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**Electrochemical detection and photochemical detoxification of hexavalent chromium (Cr(VI)) by Ag doped TiO<sub>2</sub> nanoparticles**

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**Abstract**

We are proposing a simple, green and one pot ionothermal protocol for synthesis of Ag doped TiO<sub>2</sub> nanoparticles. The prepared material was characterized by various spectroscopic techniques like P-XRD, XPS and then electrocatalytic reduction and photocatalytic detoxification ability of the materials have been explored. The amperometric studies showed the liner range, limit of detection and limit of quantification from 0.1 to 3.1 μM, 0.01 μM and 0.033 μM respectively. The material also showed better photochemical reduction of Cr(VI) in the sun light compared to UV light. About 90% reduction of Cr(VI) to Cr(III) was observed in the 120 min in sunlight whereas 88 % reduction was obtained in the UV light in the same time. The Ag doped TiO<sub>2</sub> nano particle modified glassy carbon has been used for electrochemical monitoring of Cr(VI) in natural water samples.

**Keywords:** Ionic liquid, Electrocatalytic reduction, photochemical detoxification, Amperometry

## Introduction

TiO<sub>2</sub> is widely used photocatalyst as well as electro catalyst due to its wide band gap, chemical stability, high catalytic activity as well as low price<sup>1-3</sup>. The electrocatalytic and photocatalytic activity of TiO<sub>2</sub> nanoparticles can be enhanced by doping as well as by tailoring the structure<sup>4-5</sup>, size and shape of TiO<sub>2</sub> nanoparticles. Among all the dopants, Ag is one of the most promising dopant, which alters the surface modification and fabrication and creates more active sites on the surface of TiO<sub>2</sub> which in turn, decreases the recombination probability making more carriers available for the oxidation or reduction of surface<sup>6</sup>. For tailoring the structure, size and shape, ionothermal method is advantageous because the interaction of ILs with nanoparticle precursors involves the nucleation and growth of nanoparticles<sup>7</sup>. In the present study, we have successfully used methoxy ethyl methyl imidazolium methane sulfonate (MOEMIMS) as the reaction medium for the synthesis of Ag doped TiO<sub>2</sub> nanoparticles. As prepared Ag doped TiO<sub>2</sub> nanoparticles materials were employed for both photocatalytic reduction and electrocatalytic determination of Cr(VI). As Cr(VI) proved to be toxic, carcinogenic and mutagenic, WHO sets the 0.96 μM as threshold limit in drinking water<sup>8</sup> so; it is very important to monitor its flux followed by detoxification in various environmental matrixes. So many photochemical and electrochemical methods using TiO<sub>2</sub> particles are reported for detoxification and determination of Cr(VI)<sup>9-10</sup>. But there is no report utilizing the single material for photochemical as well as electrochemical reduction of Cr(VI) to Cr(III).

In this manuscript, we are reporting the ionothermal synthesis of Ag doped TiO<sub>2</sub> nanoparticles and explored the possibility of utilizing the synthesized materials both as photochemical detoxification of Cr(VI) to Cr(III) as well as for the electro catalytic reduction of Cr(VI) to

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3 Cr(III). The catalytic electrochemical reduction is utilized in amperometric detection of Cr(VI) in  
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5 various environmental effluents.  
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## 8 **Experimental**

### 9 **Materials and Methods**

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11 Titanium tetra chloride, silver nitrate and potassium dichromate were purchased from Sigma  
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13 Aldrich chemicals, India. All the chemicals used were of analytical grade. Doubled distilled  
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15 water used throughout the experiment.  
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#### 19 **Preparation of Ag doped TiO<sub>2</sub> nanoparticles**

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21 Ag doped TiO<sub>2</sub> nanoparticles have been synthesized according to our earlier report <sup>11</sup>. Briefly 0.5  
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23 mL TiCl<sub>4</sub> was added to the Teflon tube containing 12.0 mg silver nitrate and 10 mL methoxy  
24  
25 ethyl methyl imidazolium methane sulfonate ionic liquid under constant stirring for  
26  
27 homogenization. After 5 min, 1 mL of water was added. The homogeneous solution was  
28  
29 subjected to ionothermal treatment at 120 °C for 24 h. When the reaction was complete,  
30  
31 autoclave was cooled to room temperature. The obtained product was mixed with acetonitrile  
32  
33 and stirred overnight to remove the ionic liquid and finally Ag doped TiO<sub>2</sub> nanoparticles were  
34  
35 separated by centrifugation. The final product was calcined at 400 °C for 3 h.  
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#### 40 **Preparation of Ag doped TiO<sub>2</sub> modified glassy carbon electrode**

41  
42 Prior to modification, glassy carbon electrode (3 mm diameter) was polished on micro cloth with  
43  
44 1.0, 0.3 and 0.05 micron size alumina. Then the electrode was sonicated in water for about 10  
45  
46 min followed by ethanol. Finally, the electrode was allowed to dry in the room temperature.  
47  
48 About 10 mg of Ag doped TiO<sub>2</sub> nanoparticle composite was dispersed well in the solution (2 mL  
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50 distilled water + 10 μL 0.2 % nafion) by sonicating for 30 min. Then 20 μL of above suspension  
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3 was cast on to the pre-treated glassy carbon electrode and allowed to dry for 2 h in room  
4  
5 temperature.  
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### 7 8 **Techniques**

9  
10 Electrochemical measurements were performed at a standard three-electrode electrochemical cell  
11 with a CHI 800 electrochemical workstation (CH Instrument, USA) with a TiO<sub>2</sub>: Ag  
12 nanoparticles modified glassy carbon electrode as the working electrode, a platinum wire as the  
13 counter electrode and a saturated calomel electrode (SCE) as the reference electrode,  
14 respectively. All pH measurements were done using digital pH meter MK VI of Systronics make.  
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### 22 **Electrochemical monitoring of Cr(VI) in aqueous samples**

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24 Amperometric measurements were performed in stirred solution with an applied potential of 0.29  
25 V. The electrolyte was deaerated with nitrogen gas for 30 min. before each measurement.  
26  
27 Aliquot of tap water was directly injected into the electrolyte (0.1M HCl) for amperometric  
28 analysis of Cr(VI) where as the lake water samples were filtered using Whatman filter paper  
29 before analysis.  
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### 36 **Photocatalytic degradation of Cr(VI) to Cr(III)**

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38 Photocatalytic experiments were carried out in a 150 × 75 mm batch reactor in the month of  
39 April- May 2014 Bangalore for 4 h (Lat, Long from 11:30 to 15:00 h) with a intensity of sun  
40 light ~950 Wm<sup>-2</sup> and UV-light with 125 Wm<sup>-2</sup> intensity. An aqueous suspension was prepared by  
41 adding 0.1 g Ag doped TiO<sub>2</sub>: nanoparticles to 100 mL (1 mM) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution with pH ~ 4, the  
42 initial pH was adjusted by the addition of 0.05 M H<sub>2</sub>SO<sub>4</sub>. During the photocatalytic experiments,  
43 the slurry composed of solution and catalyst was placed on the reactor and stirred magnetically  
44 for agitation with simultaneous exposure to both Sun and UV- light for 120 min. A known  
45 volume (3 mL) of the exposed solution was withdrawn at specific intervals of time (30 min). Ag  
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3 doped TiO<sub>2</sub> nanoparticles were removed from the solution by centrifugation to assess the extent  
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5 of degradation. The concentration of the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution was measured using UV-Visible  
6  
7 spectrophotometer.  
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## 10 **Results and discussion**

### 11 **Characterization of Ag doped TiO<sub>2</sub> nanoparticles**

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13 The synthesized Ag doped TiO<sub>2</sub> nanoparticles has been characterized by XRD, XPS, FT-IR, UV-  
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15 Visible, TGA, SEM, TEM and EDX and it has been discussed in our earlier report <sup>11</sup>. The SEM  
16  
17 images of Ag doped TiO<sub>2</sub> nanoparticles are as given in the Fig. 1. Fig. **1a** show SEM image of  
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19 Ag doped TiO<sub>2</sub> nanoparticles prepared via ionic liquid assisted hydrothermal method at very  
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21 high magnification and we can clearly observe the presence of nanoparticles. In Fig. **1b** Ag  
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23 doped TiO<sub>2</sub> nanoparticles are closely resembles fern-like phyllotaxy. i.e. shows hyper branched  
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25 structure, grows with pronounced trunks with 100 μm and 30 μm dimensions respectively. Ag  
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27 doped TiO<sub>2</sub> nanoparticles, which have corrugations and ordered branches that are symmetrically  
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29 distributed on opposite sides of the trunks. Fig. **1c** shows the EDS spectrum of Ag doped TiO<sub>2</sub>  
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31 nanoparticles, EDS mainly used to identify the elements present in the prepared materials and it  
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33 clearly shows the presence of Ti, O, and Ag <sup>11</sup>. The TEM images of the Ag doped TiO<sub>2</sub>  
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35 nanoparticles particles are as given in the Fig. 2. **Fig. 2a to 2d** shows the TEM images of Ag  
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37 doped TiO<sub>2</sub> nanoparticles prepared at 120 °C for 1 day, and are looking like almost rice shape  
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39 and the size of the nanoparticle is found to be ~ 60 nm. Due to the large atomic radius of the  
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41 silver atom, they cannot interpenetrate in TiO<sub>2</sub> crystals to form solid solution alloy. Therefore,  
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43 silver metal distributes in the form of separated nanoparticles. In general, the TiO<sub>2</sub> particles  
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45 appear transparent. Dark region indicated by arrow clearly indicates the presence of almost  
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47 spherical shaped Ag particles <sup>11</sup>. The same material is used for electrochemical monitoring of  
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49 Cr(VI) in aqueous samples and Photocatalytic degradation of Cr(VI) to Cr(III).  
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## Electrochemical reduction studies of Cr (VI)

The electrocatalytic properties of the Ag doped TiO<sub>2</sub> nanoparticles towards Cr(VI) reduction was evaluated by the CV studies. Various parameters that affect the electrochemical reduction of the Cr(VI) were evaluated.

### Optimization of the electrolytic medium and its concentration

It was proved that acidic environment plays a crucial role in electrocatalytic reduction of Cr(VI)<sup>12-13</sup>. Various acidic electrolytes were tested for electrocatalytic reduction of Cr(VI) by CV studies. From Fig. 3(a) it was evident that HCl was suitable electrolyte for the electrochemical reduction of Cr(VI) because the well-defined irreversible reduction peak for 0.1 mM Cr(VI) was obtained compared to HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. As chloride, ions are normally present in natural samples it is advisable to use the same medium for electro reduction process. To get further mechanistic insights, the effect of pH was studied in different concentrations of HCl. From Fig. 3(b), it is clear that the reduction current increases initially with the concentration of the acid (up to 0.1 M) but later the trend reversed. The decrease in the reduction current at higher concentrations (beyond 0.1 M) of the HCl medium may be due to the increase in Cl<sup>-</sup> ion concentration in the medium. Therefore, 0.1 M HCl was used as electrolyte in all electrochemical studies.

### Cyclic voltammetric studies

Fig. 4 shows the cyclic voltammograms obtained for Cr(VI) in 0.1 M HCl medium on bare GC as well as Ag doped TiO<sub>2</sub> nanoparticles composite modified GC. There is an reduction peak around 0.289 V on Ag doped TiO<sub>2</sub> nanoparticles composite modified GC where as there is no such peak obtained for same concentration of Cr(VI) on bare GC electrode. This confirms that the Ag doped TiO<sub>2</sub> nanoparticles composite materials catalyzed electrochemical reduction



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3 process otherwise the reduction is very insignificant on bare GC and can't be used for detection  
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5 of Cr(VI) in microgram levels. From Fig. 5 it is clear that the reduction current increases linearly  
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7 with the concentration of Cr(VI). The interesting thing in the present studies is that, the reduction  
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9 potential obtained around 0.29 V, which is more positive potential than some of the reported  
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11 gold based electrodes and with increase in scan rate there is a negative shift in reduction  
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13 potentials indicating that the electrochemical process is irreversible <sup>14</sup> Fig. 6(a) . Fig. 6(b) shows  
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15 the relation between reduction peak currents and scan rates. Further, the reduction peak currents  
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17 are linearly related to square root of the scan rates. This confirms that the kinetics of the reaction  
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19 is diffusion controlled.  
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#### 24 **Determination of Cr(VI) by amperometry**

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26 The analytical characteristics of the Ag doped TiO<sub>2</sub> nanomaterials modified GC electrode  
27  
28 towards Cr(VI) monitoring was evaluated by amperometry. Under optimized conditions the  
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30 method has shown liner range from 0.1 to 3.1 μM with the R<sup>2</sup>= 0.99479 (Fig. 7(a)). The response  
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32 time was very quick and the limit of the detection was found to be 0.01 μM. The obtained  
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34 detection limit was lesser than that of the WHO value, from this it clear that our protocol can be  
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36 readily utilized for monitoring the Cr(VI) in drinking water. Then the possible interference from  
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38 the other reducible species commonly present in natural water sample was studied. From Fig.  
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40 7(b), it is confirms that there is no change in reduction current even after the addition of 10 μM  
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42 Fe<sup>3+</sup> and 10 μM Cr(III) ions. Then there is no decrease in reduction current of 10 μM Cr(VI) in  
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44 the presence of above said ions in the medium. The threshold limit values of the various cations  
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46 and anions present commonly in water for Cr(VI) determination was given in **Table-1**. To check  
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48 the practical applicability of the method we had carried out the chromium detection in natural  
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50 water samples collected from the lakes and in tap waters. The results are presented in **Table-2**.  
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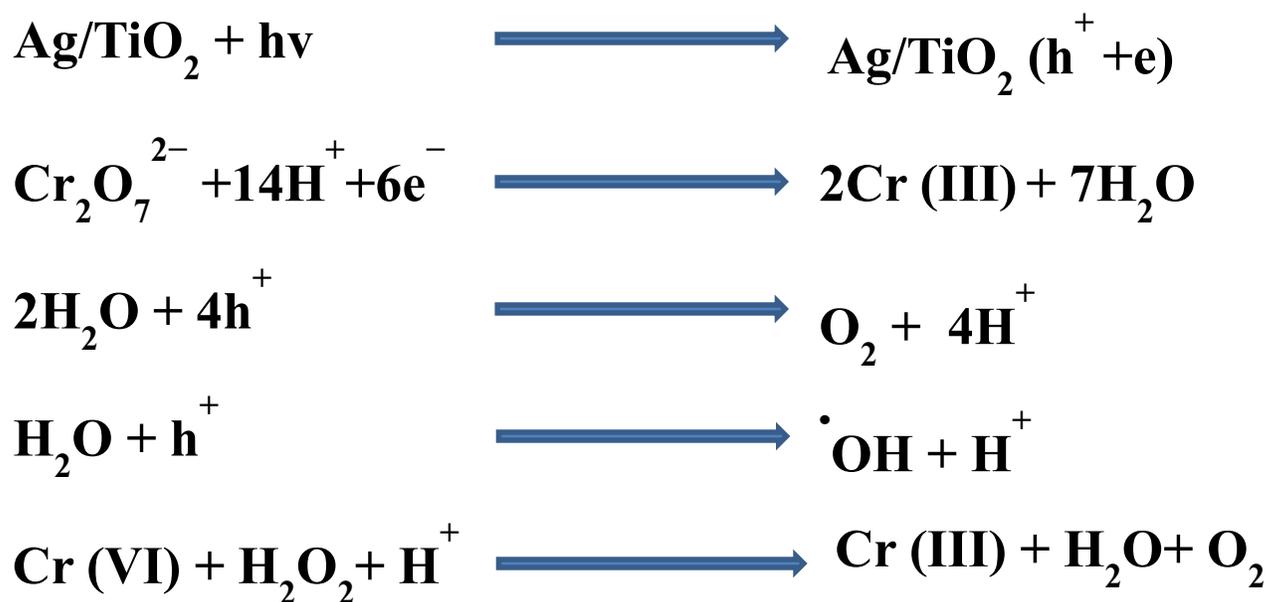
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3 The chromium was not detected in the tap water as well as lake water samples, then we spiked  
4 the samples with Cr(VI) and recovery studies have been carried out and the recovery values are  
5 found to be more than 95 %. The results obtained with our method were validated by analyzing  
6 the samples by ICP-AES technique and the results of proposed method were found to be in good  
7 agreement with ICP-AES analysis results.  
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### 10 11 12 13 14 **Repeatability, reproducibility and stability of the sensor**

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16 For any sensor the above parameters are very important. In order to assess the repeatability of the  
17 sensor five replicate CV measurements were performed with 0.1 mM Cr(VI) with scan rate 0.1  
18 mV s<sup>-1</sup> in 0.1 M HCl. The cathodic peak currents obtained were of same and RSD of these five  
19 measurements were found to be 1.2 %. This study confirms the sensor has considerable  
20 repeatability for Cr(VI) reduction. Then for reproducibility 5 electrodes (Ag doped TiO<sub>2</sub>  
21 nanoparticle modified GC) were prepared in the similar manner and Cr(VI) reduction was  
22 studied by CV with 0.1 mM Cr(VI) with scan rate 0.1 mV s<sup>-1</sup> in 0.1 M HCl. The differences in  
23 cathodic peak currents obtained were of negligible and the RSD of these measurements were of  
24 3.9 %. Finally, the stability of the sensor was studied by conducting the CV measurements with  
25 0.1 mM Cr(VI) with scan rate 0.1 mV s<sup>-1</sup> in 0.1 M HCl with Ag doped TiO<sub>2</sub> nanoparticle  
26 modified GC electrodes stored in the ambient temperatures for about 4 months. The electrode  
27 exhibits same performance i.e. almost same cathodic peak currents even after 4 months with  
28 retention of 93 % to that of peak current obtained in the initial days (Fig.8). All these studies  
29 clearly indicate that the present sensor is highly reproducible, repeatable and exhibits stability for  
30 longer time.  
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### Photochemical detoxification of Cr(VI)

Photochemical detoxification of Cr(VI) to Cr(III) in presence of sun light and UV light as shown in Fig. 9(a) and Fig. 9(b) respectively. Our catalyst is found to be more active in sun light compared to UV light. The photocatalytic reduction of  $K_2Cr_2O_7$  ( $1 \times 10^{-3}$  M) having pH 4, was done by adding 0.1 g Ag doped  $TiO_2$  nanoparticles in photocatalytic reactor in Sun light it is cleared within 120 min about 90% reduction was achieved. Where as in UV light about 88% reduction was achieved. This clearly indicates that our material showed good photocatalytic reduction from Cr(VI) to Cr(III) in Sun light than the UV-light. This may be due to the decrease in the band gap of  $TiO_2$  particles achieved by doping of Ag. Mechanistic pathway of photocatalytic reduction from Cr(VI) to Cr(III) as shown in the Scheme.1



**Scheme-1** Mechanistic pathway of photocatalytic reduction from Cr(VI) to Cr(III)

### Conclusions

In this work, we have demonstrated a simpler and greener protocol for ionic liquid- assisted hydrothermal synthesis of Ag doped  $TiO_2$  nanoparticles for photochemical detoxification as well

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3 as electrocatalytic reduction of Cr(VI) to Cr(III). The prepared materials showed better  
4 photocatalytic activity in the sun light compared to UV light, which is advantageous in photo  
5 catalytic studies. The above material also showed better electrochemical reduction properties in  
6 the shifting the reduction current of Cr (VI) to positive side when compared to some of the  
7 reported ones (Table 3). More importantly, the detection limits obtained were less than that of  
8 the WHO guidelines. Hence, our material can be scaled -up for the development of online  
9 monitoring electrochemical systems for Cr(VI) for drinking water analysis and photocatalytic  
10 reacting systems for detoxification of the drinking water.  
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## 24 **Acknowledgement**

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## Figure and table Captions

**Fig. 1** SEM images of Ag doped TiO<sub>2</sub> nanoparticles

**Fig. 2** TEM images of Ag doped TiO<sub>2</sub> nanoparticles

**Fig.3** CV graphs obtained (a) On Ag doped TiO<sub>2</sub> nanoparticle modified GC, in different 0.1 M acidic mediums as electrolytes (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 mM Cr(VI)). (b) In different concentrations of HCl (0.05 to 0.2 M) as electrolytic medium (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 mM Cr (VI)).

**Fig.4** CV graphs obtained (a) On different electrodes (A) bare GC electrode in the absence of 0.1 mM Cr(VI) (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 M HCl electrolyte) (B) bare GC electrode in the presence of 0.1 mM Cr(VI) (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 M HCl electrolyte) and presence of 0.1 mM Cr(VI) (C) Ag doped TiO<sub>2</sub> nanoparticle modified GC in the absence of 0.1 mM Cr(VI) (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 M HCl electrolyte) (D) Ag doped TiO<sub>2</sub> nanoparticle modified GC in the presence of 0.1 mM Cr(VI) (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 M HCl electrolyte).

**Fig.5** CV graphs with different concentration of Cr(VI) (0- 8 μM) (Scan rate 0.1 mV s<sup>-1</sup> and 0.1 M HCl electrolyte).

**Fig.6** CV graphs obtained (a) With different scan rates, from 0.1 to 1.0 mVs<sup>-1</sup> (Scan rate 0.1 mV s<sup>-1</sup>, 0- 8 μM Cr(VI) and 0.1 M HCl electrolyte). (b) The liner relation of currents vs square of scan rate (0- 8 μM Cr(VI) and 0.1 M HCl electrolyte).

**Fig.7** Amperometric graphs obtained on the Ag doped TiO<sub>2</sub> nano materials modified GC electrode (a) Potential 0.29 V, electrolytic medium 0.1 M HCl and Cr (VI) (0 to 3.1 μM), (b) Interference studies carried out with a potential 0.29 V, electrolytic medium.

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3 **Fig.8** Photochemical; detoxification of Cr(VI) to Cr(III) in presence of (a) Sun light and (b) UV  
4 light.  
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7 **Fig.9** Stability and reproducibility of Ag doped TiO<sub>2</sub> nano materials modified GC electrode at  
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9 different time intervals (a) 1<sup>st</sup> month, (b) 2<sup>nd</sup> month (c) 3<sup>rd</sup> month and (d) 4<sup>th</sup> month.CV carried  
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11 out in electrolytic medium 0.1 M HCl and 0.1 mM Cr(VI) with scan rate 0.1 mV s<sup>-1</sup> .  
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14 **Table 1.**Interferent studies  
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16 **Table 2.**Determination of Cr(VI) in natural water samples.  
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19 **Table 3.** Comparison of the analytical parameters of the proposed method with the reported  
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21 protocols.  
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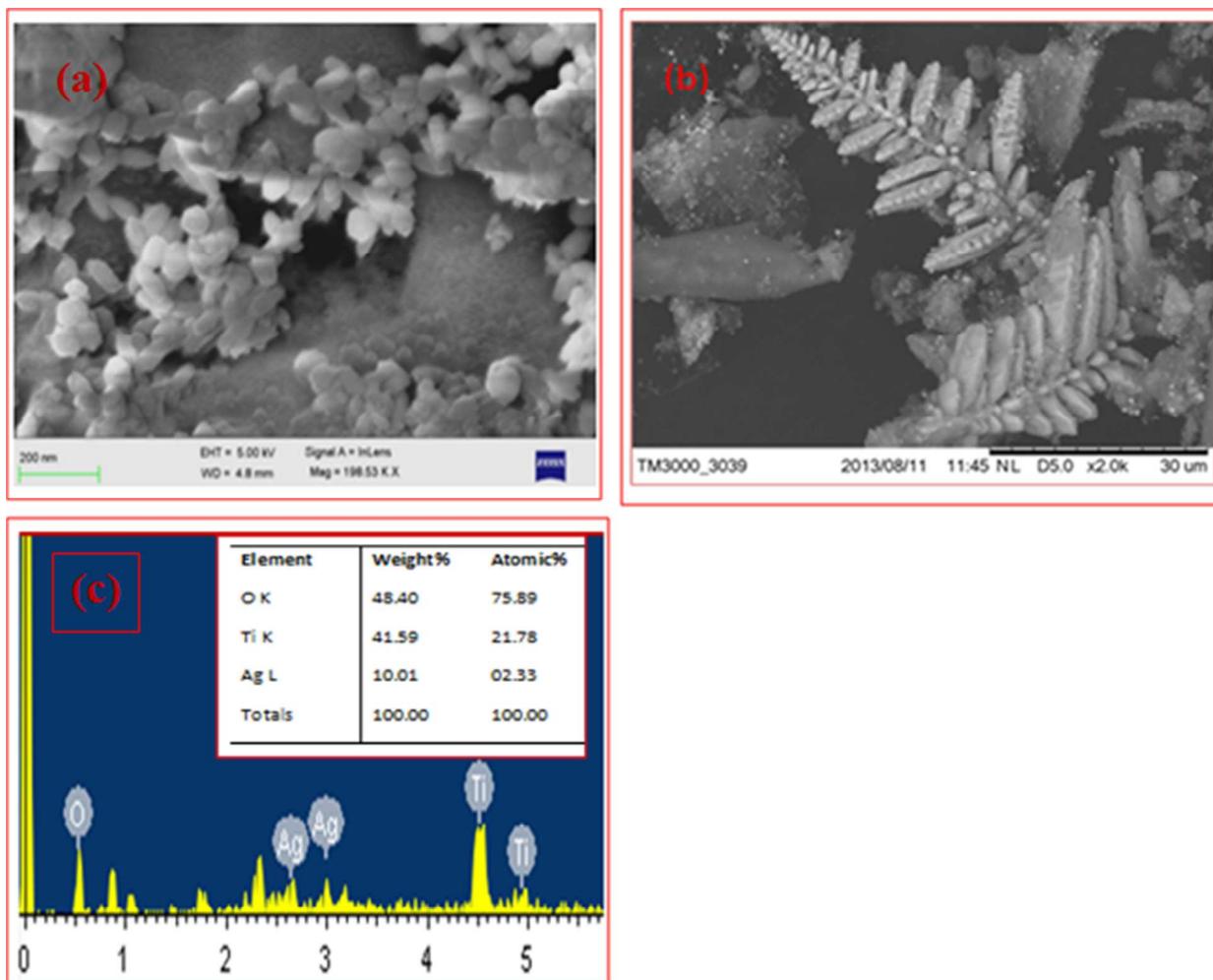


Fig. 1.

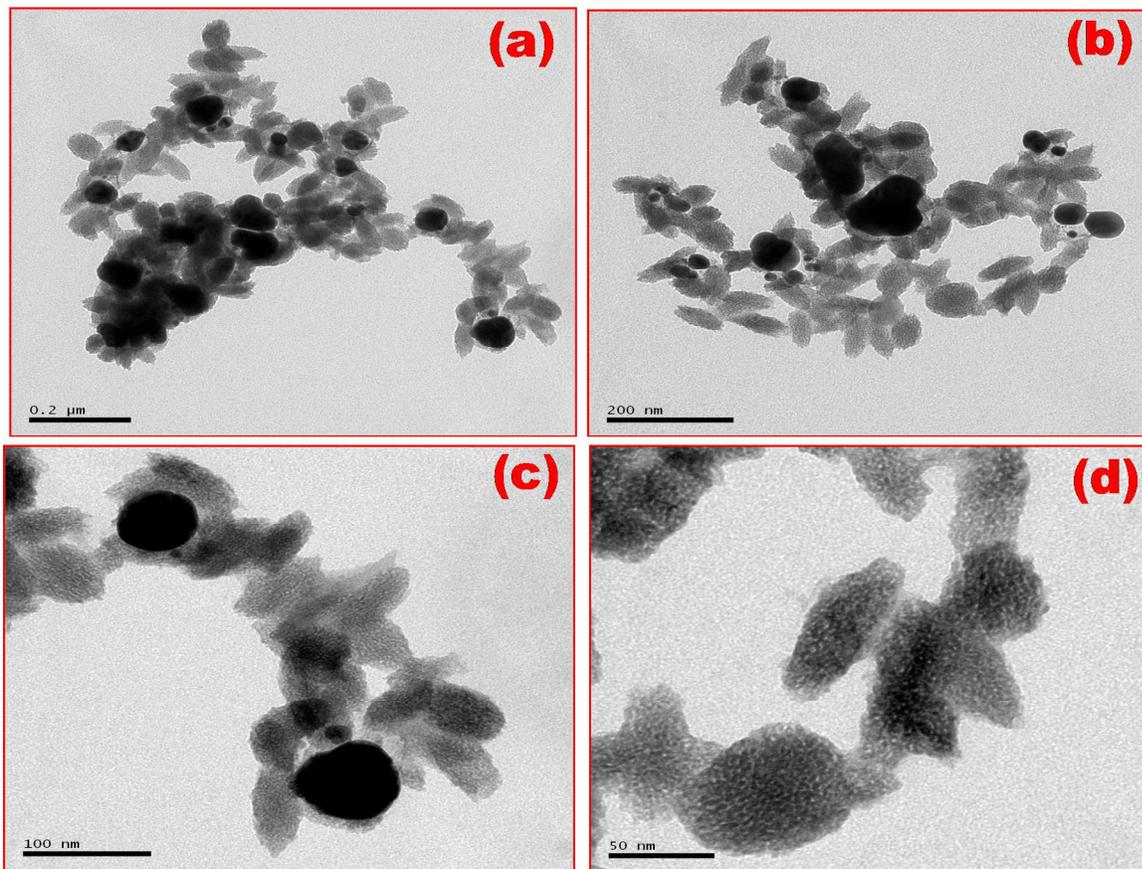


Fig. 2.

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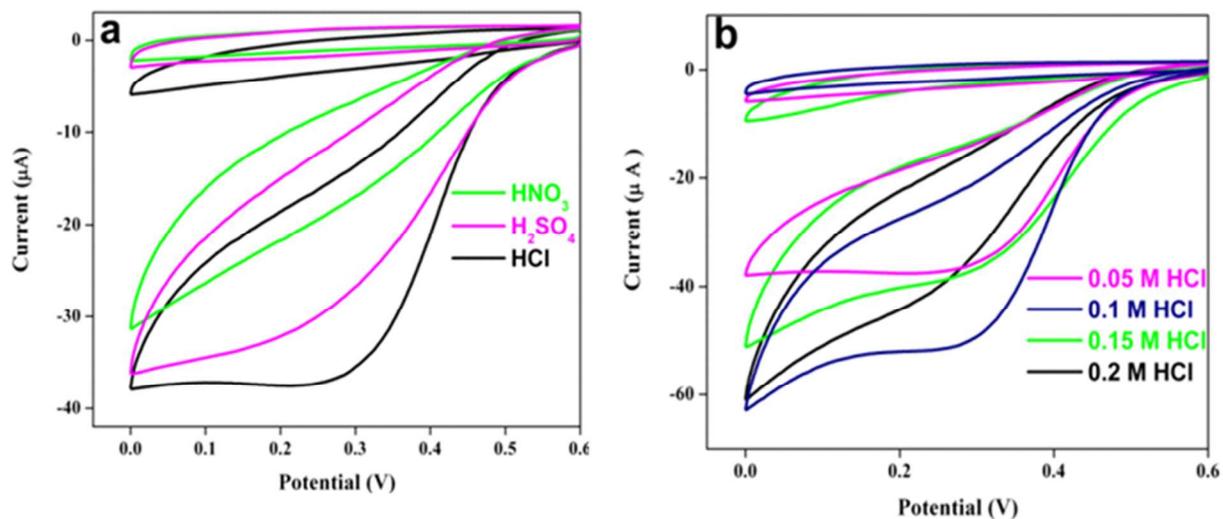


Fig. 3.

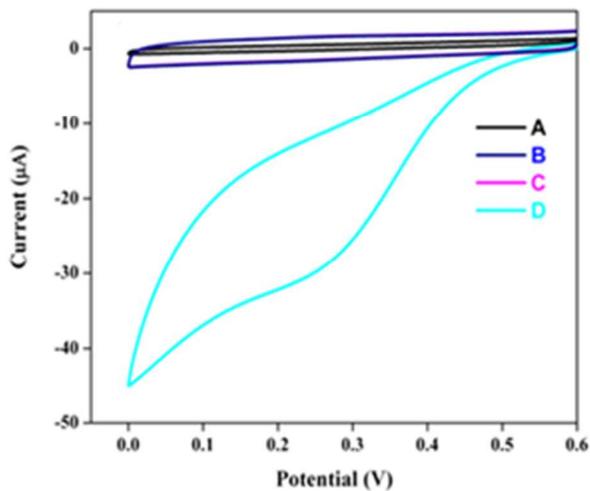


Fig. 4.

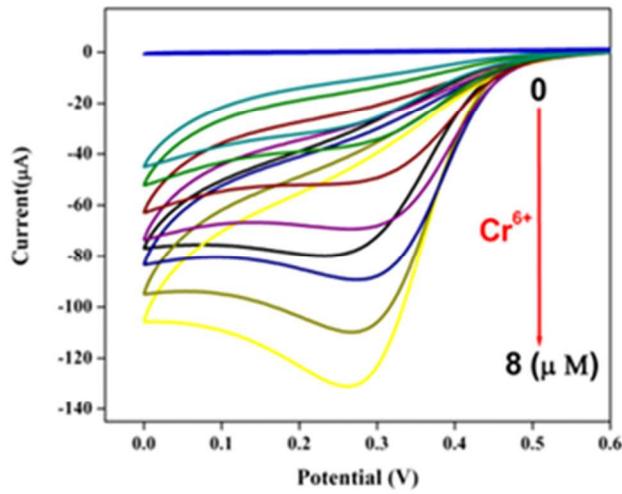


Fig. 5.

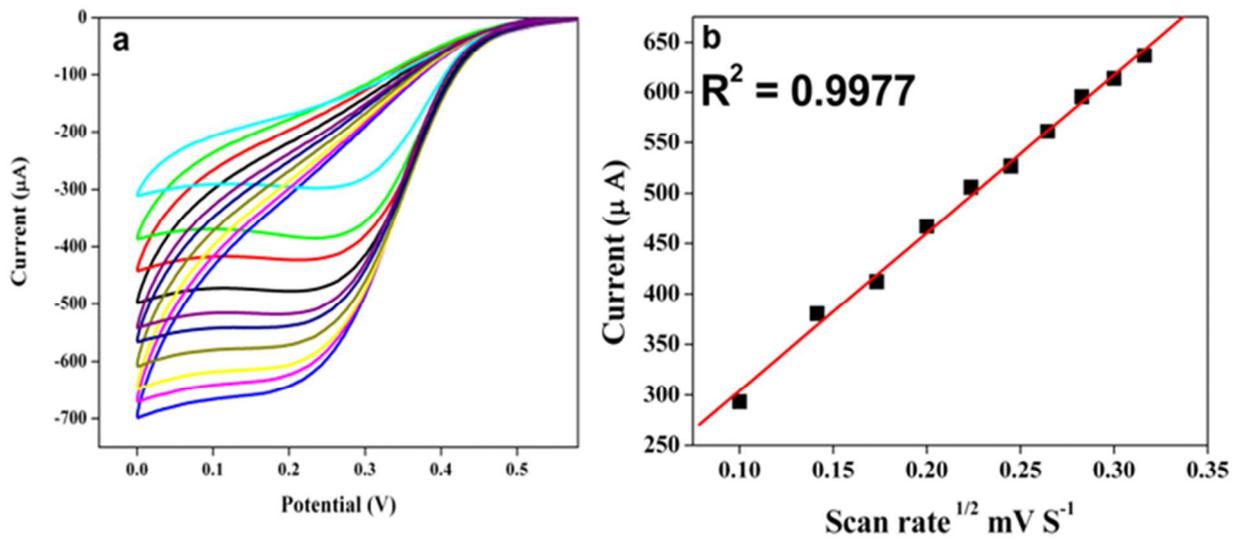


Fig. 6.

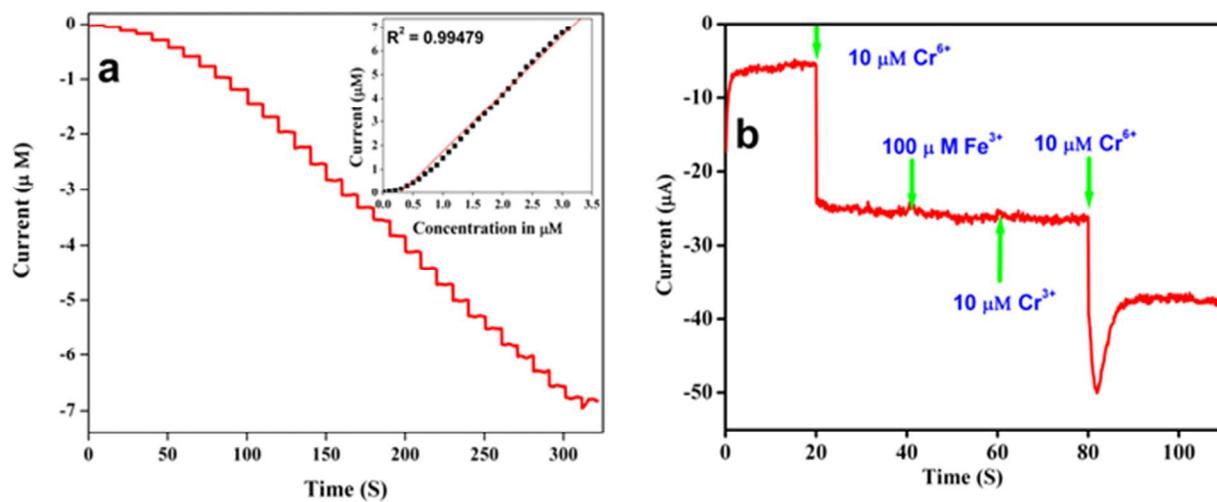


Fig. 7.

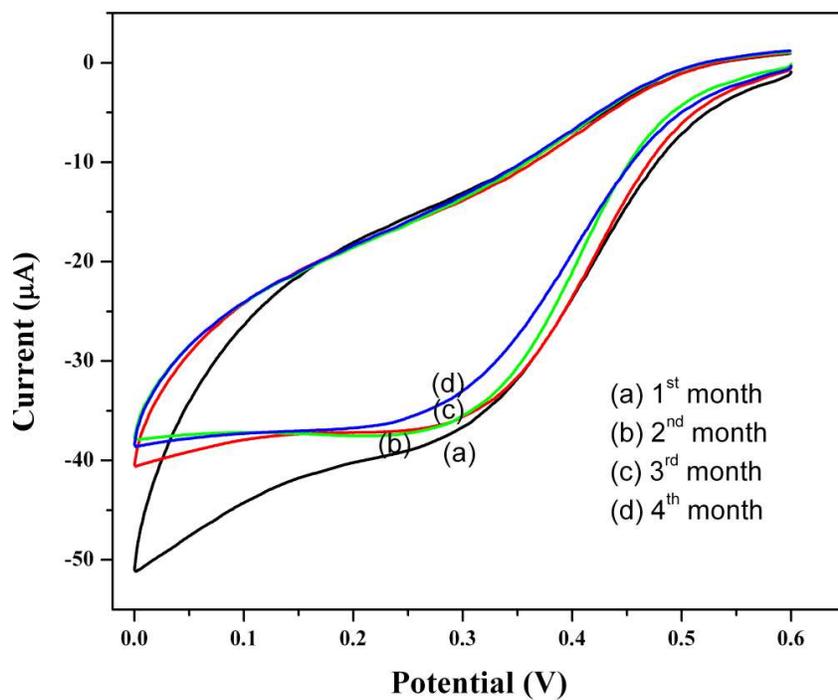


Fig. 8.

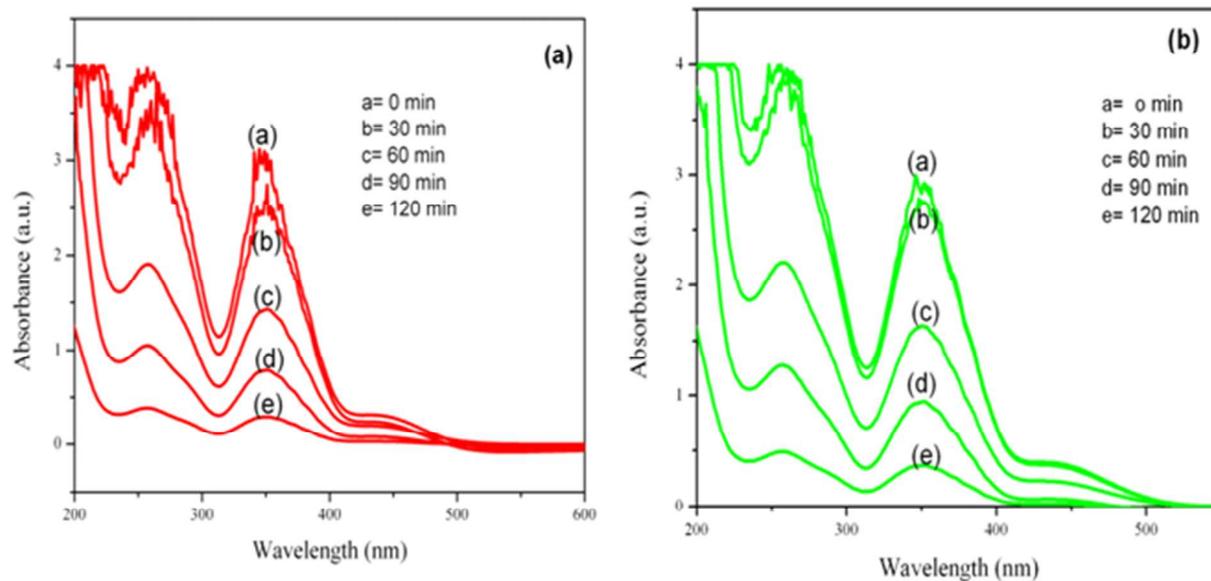


Fig. 9.

Interferent ion	Threshold limit ( $\mu\text{M}$ )
$\text{Fe}^{3+}$	1000
$\text{Cr}^{3+}$	1000
$\text{Mn}^{7+}$	500
$\text{K}^+$	2000
$\text{Na}^+$	2000
$\text{Mg}^{2+}$	2000
$\text{Ca}^{2+}$	2000
$\text{NO}^{3-}$	500

Table 1.

Sample	Found Cr(VI) $\mu\text{M}$		Added Cr(VI) $\mu\text{M}$	Total Cr(VI) $\mu\text{M}$		Recovery %	
	Proposed method	ICP-AES method		Proposed method	ICP-AES method	Proposed method	ICP-AES method
Tap water	Not detected	Not detected	0.5	0.4901 $\pm$ 0.090	0.4999	98.02	99.80
	Not detected	Not detected	1.0	0.9876 $\pm$ 0.008	0.9986	98.76	99.86
	Not detected	Not detected	3.0	3.0010 $\pm$ 0.221	3.1001	100.03	103.33
Lake water	Not detected	Not detected	0.5	0.4983 $\pm$ 0.008	0.49996	99.66	99.992
	Not detected	Not detected	1.0	0.9987 $\pm$ 0.001	1.001	99.87	100.1
	Not detected	Not detected	3.0	2.9985 $\pm$ 0.120	2.9995	99.95	99.98

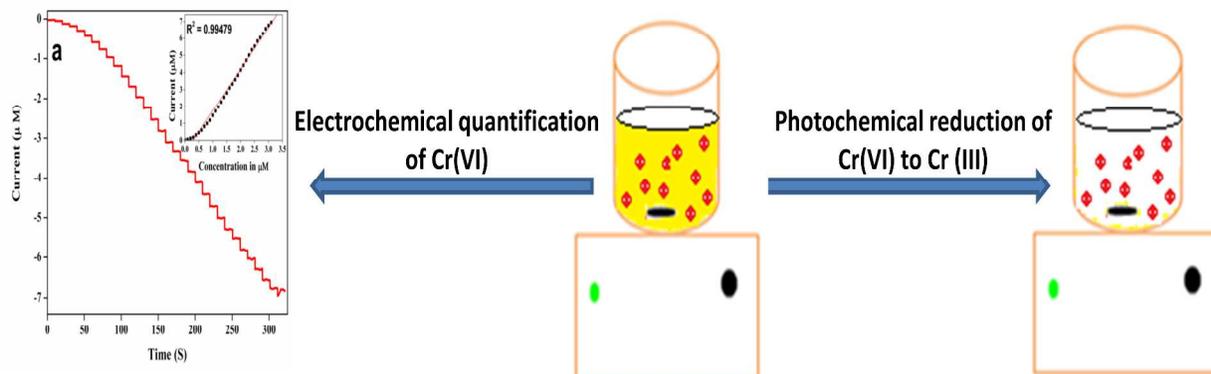
Table 2.

Electrode	Reduction potential (V)	Linear range ( $\mu\text{M}$ )	Limit of detection ( $\mu\text{M}$ )	Reference
Gold electrode	-----	-----	4.3	8
Gold plated carbon based composite	0.5	20-2000	4.4	15
Graphite screen printed electrode	0.025	100-1000	19.0	16
Gold screen printed macro electrodes	-----	10-1600	4.4	17
Au nanoparticle-decorated titania nanotubes on Gold electrode	-----	0.1-105	0.03	14
Ag doped $\text{TiO}_2$ on Glassy carbon	0.289	0.1 - 3.1	0.033	Present work

Table 3.



## Graphical abstract



Schematic representation of electrochemical reduction and photochemical detoxification of Cr(VI)