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Evaluation of photocatalytic activity of commercial red phosphorus towards the disinfection of \textit{E. coli} and reduction of Cr (VI) under direct sunlight

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Abstract

Elemental photocatalysts are getting the attention of material scientists as a new class of visible light photocatalysts in recent years. Hence it is important to understand and evaluate their photocatalytic activity for the rationale design and development of new catalysts at low cost. In this regard, we choose commercial red phosphorus as elemental photocatalyst and we evaluate its activity towards the disinfection of \textit{E. coli} and reduction of Cr (VI) under natural sunlight. The measured bandgap of red phosphorus is 2.0 eV matches with theoretical value and indicates the suitability of the material as photocatalyst under direct sunlight. Moreover, red phosphorus also has optimum valence and conduction band levels for the successful photo-generation of reactive oxygen species (ROS). These photogenerated ROS could help to achieve the disinfection of \textit{E. coli} in 50 min. In the case of photocatalytic reduction of Cr (VI), 98% of Cr (VI) reduction has been achieved in 60 min at pH 2. The rate of Cr (VI) reduction decreases with an increase in pH value similar to the reports with other metal oxide photocatalysts.

Introduction

Various pollutants present in waste water can considerably affect the human health and environment. Pollutants present in water promote the formation of harmful algal blooms or the release of cyanotoxins and they also decrease the dissolved oxygen levels that could significantly affect aquatic biota and ecological balance [1]. The main contaminants in water are broadly classified as (i) biological contaminants (ii) inorganic contaminants and (iii) organic contaminants [2]. In the view of rapid industrialization and urbanization in the developing counties, providing contaminants free drinking water for affordable prices is a challenging task. Although chlorination, ozonation and UV treatment are the commonly used water disinfection methods [3], they associate with the serious limitations such as (i) non-environmental friendly nature (chlorination) (ii) generation of harmful and carcinogenic by-products [4–8]. UV treatment method is ineffective for UV resistant bacteria, moreover it is not the first choice in terms of economic feasibility [9]. In this regard, cost effective solar water disinfection (SODIS) process was proposed to low and middle income countries to get safe drinking water at nominal prices [10]. SODIS is a low cost method that does not produce any harmful by-products. However the process takes longer reaction times and the rate of disinfection in SODIS process depends on the intensity of sunlight. Hence by integrating the process with photocatalysis, the reaction kinetics of SODIS process can be accelerated [11, 12].
an outcome from the experiments of Fujishima and Honda, photocatalysis is evolved as a powerful green technology for H2 generation and environmental remediation. Among the three major contaminants of water which are mentioned earlier, removal of organic contaminants using photocatalytic technology is well established [13]. Researchers have also used the photocatalysis for removal of biological contaminants, i.e. disinfection of water using different light sources and different transition metal-based photocatalysts [14]. Wide bandgaps of these photocatalysts (generally >3 eV) generates a necessity to use an external UV light source. Moreover, these photocatalysts (with bandgap >3 eV) can absorb only UV radiation, not visible light radiation and the Sunlight contains only 5% UV light, hence they are not prominent to accelerate the SODIS process. In this regard, the development of novel solar light/visible light photocatalysts [15] and effective light trapping with bio-inspired/biomimetic catalyst designs [16, 17] that address integration of photocatalysis in a circular process, minimizing the residues generation [18, 19] got much attention in recent years.

In continuation to the above discussion on water purification, inorganic contaminants are another major sources of drinking water pollution. These inorganic contaminants include the presence of heavy metals such as arsenic, mercury, chromium etc. Cr (VI) is released to water by electroplating and leather industrial effluents and its presence in water causes health problems related to the liver and kidney [2, 20]. Application of photocatalysis for the removal of Cr (VI) using visible light photocatalysts has evolved as green technology in recent years as it converts the hazardous Cr (VI) to non-hazardous Cr (III) [20–22].

Proposed visible light photocatalysts in literature are broadly classified as (i) metal-based photocatalysts (ii) non-metallic/elemental photocatalysts. Due to the photo corrosion of metal based photocatalysts [23], elemental/non-metallic photocatalysts need to be explored more as an alternative to metal-based visible light photocatalysts. g-C3N4, α-sulfur, boron, red phosphorus are few non-metallic/elemental based materials that are investigated for visible light photocatalytic applications [24–27]. In particular, for the photocatalytic disinfection application, g-C3N4 was well established [28, 29]. Red phosphorus is another important visible light active elemental photocatalyst with a suitable bandgap (1.4–2.0 eV) [27, 30–38]. It exists in several allotropic forms which are categorized as: Type I (amorphous); Type IV (Hittorf; crystalline) and Type V (fibrous, crystalline) [39–41]. Type II and Type III also exist but their synthesis and structural information are not well established. Crystalline allotropes of red phosphorus/their composites were examined as photocatalysts, and these materials were mainly derived from the commercially available amorphous red phosphorus [30, 31, 42–47]. Hence it is important to understand the photocatalytic activity of commercial amorphous red phosphorus for the critical evaluation of the visible light photocatalytic activity of red phosphorus based photocatalysts. Moreover, it is available at low price, hence it can be a promising photocatalyst to accelerate the SODIS process and scale-up of the photocatalytic processes at nominal price.

Very few reports exist on the red phosphorus as photocatalysts for the disinfection and Cr (VI) reduction. Xia et al studied red phosphorus as green photocatalysts for the bacterial inactivation [33]. Nevertheless, the calculation of bandgap (1.4 eV), valence band (VB) and conduction band (CB) positions need to be mentioned more clearly. In addition to this, the use of Xe lamp as light source compromises the economic feasibility of the process. Li et al used nanosized red phosphorus for the photocatalytic reduction of Cr (VI) with Xe lamp as light source [48]. Liu et al synthesized g-C3N4/red P photocatalyst for the reduction of Cr (VI) and dye degradation [49]. A ternary composite of red phosphorus (MoS2/Red P/rGO) for the removal of Cr (VI) and organic pollutants was demonstrated by Bai et al [50, 51].

In this context, we evaluate the commercial red phosphorus as photocatalyst for the disinfection of water where E. coli was used as model biological pollutant and Cr (VI) was taken as a model inorganic pollutant. We believe that the present study gives a comprehensive overview of the photocatalytic activity of red phosphorus and helps to design structurally novel and efficient red phosphorus based elemental photocatalysts by engineering the material at atomic level.

Methodology

Commercial red phosphorus was obtained from AlfaAesar (99%). To remove the surface oxide layers on commercial red phosphorus, 2 g of commercial red phosphorus was taken in Teflon vessel that contains 20 ml of Millipore water. Tellon vessel was enclosed in a hydrothermal autoclave and heated at 200 °C for 12 h. After that, vessel was cooled to room temperature and surface water was removed. The material at the bottom of the vessel was washed with Millipore water for two times and the sample was dried in an oven at 80 °C–90 °C for 1 h (supporting information S1 is available online at stacks.iop.org/MRX/7/104002/mmedia).

Computational methodology

Amorphous Red Phosphorus was modelled by using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [52–54]. The calculations were done by the projector augmented...
wave method (PAW) using the GGA-PBE [55, 56] exchange correlation functional with a plane wave cut-off of 500 eV. The amorphous structure consisting of 126 atoms was simulated using the melt-quench approach in a canonical ensemble (NVT) with Nose-Hoover thermostat for temperature control [57]. The system was heated at a temperature of 800 K way above its melting point of 317 K. The system was then quenched at 300 K at a cooling rate of 125 K ps\(^{-1}\). All the calculations were carried out with a single k-point sampling at the Γ point of Brillouin Zone for energy convergence. The band structure calculations were computed using HSE06 functional [58].

**Characterization**

Morphology of the hydrothermal activated red phosphorus was examined by SEM using a Carl Zeiss Evo 18 instrument. Photocatalyst was characterized with Rigaku UltimaIV X-ray diffractometer (Rigaku America, Woodlands, TX, USA), Raman analysis was carried out by using a Lab RAM HR (Horiba JobinYvon, France) employing a 514.5 nm laser at an intensity of 1.3 mW. UV–vis diffuse reflectance spectrum of the sample was recorded using Shimadzu UV–vis-nIR spectrophotometer (model 3600+). Mott-Schottky analysis was carried out using Bologic SP150 instrument. Photocatalyst modified glassy carbon was used as a working electrode, Pt foil as a counter electrode and Ag/AgCl as a reference electrode. The analysis was carried out using 5 mM of potassium ferricyanide along with 1.0 M KCl at 1 kHz.

**Photocatalytic experiments**

**Photocatalytic inactivation of E. coli**

Sterilization of all required accessories such as glassware, Eppendorf tubes, micropipette tips, centrifuge tubes, Luria broth, nutrient agar, and DI water was carried out in an autoclave at 121 °C for 15 min. E. coli (DH5α) was taken as a model microorganism for photocatalytic disinfection experiments. To 30 ml of sterilized Luria Bertani broth (HiMedia, India), a loop of viable bacterial colony was inoculated and the broth was kept in a shaking incubator with 180 rpm at 37 °C for 6 h. The bacteria pellet was obtained after centrifuging culture at 4000 rpm for 15 min. The pellet was washed twice with DI water and re-suspended with 30 ml of sterilized DI water. Red phosphorus photocatalyst (0.15 g l\(^{-1}\)) was loaded to the re-suspended bacterial solution and the reaction mixture was kept under direct sunlight with constant stirring (supporting information S2). The intensity of sunlight radiation during the photocatalytic experiments was measured using solar power meter (WACO-206) and it was found to be 700–800 W m\(^{-2}\). Every 10 min interval samples aliquots were collected. Serially diluted sample aliquots were spread on solidified nutrient agar (HiMedia, India) plate. The plates were incubated for 12 h at 37 °C to get the viable bacterial count.

**Photocatalytic reduction of Cr (VI)**

100 ml of different initial concentrations of K\(_2\)Cr\(_2\)O\(_7\) (25 ppm; 60 ppm) solutions were prepared in a 250 ml beaker. To this, 40 mg of red phosphorus was added and sonicated for 5 min. After that, beaker was kept for stirring (1000 rpm) under dark conditions for 30 min to attain adsorption and desorption equilibrium. 5 mg of ammonium oxalate was added to the above solution and the reaction setup was kept under natural sunlight. As mentioned previously, the intensity of sunlight radiation during the photocatalytic experiments was measured using solar power meter (WACO-206) and it was found to be 700–800 W m\(^{-2}\). Aliquots were taken at an interval of half an hour and centrifuged at 8000 rpm for 10 min to remove the photocatalyst. The supernatant was analysed using UV–vis spectrophotometer. The progress of photocatalytic reduction of Cr (VI) to Cr (III) was monitored by observing the spectral changes at 354 nm in UV–vis spectra. Effect of pH on photocatalytic activity of red phosphorus was performed by keeping the initial Cr (VI) concentration at 25 ppm and maintaining the pH of the solutions at 2, 4, 7, 10 using HCl and NaOH solutions. The percentage reduction of pseudo first order reaction was calculated by using the following equation [59, 60].

\[
\% \text{ of Cr(VI) reduction} = \left(1 - \frac{C_t}{C_0}\right) \times 100
\]  

(1)

In the above equation, \(C_0\) is the initial concentration of Cr (VI); \(C_t\) is the concentration of Cr (VI) after time \(t\);

**Results and discussion**

Figure 1 (a) shows the PXRD of the red phosphorus that shows the broad peaks at 2θ values ~15 and ~34. These peaks positions are ascribed to the (013) and (31-8) of red phosphorus (JCPDS file No: 44–0906) respectively.
Another important characterization of amorphous red phosphorus is Raman spectrum (figure 1(b)). That contains broad peaks in the range of 300–500 cm$^{-1}$ and the peak positions at 351 cm$^{-1}$ and at ~390 cm$^{-1}$ are in good agreement with earlier reports [62]. SEM images of the sample at different magnifications are shown in the figure 2. SEM images clearly show the micron-sized particles of the photocatalyst with irregular morphologies.

The bandgap energies are calculated using DFT. In order to confirm that the theoretically simulated amorphous red P replicates the synthesized amorphous red P, its radial distribution function (RDF) was plotted (supporting information S3). Two distinct peaks present in the RDF are an indicator of short range order and long range disorder. Also, the two RDF peaks observed at 2.22 Å and 3.52 Å are in agreement with the experimentally observed first two coordination shells at 2.22 Å and 3.49 Å obtained by neutron diffraction method [63]. The band energies were calculated for Γ–X|Y–Z|Γ–Γ–R–R2–Γ–V2 band path along the high symmetry direction [64, 65]. The calculated band structure was obtained to be 2.02 eV as shown in the figure 3. Both the valence band maxima and conduction band minima lie at the Y point hinting towards a direct bandgap which leads to higher energy conversion efficiency of solar energy.

To further verify the bandgap of red phosphorus by experimental data, we studied light absorption properties of the material by UV–vis spectroscopy. The absorption edge of the material is near to 700 nm (figure 4(a)) indicating the absorption ability of major portion of the visible region of the solar spectrum. The bandgap of the material is calculated using Kubelka–Munk equation and the value was found to be 2.0 eV (figure 4(b)) which is equivalent to the theoretically predicted value. Conduction band (CB) and valence band (VB) edges of the material are calculated using the equations mentioned in the literature [66–68] and the values are found to be $E_{CB} = -0.12$ eV and $E_{VB} = 1.88$ eV. To measure the $E_{CB}$ level experimentally, Mott–Schottky analysis was also performed (figure 4(c)). The flat band potential measured from Mott–Schottky plot was observed at $-0.697$ V versus Ag/AgCl i.e. $-0.497$ V versus NHE. As the flat band potential approximately equivalent to conduction band [69, 70], hence the conduction band potential of red phosphorus can be considered as $-0.497$ V. Using the values of optical bandgap and conduction band potentials, the calculated value of valence band potential lies at 1.503 V versus NHE.
Superoxide radical anion (O$_2^-$), H$_2$O$_2$ and hydroxide radical (OH$^\cdot$) are important reactive oxygen species (ROS) that are generally produced in photocatalytic processes and these ROS are responsible for the death of bacterial cells by damaging the cell wall. Experimentally measured CB position of red phosphorus is suitable to generate H$_2$O$_2$ by two electron reduction of O$_2$ (O$_2$/H$_2$O$_2$ 0.68 V versus NHE)[71,72]. However OH$^\cdot$ cannot be generated directly from the oxidation of H$_2$O, as the reaction requires a potential of 2.38 V that is more positive than the EVB of the photocatalyst (1.503 V)[72]. Nevertheless, the generation of OH$^\cdot$ radical is possible by photolysis of H$_2$O$_2$ or from the other ROS as reported earlier[47,71,73,74]. As the experimentally measured conduction band potential is more negative (−0.497 V) than the potential required for generation of superoxide radical by single electron transfer reduction process i.e. −0.16 V versus NHE the direct formation of the O$_2^-$ could be facilitated. Moreover, the CB level is also appropriate to generate HO$_2^-$[75,76] and this HO$_2^-$ can also be generated by the following reactions [77].

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH}^- \]  
(2)

\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  
(3)

HO$_2^-$ is a conjugate of O$_2^-$ with pKa value 4.8[73,77]. Hence the superoxide radical can also be generated from HO$_2^-$ and it was detected by spectroscopic methods. In addition to superoxide radical, we also detected and confirmed the formation of the other ROS by spectroscopic methods (supporting information S4).

Figure 5(a) shows the photocatalytic disinfection of E. coli. In the absence of catalyst, an overall 0.5–0.6 log reduction in bacterial count has been observed after 60 min of the reaction. Although the reduction was minimal, it could be due to the disinfection caused by direct sunlight (SODIS). In the presence of red phosphorus catalyst, as the reaction progress, we observed 0.3, 0.5, 1 and 1.1 log reduction in 10, 20, 30, 40 min respectively. In the sample aliquot taken at 50 min, we did not observe any viable colonies and the result was consistent with 60 min sample also (figure 5(b)). This bacterial disinfection can be attributed to the photogenerated ROS that can rupture the cell wall and cause cell death as mentioned earlier.
Photocatalytic reduction of Cr (VI)

UV–vis spectra of photocatalytic reduction of Cr (VI) at different initial concentrations of Cr (VI) are shown in figure 6. The progress of the photocatalytic reduction of Cr (VI) was monitored by following the decrease in the peak intensity at ~350 nm that is attributed to HCrO$_4^-$ [78]. At higher concentrations of Cr (VI) i.e. at 60 ppm, 44% of Cr (VI) reduction was observed in 60 min (table 1) (figures 7(a) and (b)). As the reaction progress, reduction was increased to 84% in 180 min (table 1) (figures 7(a) and (b)). In the absence of catalyst, intensity of
350 nm peak was unchanged, even after 180 min of reaction time (supporting information, figure S5). When the concentration of Cr (VI) was reduced from 60 to 25 ppm, ∼90% of Cr (VI) reduction was observed in just 60 min (table 1). To understand this change, we calculated the rate constant (table 1) (figures 7(c) and (d)) of the photocatalytic reduction of Cr (VI) from the -ln(C/C₀) versus time graph. It was observed that the rate constant was doubled when the initial concentration of the Cr (VI) was reduced to 25 ppm. Here it is important to note that the volume of the reactor, sunlight intensity (lux), amount of catalysts and other reaction parameters were kept unaltered. The heterogeneous photocatalytic reduction occurs via adsorption of reactants (i.e. Cr (VI) in present case) on solid catalytic particles. Hence, more number of catalytic sites are available for Cr (VI) adsorption at lower reactant concentrations and that could lead to higher reaction rates.

To understand the effect of pH on photocatalytic reduction of Cr (VI), we further carried out the photocatalytic reduction by varying the pH of Cr (VI) solution at 2, 4, 7 and 10 using HCl and NaOH (figure 8) and other experimental conditions were kept identical. At basic conditions, linearity according to Beer–Lambert’s law is not valid if the Cr (VI) concentration is beyond 25 ppm [78]. Hence the concentration of Cr (VI) was fixed at 25 ppm to study the effect of pH on photocatalytic reduction of Cr (VI). In accordance to earlier reports [48], the high rate of photocatalytic reduction was observed at lower pH i.e. at 2. At this pH, after 30 min of reaction, the intensity of 350 nm peak was considerably decreased. After 60 min of reaction time, we observed

| Reaction conditions | k (rate constant) | R² | % of reduction (60 min) |
|--------------------|------------------|----|------------------------|
| 60 mg l⁻¹ | 0.01236 | 0.99 | 44.02 |
| 25 mg l⁻¹ | 0.02395 | 0.94 | 89.94 |

Figure 7. C/C₀ versus time and –ln C/C₀ versus time graphs of photocatalytic reduction of Cr (VI) with red phosphorus photocatalyst under direct sunlight. The experiments were carried at different initial concentrations of Cr (VI) i.e. at 60 ppm (a) and (b) and at 25 ppm (c) and (d).
that 98% of Cr (VI) was reduced. Further increase in the pH of the reaction to 4, Cr (VI) reduction was decreased from 98% to 85% for same period of reaction time i.e. 60 min. pH 10 is higher pH than the pKa value (i.e. 6.4) of HCrO$_4^-$ / CrO$_4^{2-}$. Hence the absorption maximum of UV–vis spectra was shifted from 350 nm (corresponding to HCrO$_4^-$) to 370 nm (corresponding to CrO$_4^{2-}$). It is also important to mention that molar absorbance of CrO$_4^{2-}$ (generated in basic medium) species is higher than the corresponding protonated species i.e. HCrO$_4^-$ or H$_2$CrO$_4$ [78]. Increase in pH of the solution to 10, led to the further decrease in the reduction of Cr (VI) to 69% in 60 min. The above explained variations in rate of reduction of Cr (VI) with pH could be understood on the basis of point of zero charge (PZC) of the catalyst/adsorbent. If the reaction pH is less than PZC of the catalyst, catalyst surface acquires more positive charge and anionic reactant species can easily adsorb on the positively charged catalyst surface through electrostatic interactions. If pH > PZC then the catalyst acquires a negative charge. Hence the adsorption might not be favourable with anionic reactant species. Hence at pH 10, which could be higher pH than the PZC of red phosphorus, is not a favourable pH for the adsorption of negatively charged CrO$_4^{2-}$ on negatively charged red phosphorus surface.

More anomalous result was observed for the reaction carried at pH 7. The percentage of reduction of Cr (VI) at pH 7 was high (95%) than the percentage of reduction at pH 4 (85%). To understand this unusual behaviour at pH 7, we carefully examined the UV–vis spectra of the sample aliquots. The absorption maximum of initial Cr (VI) solution at pH 7 was observed at 370 nm. pH 7 is higher than the pKa value of HCrO$_4^-$ / CrO$_4^{2-}$ i.e. 6.4. Hence, Cr (VI) exists predominantly as CrO$_4^{2-}$ with an absorbance maximum at 370 nm as mentioned earlier. However, after 30 min stirring in dark and in subsequent experiments, the absorption maximum was shifted to 350 nm. Moreover, the absorption maximum of CrO$_4^{2-}$ at 370 nm shows high molar absorbance than the
HCrO$_4^-$ at 350 nm. Hence this could lead to a large variation in the absorbance of the initial sample aliquot and subsequent sample aliquots and resulted the anomaly in the percentage of reduction at pH 7. At pH 10, for all the aliquots including the initial sample, the absorption maximum was observed at 370 nm only. Hence this was not led to any irregular behaviour in the percentage of reduction at pH 10. The vaules of rate constants, % of reduction of Cr(VI) reduction at different pHs are given in the table 2.

Table 2. Rate constant and percentage of reduction of Cr (VI) at different pH values.

| pH  | $k$ (rate constant) | $R^2$ | % of reduction (60 min) |
|-----|---------------------|-------|------------------------|
| 2   | 0.04724             | 0.999 | 98.54                  |
| 4   | 0.02268             | 0.997 | 85.39                  |
| 7   | 0.02964             | 0.991 | 95.29                  |
| 10  | 0.01368             | 0.995 | 69.37                  |

Figure 9 shows the recyclability of the catalyst for photocatalytic reduction of Cr(VI) (25 mg l$^{-1}$, pH 2) upto three cycles. After the first cycle the catalyst activity was reduced to ~70%, however the stable performance was observed in 2nd and 3rd cycles. PXRD of the used catalyst matches with the fresh photocatalyst indicating that photocatalyst did not undergo any significant changes after recycling (supporting information, S6). The initial decrease in the activity of the photocatalyst could be due to the adsorption of Cr(III) ions (which could form as a result of photocatalytic reduction of Cr(VI)) on the active sites of the catalyst. This could block the active sites of the catalyst from the access of reactant Cr(VI) ions to the active sites of the catalyst [79, 80].

Conclusions

This work summarizes the photocatalytic activity of commercial red phosphorus towards the disinfection of E. coli and photocatalytic reduction of Cr(VI) under direct sunlight. The optimum bandgap of the material shows that the red phosphorus is a promising material for the visible light photocatalytic applications. Hence the photocatalytic reactions were carried out under direct sunlight to make the process economically feasible. As the photocatalyst possesses optimum VB and CB edges for the successful generation of ROS, these photogenerated ROS could bring the disinfection of E. coli in 50 min. Red phosphorus was also proved as a good photocatalyst for the reduction of Cr(VI). At 25 ppm Cr(VI) concentration, ~90% of Cr(VI) reduction was achieved in 60 min and the percentage of reduction was increased to 98 when the pH of the reaction was maintained at 2. This study helps to design the novel non-metallic photocatalysts and operational conditions to achieve high photocatalytic efficiencies towards environmental remediation.
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Declaration of interest

None

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