Efficient Solar Energy Conversion Using CaCu$_3$Ti$_4$O$_{12}$ Photoanode for Photocatalysis and Photoelectrocatalysis

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A highly efficient third generation catalyst, CaCu$_3$Ti$_4$O$_{12}$ (CCTO) shows excellent photoelectrochemical (PEC) and photocatalytic ability. As only 4% part of the solar spectrum covers UV light, thus it is highly desirable to develop visible light active photocatalyst materials like CCTO for effective solar energy conversion. A direct band transition with a narrow band gap (1.5 eV) was observed. Under light irradiation, high photocurrent density was found to be 0.96 mA/cm$^2$, indicating the visible light induced photocatalytic ability of CCTO. Visible light mediated photocatalytic and photoelectrocatalytic degradation efficiency of CaCu$_3$Ti$_4$O$_{12}$ pellets (CCTO) was investigated for three classes of pharmaceutical waste: erythrosin (dye), ciprofloxacin (antibiotic) and estriol (steroid). It is found that the degradation process follows first order kinetic reaction in electrocatalysis, photocatalysis and photoelectrocatalysis and high kinetic rate constant was observed in photoelectrocatalysis. This was quite high in comparison to previously reported methods.

Photocatalysis has attracted great interest in recent years due to its potential to degrade various pollutants into environmental-benign chemicals at low cost$^{1-3}$. Photoelectrochemical (PEC) water splitting along with photocatalytic oxidation is a sustainable process for the conversion of solar energy for energy production. First time in 1972, Fujishima and Honda demonstrated the prospect of creating a clean and sustainable fuel through PEC process$^4$. The other aspect of using this solar energy is the degradation of harmful, widely used pharmaceutical wastes in to non- toxic chemicals in the process of water treatment. Pollutants from pharmaceuticals and industrial wastages have serious and long-term effects on human health and aquatic environment. These pollutants enter into the environment through the discharge of manufacturing plants, industrial waste water and sewage treatment plants (STP). Pharmaceutical waste water contains dyes, antibiotics, estrogens, steroids and other drugs$^{5-7}$. Fluoroquinolone antibiotics and estrogenic hormones such as ciprofloxacin, norfloxacin, enrofloxacin, 17$\beta$-estradiol (E2), 17$\alpha$-ethylestradiol, and estriol are largely used to treat diseases and infection. However, incomplete degradation of these drugs releases harmful residual components in surface water$^{8,9}$. Similarly, a low concentration of antibiotics, which are commonly used in agriculture to promote growth and prevent disease, can cause proliferation of drug resistant bacteria causing a potential threat for human health and ecosystem$^{10,11}$. For example, Erythrosine which is extensively being used for artificial coloring for foods and drugs like ibuprofen, its toxicological test shows sensitivity to light and increase thyroid hormone levels and lead to hyperthyroidism$^{12,13}$. Thus alternative cost-effective techniques are highly required to degrade this environmental discharge of pharmaceuticals and hazardous dyes.

A PEC cell provides a sustainable process to transform solar energy into chemical fuel and electricity. This is a highly efficient operation can be triggered simply by sunlight. PEC water splitting is the most direct mechanism which can be used for hydrogen generation, solar energy harvesting and waste water treatment. Water splitting is an endergonic process requiring an energy input of 237 kJ/mol of water. Solar light can be an efficient source for the necessary energy input. However, that energy needs to be efficiently collected through absorption processes.

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A site and Ti$^{4+}$ on the B site. It is extensively studied for the energy storage and microelectronics applications due to its high dielectric constant$^{28-31}$. In this paper, we demonstrate the visible light induced photoelectrochemical behavior and photocatalytic activity of CCTO ceramic for the three different classes of pharmaceuticals: dyes, antibiotics and steroid hormones. To the best of our knowledge, this is the first report for the enhanced visible light photocatalytic activity of CCTO ceramic pellets for the pharmaceutical pollutants.

Results and Discussion
Ceramic samples of CCTO prepared from the oxalate precursor route had been studied by different characterization techniques. The X-ray diffraction patterns were recorded on the as prepared CCTO powders (Fig. 1a(i)), the pellets sintered at 1130°C (Fig. 1a(ii)) are compared well with ICDD data file card no. 01-075-1149 (Fig. 1a(iii)), demonstrating the single phase nature of CCTO. In the XRD-pattern of sintered CCTO pellet, there is not any peaks for CuO and TiO$_2$ which shows that phase pure CCTO can be synthesized using this process. The crystallite size was calculated using Scherer formula and observed as 26 nm for powder and 64 nm for sintered pellets of CCTO. The heat treatment around 1130°C resulted sintering of the particles and increment in crystallite size. Figure 1b shows the SEM micrograph of CCTO pellets sintered at 1130°C for 2h.

The optical properties of CCTO had been studied using UV-visible spectroscopy$^{32}$ and Fig. 2a shows the diffuse reflectance spectra for the CCTO powder. A broad absorption band was observed between 200–700 nm with highest absorption at 305 nm. The absorption cutoff wavelength for the CCTO powder is 750 nm. Figure 2b shows the plot between Kubelka-Munk function $(FR)/(RT)$ and photon energy $(h\nu)^{33}$. A direct transition of 1.5 eV was estimated from the tangent line in the plot which corresponds to the visible light absorption and low band gap of CCTO powder. In CCTO, three possible mechanisms are attributed for photogenerated hole formation for 3d$^9$ (i) $d_{x^2-y^2} \rightarrow d_{g}$, (ii) $d_{x^2-y^2} \rightarrow d_{e}$, (iii) $d_{x^2-y^2} \rightarrow d_{t_2g}$, $Clark et al.$ reports the visible light activity of Pt-CCTO complex for dye degradation$^{34}$. The observed absorbance data shows that CCTO has a direct transition in the visible region. In CCTO, the higher energy absorption edge arises due to direct transition from Cu 3d–O 2p hybridized valance band to the Ti 3d conduction band and the lower energy absorption is attributed as transition between valance band and unoccupied Cu 3d band. CCTO have visible light activity due to photo-induced charge transfer from Cu$^{2+}$, Ti$^{4+}$ ground state to Cu$^{3+}$, Ti$^{3+}$ excited state$^{35}$. The visible light activity and the photo induced charge transfer show their potential for photoelectrochemical solar cell and photocatalytic pollutant removal process. CCTO has
large absorption spectrum in visible region which is favorable for activity of CCTO as catalyst under visible light. Therefore, CCTO was used for pollutant degradation and photoelectrodes under visible light irradiation.

The photocatalytic activity of as prepared CCTO pellet was evaluated by the degradation of erythrosine, ciprofloxacin and estriol. Fig. 3a shows the variation in absorbance spectra of an aqueous solution of erythrosine in the presence of CCTO pellets irradiated by a visible light source. The absorption peak corresponding to erythrosine dye was observed at 525 nm and the peak intensity decreases rapidly with the prolonged exposure time. The pink solution of erythrosine turned into colorless solution after only 40 minute exposure. Erythrosine dye molecules react with \( \cdot O_2 \) or \( \cdot OH \) radicals generated during splitting of \( H_2O \) in photocatalysis process which further perform...
mineralization of erythrosine molecules. Figure 3b shows the images of time dependent degradation of erythrosine in the presence of CCTO. Under visible light irradiation, the pink color of the erythrosine started fading within 15 minutes and turned colorless within 30 minutes. However, in the dark, we did not observe any detectable color change. That indirectly proves that CCTO is photocatalytically degrading the erythrosine molecules. Figure 3c shows the change in concentration of ciprofloxacin aqueous solution during photocatalysis with CCTO pellet under exposure of visible light. The results show that the absorption peak of ciprofloxacin molecules decreases with the irradiation time at 276 nm. Photocatalytic degradation of estriol using CCTO pellet was analyzed by fluorescence spectroscopy. Estriol shows a strong emission peak at 306 nm when excited with 240 nm source wavelength. Figure 3d shows the rapid decrease in fluorescence intensity of estriol molecules during photocatalysis using CCTO pellets under visible light exposure which attributed as degradation in concentration of estriol molecules.

The degradation efficiency (D %) of CCTO pellets for the pollutants is calculated using:

$$D\% = 100 \times \left[ \frac{C_0 - C_t}{C_0} \right]$$

where $C_0$ is the initial concentration of drug and $C_t$ the concentration of drug after time ($t$) exposure. Figure 4a shows the comparative degradation (%) of erythrosine, ciprofloxacin and estriol in photolysis and photocatalysis under the visible light exposure ($\lambda > 420$ nm). In the photolysis, no significant degradation was observed for all the pollutants. CCTO photocatalytic pellet shows maximum degradation efficiency for the erythrosine dye under visible light which is better than previous reported methods. The dye molecules degraded up to 70% in visible light irradiation of 40 min while under dark light no degradation of pollutant was observed. The prepared CCTO ceramic pellets degrade 60% of ciprofloxacin concentration in 60 min while for estriol molecules, CCTO pellet saturates earlier. Upto 50% degradation was performed in 40 min using prepared CCTO pellets which are higher than earlier used catalysts for visible light mediated degradation.

The kinetic behavior of CCTO photocatalyst for the degradation of erythrosine, ciprofloxacin and estriol were investigated using Langmuir-Hinshelwood kinetic equation:

$$-r = \frac{d[C]}{dt} = K[C]$$

$$\int_{[C_0]}^{[C]_t} \frac{d[C]}{[C]} = \int_{t=0}^{t=t} K dt$$
where $C_0$ and $C_t$ are the initial concentration and concentration after time t for pollutants. $K$ is the first order catalytic rate constant which is represented by slope of the $\ln \left( \frac{A_t}{A_0} \right)$ and degradation time ($t$) plot. Figure 4b shows the kinetics decay plots for the degradation of erythrosine, ciprofloxacin and estriol. All three of the pollutants show first order decay for the visible light catalysis using CCTO ceramic pellets. The kinetic rate constants for the erythrosine, ciprofloxacin and estriol are calculated as $k_1$ (0.0289 min$^{-1}$), $k_2$ (0.01682 min$^{-1}$) and $k_3$ (0.0166 min$^{-1}$). Figure 4c shows the degradation rate for all the three pollutants in the repeated photocatalytic process using CCTO pellet as catalyst. In all the five cycle, constant degradation rate was observed which attributed as stability and reusability of the catalyst.

Mass spectroscopy was used to probe the generated byproduct after photocatalysis of erythrosine. Figure 5 shows the mass spectra for erythrosine aqueous solution before and after photocatalysis. The intermediates with $m/z$ 467.44 and 657.34 corresponding to the fragments of erythrosine and gradually disappeared after irradiation for 30 minutes in presence of CCTO. Photocatalytic degradation pathway of erythrosine can be analyzed from the transformation of the intermediate species analyzed in mass spectroscopy40. Erythrosine dye molecules reacts with photogenerated holes and $\dot{O}_2$ or $\dot{OH}$ radicals which are generated during water splitting. Erythrosine transformed into 2,5-dihydroxybenzoic acid and phthalic acid41,42. The intermediate products further react with $\dot{OH}$ radicals and converted into CO$_2$ and water by ring opening and mineralization process43.

In the photocatalytic degradation of ciprofloxacin both $\dot{OH}$ radical and photogenerated holes play role in complete oxidation of molecule and intermediates. The photogenerated holes attack on the N12 position in ciprofloxacin. On the other hand, the addition of $\dot{OH}$ radical occurs at C10 and C5 position in quinolone ring. The intermediates formed in the process are further oxidized with hydroxyl radicals and perform a complete oxidation in CO$_2$. The conduction band in CCTO which contributed by Ti (3d) state, plays important role to return the quinolone molecule in ground state by transferring electron into conduction band after photo-excitation. The electron in conduction band further transferred to donor quinolone molecules45. In the photocatalytic degradation process of estriol, the active $\dot{OH}$ radicals formed at photocatalyst surface by water splitting. These $\dot{OH}$-radicals are more likely to attack the benzene ring at C2 and C4 of estriol followed by reaction with oxygen and elimination of HOO$\cdot$ group46,47. $\epsilon$-17β-dihydroxy-1, 4- estradien-3-one (DEO) and testosterone like species are generated as intermediate products in photocatalytic degradation of estriol. These species are further completely mineralized into CO$_2$. The intermediates and final products did not have any estrogenic activity due to the complete dissociation of phenol group which is highly responsible to initiate estrogenic activity48.

To demonstrate the enhanced electron transfer in the CCTO system, some PEC tests were carried out. The photoelectrochemical activity of CCTO under visible light was analyzed by measuring the photocurrent using linear sweep voltammetry (LSV) in the dark and under visible light irradiation as shown in Fig. 6. Cyclic voltammetry observations attributed as high stability of CCTO photo-anode in the electrolyte during electrochemical measurements. The higher photocurrent density was observed under the light illumination for the CCTO pellets which was attributed as light harvesting ability and narrow band gap of CCTO. The photocurrent density ($J_p$) was observed as 0.97 mA/cm$^2$ under light irradiation. The interband electron transition due to photon absorption during visible light irradiation results into the generation of photocurrent and four fold increase of current density. LSV and cyclic voltammetry showed that the CCTO can be used effectively as photocatalysts and photoelectrode materials.

In order to understand the origin of photoactivity enhancement in the PEC system, the flat band potential was measured. Here, the flat band potential of electrodes was determined by the Mott–Schottky relation49:
\[
\frac{1}{C^2} = \left( \frac{2}{\varepsilon \varepsilon_0 N_d} \right) \left[ V_a - V_{fb} - \frac{kT}{e} \right]
\]

Where \( C \) = space charge layers capacitance, \( e \) = electron charge, \( \varepsilon \) = dielectric constant, \( \varepsilon_0 \) = permittivity of vacuum, \( N_d \) = electron donor density, \( V_a \) = applied potential and \( V_{fb} \) = flat band potential.

The flat band potential (\( V_{fb} \)) was determined by taking the x intercept of a linear fit to the Mott–Schottky plot (See supporting information, Fig. S1), \( 1/C^2 \), as a function of applied potential (\( V_a \)). The apparent donor density of the CCTO photoanode was calculated as \( 1.9 \times 10^{15} \). Flat band potential of \( 0.4 \) V vs SCE was observed for CCTO photoanode. Electrochemical impedance spectroscopy (EIS) was performed to investigate the electrochemical behavior of CCTO photoanode. Figure S2 (See supporting information) shows EIS results presented in the form of Nyquist plot. CCTO electrode exhibits \( R_{ct} \) (2.8 k\( \Omega \)) indicating the more favorable environment for hole transfer to the electrolyte.

Figure 7a,b show the electrocatalytic and photoelectrocatalytic degradation of erythrosine by CCTO. The cyclic voltammogram data (Fig. 7a,b) show a sharp oxidation peak at 0.62 V (vs SCE). This peak intensity decreased on the progression of scans (with the increased number of cycle). The decrease in the anodic peak current can be attributed as oxidative degradation of erythrosine on CCTO electrode as the visible change in the color of the electrolyte was also observed. Careful investigations of the CCTO pellet after electrochemical and photoelectrochemical studies shows no noticeable change (see supporting information), indicating that decline of the peak intensity in CV was due to the degradation of electrolyte materials and not accountable for the structural or chemical degradation of CCTO. The photoelectrochemical performance of CCTO pellets shows significantly higher current density during the visible light assisted electrocatalytic degradation (Fig. 7b). In photoelectrochemical study, higher degradation rate was observed in comparison to the electrochemical degradation of erythrosine. Figure 7c shows the degradation plots for photocatalysis and photoelectrocatalysis of erythrosine, ciprofloxacin and estriol. The kinetic decay constants for the degradation of all three pollutants was found to be higher under photoelectrocatalytic degradation which is attributed as role of photocurrent in generation of more \( \cdot OH \) radicals for catalysis and effective separation of charge carriers. The stability of the catalyst has been verified using XRD before and after catalysis. The XRD data shows indifference with the pre-catalysis data collected as shown in Fig S3. (See supporting information).

The photocatalytic activity is controlled by both the ability of light-harvesting and the separation of \( e^-/h^+ \) pair. The \( e^-/h^+ \) pair generated due to light absorption will recombine if they are not separated quickly. A high photocurrent indicates that CCTO has a strong ability to generate and transfer the photo-excitied charge carriers and rapidly production of \( \cdot OH \) radicals during electrochemical water splitting under light illumination. These \( \cdot OH \) radicals plays major role in the photocatalytic degradation of pollutants. Time-dependent fluorescence experiments had been carried out to identify these \( \cdot OH \) (See supporting information, Fig. S4). Previous reports and the experimental results indicated that photocatalytic degradation of pharmaceuticals initiated by excitation of electron form the valence band to the conduction band after irradiation of light.\(^{2,14,49}\). The photocatalytic performance of catalyst is depends upon its light absorption ability and electron transfer ability. The process starts only when the incident light energy is equal to or larger than band gap. CCTO photocatalyst is a novel material for visible light catalysis which is attributed as role of photocurrent in generation of more \( \cdot OH \) radicals for catalysis and effective separation of charge carriers. The process followed by the direct oxidation of pharmaceuticals by photo generated hydroxyl radicals and holes. The indirect oxidation is performed by the \( \cdot OH \) radicals generated by water splitting.

**Conclusion**

In conclusion, a novel visible light active CaCu3Ti4O12 ceramic was synthesized from the oxalate precursor route. CCTO have broad absorbance spectrum for visible light and narrow band gap which makes it a potential material for visible light induced photocatalysis and photoelectrochemical cell. Under visible light irradiation, CCTO pellet electrodes show high photocurrent density 0.97 mA/cm\(^2\). It shows the potential of CCTO photoanode for the
High performance PEC solar cells for energy conversion. CCTO ceramic pellets have more efficient photocatalytic ability to degrade erythrosine, ciprofloxacin and estriol than any other catalyst under visible light. The catalysis was performed by using CCTO pellets and does not require any additional filtration process to remove the catalyst which is an added advantage over the catalysis in powder form. This study has demonstrated fabrication of third generation photocatalyst with two distinct transition metals for the visible light mediated photoelectrochemical and photocatalytic degradation for three different classes of pharmaceutical water pollutants which can be applied to develop new class of visible light active catalysts for other pollutants.

**Methods**

**Synthesis of CaCu₃Ti₄O₁₂.** Ceramic samples of CaCu₃Ti₄O₁₂ (CCTO) were prepared from the oxalate precursor route. In a typical preparation, initially, the titania gel was prepared from the aqueous TiOCl₂ (0.05 M) by adding NH₄OH at room temperature till the pH reaches ~8.0 and washed with water to remove NH₄Cl. Synthesized titania gel was powdered and dissolved in H₂C₂O₄.2H₂O. In the obtained solution, calcium carbonate was added and stirred. The solution remained clear without any precipitate formation. Cupric chloride solution in acetone and water (80:20) was added slowly and stirred continuously at 10 °C. The thick precipitate was separated, washed several times with acetone to make it chloride-free and dried in air. The precipitate thus prepared was isothermally heated above 680 °C to get the ceramic powders of CaCu₃Ti₄O₁₂. The resultant powder was ground thoroughly, ball milled for 2 h and granulated by adding polyvinyl alcohol (PVA) and poly ethylene glycol (PEG), then pressed into pellets at 150 MPa with a diameter of 12 mm and thickness of 2 mm. The green pressed pellets were slowly heated to 600 °C to get rid of the binder. Finally, the pellets were sintered in air at 1130 °C for 2 h. Pellet densities were measured by the Archimedes principle using xylene as the liquid medium.

**Material Characterization.** After sintering, X-ray powder diffraction studies were carried with an X'pert diffractometer (Philips, Netherlands) using Cu Kα₁ radiation (λ = 0.154056 nm) in a wide range of 2θ (10°–90°) with 0.02 step size to examine the phase constitutes of the specimens. Scanning electron microscope (FEI-Technai SEM-Sirion) was used to observe the microstructure of the sintered pellets. Optical properties of CCTO powder were analyzed by UV-vis absorbance spectroscopy.

**Photoelectrochemical Characterization.** A scanning potentiostat (Metrohom, Autolab) was used to perform cyclic voltammetry and electrochemical impedance studies in a three-electrode photoelectrochemical cell with CCTO pellet as the working electrode, a calomel electrode as the reference, a platinum wire as the counter electrode and 1M L⁻¹ KOH as electrolyte. To fabricate the working electrode, a copper wire was attached with the silver paste at side of pellet and sealed with epoxy to avoid the copper contact with electrolyte.
Table 1. Applications and toxicological effects of chemicals under study.

| Chemical   | Application                                                                 | Toxicological Effect                                                                 |
|------------|----------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Erythrosine| Used in artificial colouring of cosmetics and food                           | Chromosome damage and thyroid tumours. When combined with blue dyes such as brilliant blue or indigo carmine, erythrosine may cause bronchial constriction. |
| Ciprofloxacin | Used to treat certain bacterial infections of the urinary tract, lower respiratory (lung) tract, skin, bone, joint, stomach, sinuses, and prostate. | Adverse developmental effects: tadsopes and zebra fish embryos. Development and rapid global transmission of resistant pathogens |
| Estriol    | Used in hormone replacement therapy (HRT)                                    | Feminization of male fish, Play role in the development of breast cancer.             |

Voltammetry and Linear Sweep Voltammetry (LSV) scan were performed between −1 V to 0.5 V vs. SCE at scan rate of 2 mV s⁻¹. For photocurrent measurements, PEC cell was assembled using a CCTO pellet electrode with an area of 1 cm² as a photoanode, Pt wire as a counter electrode and 1 M L⁻¹ KOH as electrolyte. A halogen lamp with a power of 100 mW/cm² was used as the incident light source and placed at 10 cm distance from the electrochemical cell.

Visible Light Photocatalysis. Pharmaceutical dye erythrosine, antibiotic ciprofloxacin and estriol were used to test the photocatalytic activity of sintered CCTO pellets. Table 1 shows the chemical structures, applications and toxicological effect of pollutants which are used for photocatalytic degradation in this paper. The photocatalytic degradation experiments were carried out by using 10 ml solution of 10 mg/L ciprofloxacin, 10 mg/L erythrosine and 1 mg/L of estriol in deionized water. A total of 10 ml solution of pharmaceutical compound was transferred in pyrex glass vessel and the sintered CCTO pellet was placed vertically in vessel. The vessel was kept in dark for 30 min to allow stabilization and pre adsorption of pharmaceutical species on catalyst pellet. The photocatalytic degradation process was initiated by exposing the reaction vessel with visible light 150 W halogen lamp with UV-light cutoff filter (λ > 420 nm). During light exposure, cold water was circulated around the vessel to maintain at room temperature. Sample aliquots of pharmaceuticals were collected at various time intervals and analyzed for change in concentration. The concentration of erythrosine and ciprofloxacin were analyzed using Shimadzu-2450 UV-vis spectrophotometer by measuring the peak intensity. The degradation of estriol was investigated by fluorescence spectrophotometer. The analysis was performed using 3 ml of sample aliquots. High resolution mass spectroscopy analysis was performed to analyze the subsequent species produced during photocatalytic degradation of erythrosine.

Photoelectrocatalysis. Photoelectrocatalytic degradation of erythrosine was carried out in a single photoelectrochemical compartment. The CCTO photoanode (12 mm diameter and 1 mm thickness) and a platinum wire cathode were placed in parallel in a cuboid glass reactor (volume of 100 mL) with a SCE reference electrode. All electrodes were connected to a Metrohm, Autolab electrochemical station. A halogen lamp placed outside the glass reactor and paralleled to the CCTO photoanode. A bias potential applied on the CCTO photoanode to electrochemical compartment. The CCTO photoanode (12 mm diameter and 1 mm thickness) and a platinum wire as a counter electrode and 1 M L⁻¹ KOH as electrolyte. A halogen lamp with a power of 100 mW/cm² was used as the incident light source and placed at 10 cm distance from the electrochemical cell.

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Author Contributions

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H.S.K. and P.T. designed/carried out the experiments, preformed the sample characterization measurements and analyzed all the results. H.S.K. and R.V. wrote the manuscript. A.H. performed electrochemical measurements.
R.V., A.H., N.A.M. and B.I. were involved in the design of experiments, editing of the manuscript and discussions throughout the work. All authors reviewed the manuscript.

**Additional Information**

Supplementary information accompanies this paper at [http://www.nature.com/srep](http://www.nature.com/srep)

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