlation coefficient (R^2) respectively (Table 1). Good agreement of the R^2 values (Table 1) of the pseudo- second order kinetic indicated that the sorption of Pb^{2+} in the synthesized layered dititanate obeys pseudo- second order kinetics.

Table 1: Second order kinetic constants, correlation coefficients (R^2) for the adsorption of Pb (II).

K	h	q_e	R^2
2.8×10^{-7}	0.0019	82.3	1
9.1×10^{-8}	0.0014	123.96	1
7.5×10^{-7}	0.0261	186.1	0.998
6.5×10^{-7}	0.0287	210	0.995
7.3×10^{-7}	0.0280	194.9	0.996
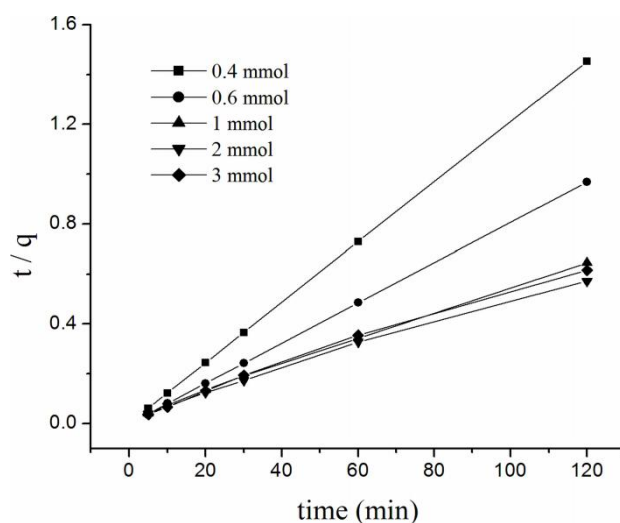
Fig. S12.   Pseudo-second-order plots of Pb(II) adsorption on layered titanate at different molar concentrations.

Adsorption Isotherms:

Equation 2 and 3 are the expression for Freundlich and Langmuir adsorption isotherm.

$$log\ q_e = log\ K_F + \frac{1}{n} log\ C_e \qquad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{1}{K_L} C_e \qquad (3)$$

Where, q_e is the amount adsorbed (mg g^{-1}) at equilibrium, C_e is concentration (mg/l) in solution at equilibrium, K_F is Freundlich constant and $1/n$ is the heterogeneity factor, while a_L and K_L are Langmuir constants.

Freundlich isotherm was obtained by ploting log q_e versus log C_e (Fig. S13) where as Langmuir isotherm (Fig. S14) was obtained by ploting C_e/q_e against C_e. Linier fit of these respective isotherms gave the value of R^2. These values of R^2 along with saturation capacity (Q_m), and Freundlich and Langmuir constants K_f and K_L are listed in (Table 2). Langmuir isotherm was well correlated ($R^2 = 0.998$) compared to the Freundlich isotherm ($R^2 = 0.8612$) suggesting monolayer adsorption of Pb (II) on the surface of layered sheets of dititanate, occurred by proton exchange.

Table 2: Freundlich and Langmuir constants and correlation coefficients (R^2) for Pb(II) adsorption on layered titanate sheets.

Freundlich constants			Langmuir constants		
K_F	$1/n$	R^2	K_L	Q_m(mg g^{-1})	R^2
15.5521	0.5979	0.8612	0.0048	526.315	0.998
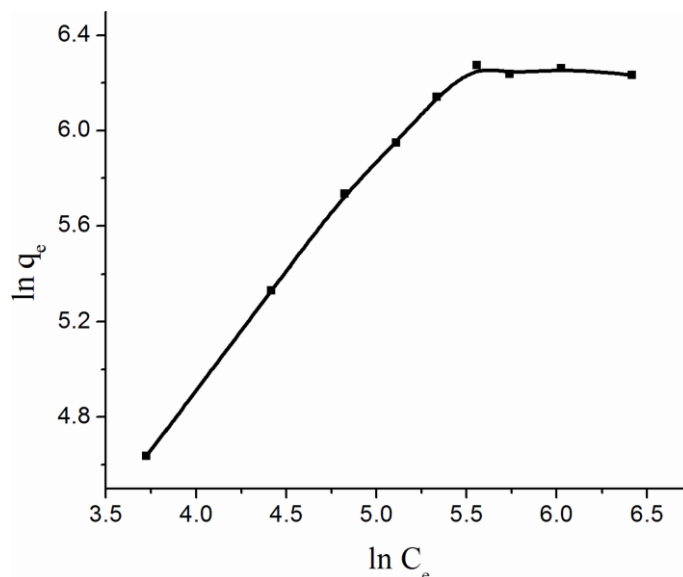
Fig. S13   Freundlich isotherm for Pb(II) adsorption on tiatnate sheets. $C_e=$ equilibrium concentration (mg L^{-1}) for different concentration of Pb(II) after adsorption of 120 min with layered titanate. $q_e =$ amount of Pb(II) adsorbed at equilibrium (mg L^{-1}).
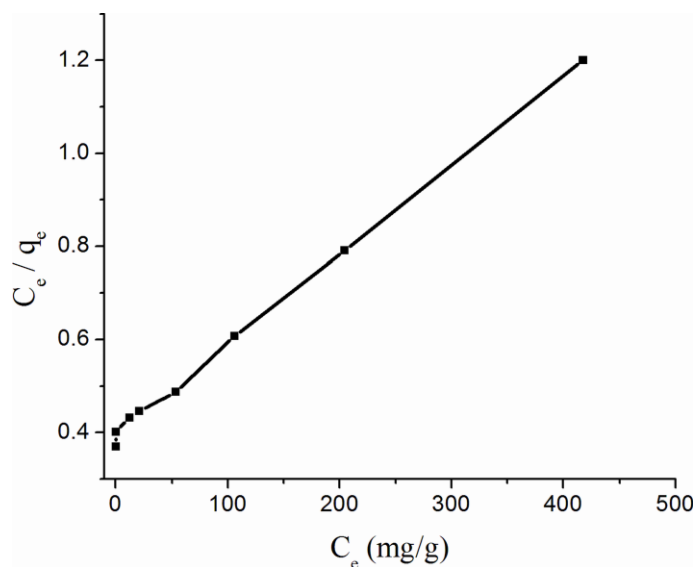
Fig. S14   Langmuir isotherm for Pb(II) adsorption on layered titanate sheets $C_e=$ equilibrium concentration (mg L^{-1}) for different concentration of Pb(II) after adsorption of 120 min with layered titanate. $q_e =$ amount of Pb(II) adsorbed at equilibrium (mg L^{-1}).
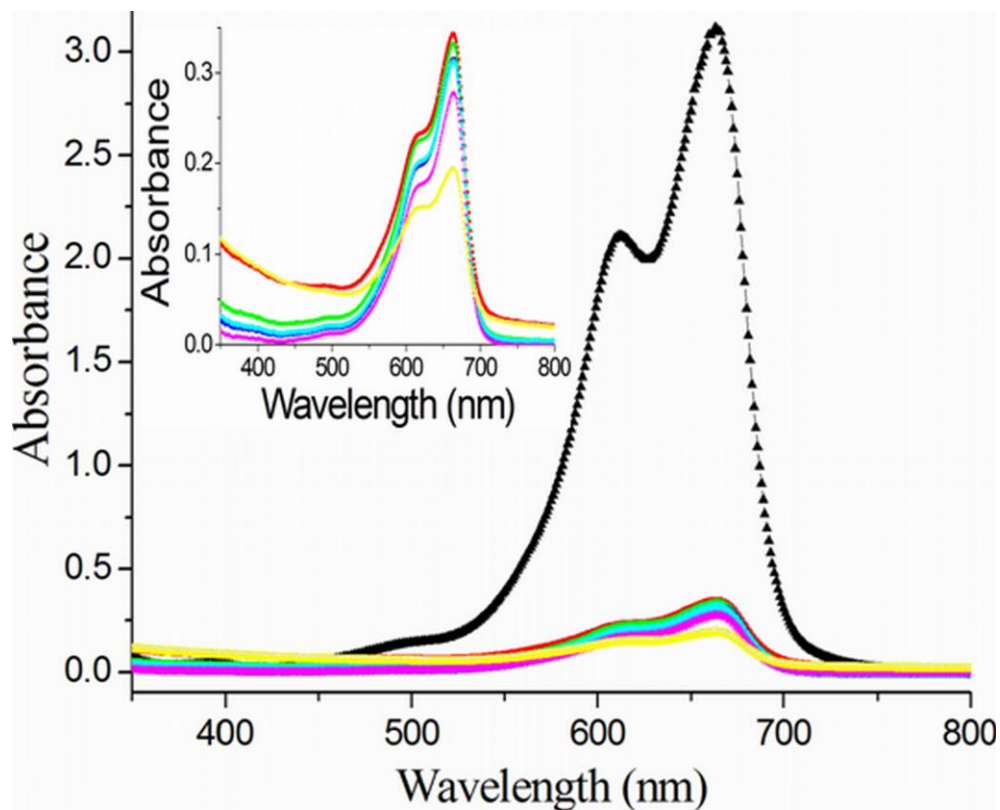
Fig. S15   Adsorption spectra of methylene blue solution at 0 (▲), 5 (■), 10 (●), 20 (▼), 30 (♦), 60 (*), 120 (▶) min of 10mg synthesized layered titanate. Inset represents the photograph of methylene blue solutions after adsorption in varying time.

Reference.

(1)   Gregg, S. J.; Singh, K. S. W. *Adsorption, Surface Area and Porosity, Academic Press*, London, UK, 2nd ed., **1982**.

(2)   Flanagan, J.; Jones, D. P.; Griffith, W. P.; Skapski, A. C.; West, A. P. *J. Chem. Soc., Chem. Commun.* **1986**, 20.

(3)   Nag, M.; Ghosh, S.; Rana, R. K.; Manorama, S. V. *J. Phys. Chem. Lett.* **2010**, *1*, 2881.