*Supplementary material*

# In Situ Decoration of $ZnSnO_3$ Nanosheets on the Surface of Hollow $Zn_2SnO_4$ Octahedrons for Enhanced Solar Energy Application

**Zhengdao Li [1,2,*], Kecheng Liu [1], Ruixue Sun [1], Chuanyun Yang [1,2] and Xiaodi Liu [1,*]**

[1] Chemistry and Pharmaceutical Engineering College, Nanyang Normal University, Nanyang 473061, China; iukecheng2006@126.com (K.L.); ruixuesun@126.com (R.S.); ycy_chemistry@163.com (C.Y.)
[2] Engineering Technology-Research Center of Henan Province for Solar Catalysis, Nanyang Normal University, Nanyang 473061, China
* Correspondence: nylzd@nynu.edu.cn (Z.L.); liuxiaodiny@126.com (X.L.); Tel: +86-377-63-513-735 (Z.L.)

**Materials Synthesis**

Preparation of solid $Zn_2SnO_4$ octahedrons (sample 1: $S_1$): 0.26 g of zinc acetate dehydrate ($ZnAc_2{\cdot}2H_2O$), 0.22 g of chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), 0.29 g of sodium hydroxide (NaOH) and 0.25 g of hexadecyl trimethyl ammonium bromide (CTAB) were mixed in 30 mL of deionized water. Then, the mixture was put into an autoclave (50 mL) and heated for 6 hours at 200 °C. The precipitate was collected and washed many times with water and dried at 60 °C.

Preparation of hollow $Zn_2SnO_4$ octahedrons (sample 2: $S_2$): 0.5 g of $Zn_2SnO_4$ solid octahedrons was dispersed in 1 M nitric acid solution (50 mL) under ultrasonic condition for 5 minutes, whereafter, the powder was bathed in acid solution at room temperature for 3 hours. This product was washed after centrifuging and dried at 60 °C in air for 6 hours.

Preparation of $ZnSnO_3$ nanosheets: 0.29 g of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), 0.27 g of sodium sulfite trihydrate ($Na_2SnO_3{\cdot}3H_2O$), 10 mL of ethanol and 20 mL of $H_2O$ were added to an autoclave (50 mL) with agitation at room temperature. A solvothermal process proceeded for 20 hours at 200 °C, and the product was collected after washing and drying at 80 °C.

Hierarchical $ZnSnO_3/Zn_2SnO_4$ hollow octahedrons (sample 3: $S_3$) were prepared in two steps: the first step was the preparation of $ZnSnO_3$ sol, 4.38 g of $ZnAc_2{\cdot}2H_2O$ was dissolved in 100 mL of ethylene glycol monomethyl ether ($HOCH_2CH_2OCH_3$) to form white suspension under vigorous stirring conditions. An amount of 2 mL of monoethanolamine ($HOCH_2CH_2NH_2$) and 7.0 g of $SnCl_4{\cdot}5H_2O$ were added into the mixture, stirring constantly for 1 hour. This transparent and colorless liquid was heated to reflux for 4 hours at 80 °C to obtain transparent, homogeneous and pale-yellow sol. The as-prepared $Zn_2SnO_4$ hollow octahedrons were immersed in the $ZnSnO_3$ sol for 12 hours to gain the $ZnSnO_3$ seed layer on the surface of $S_2$. The second step was the preparation of $ZnSnO_3$ sheets on the surface of $Zn_2SnO_4$ hollow octahedrons. An amount of 0.15 g of $ZnSnO_3$-seeded $S_2$ was dumped into a mixture consisting of 0.29 g of $Zn(NO_3)_2{\cdot}6H_2O$, 0.27 g of $Na_2SnO_3{\cdot}3H_2O$, 10 mL of ethanol and 20 mL of $H_2O$. Next, the obtained slurry was put into an autoclave (50 mL) and the solvothermal reaction continued for 20 hours at 200 °C. The obtained precipitate was centrifuged, washed, and the dried solid powder was calcined for 3 hours at 600 °C in air with a heating rate of 5 °C.

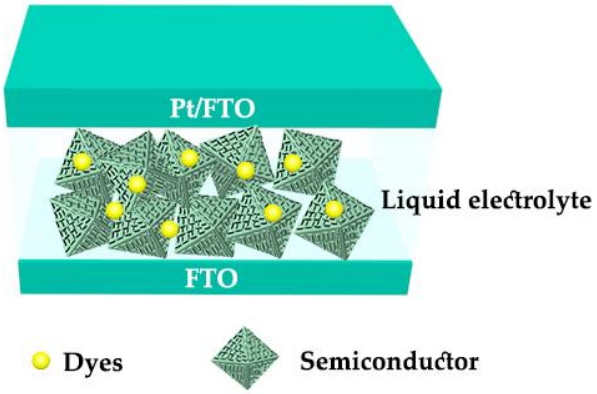


**Figure S1.** Schematic of the dye-sensitized solar cell.

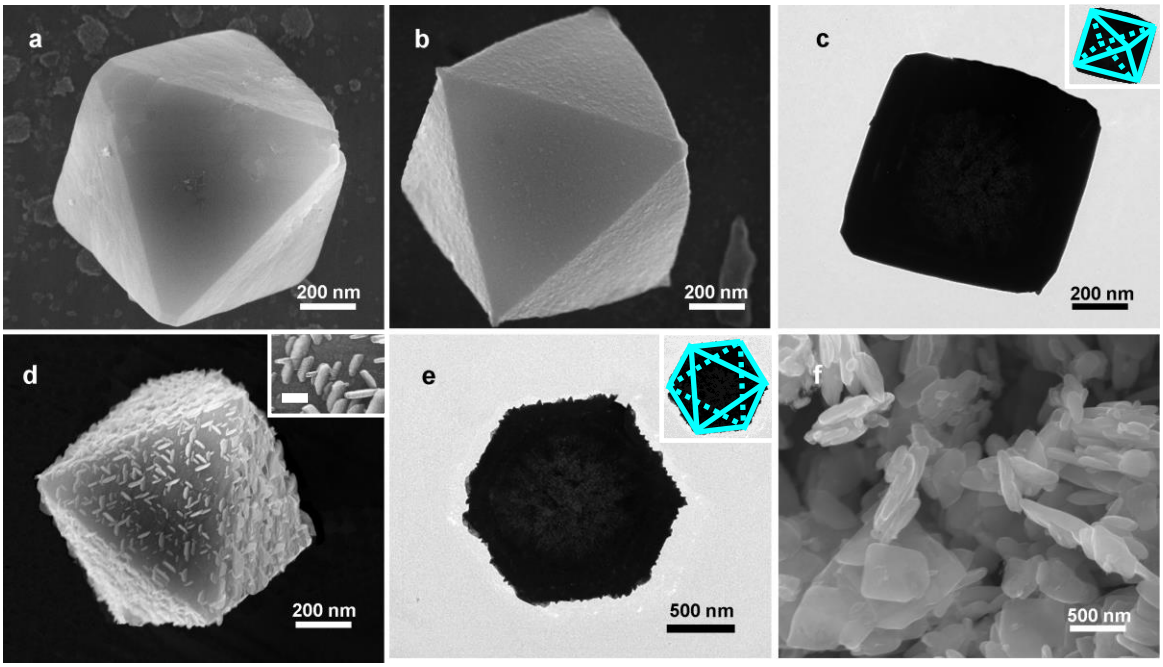


**Figure S2.** SEM images of (**a**) $S_1$, (**b**) $S_2$, (**d**) $S_3$ and (**f**) $ZnSnO_3$ nanosheets; TEM images of (**c**) $S_2$ and (**e**) $S_3$. Inset: the scale bar is 50 nm in (**d**).

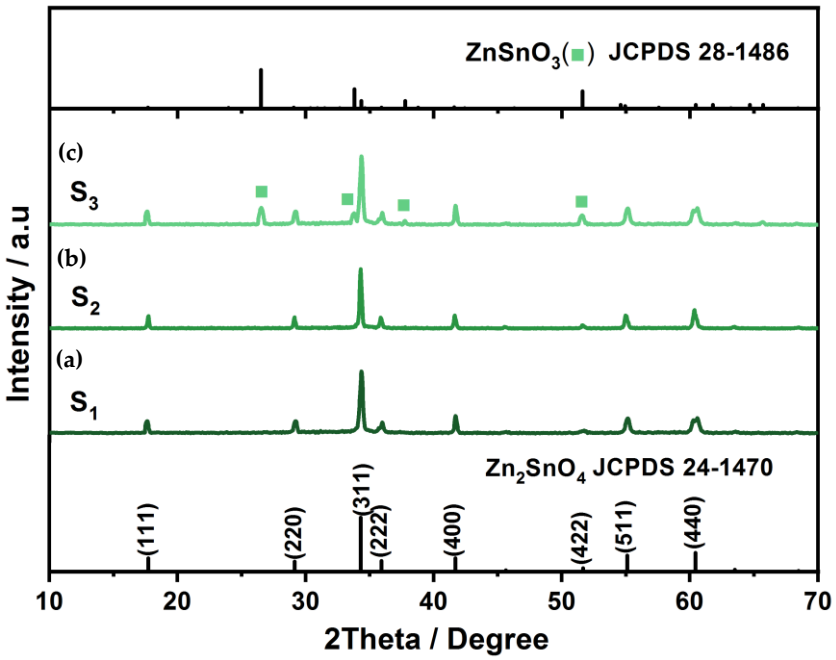


**Figure S3.** XRD patterns of (**a**) $S_1$, (**b**) $S_2$ and (**c**) $S_3$.

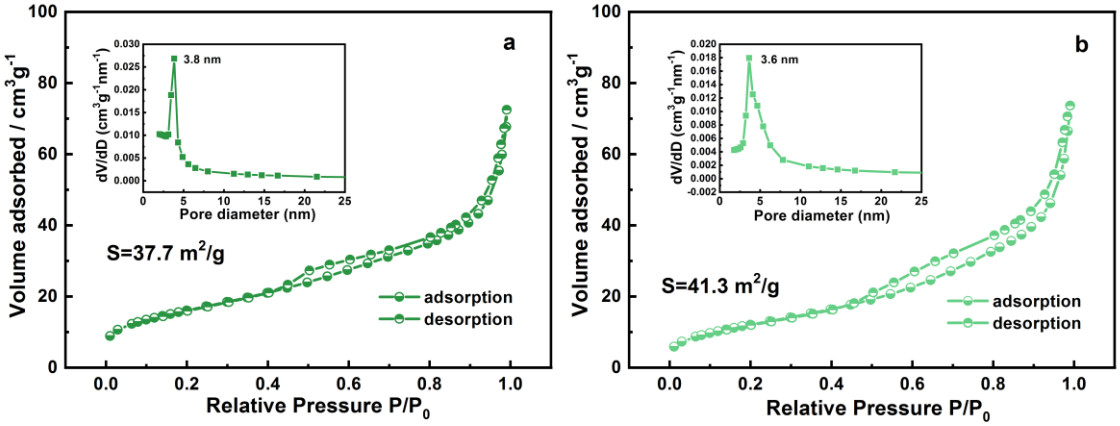


**Figure S4.** $N_2$ adsorption/desorption isotherms: (**a**) $S_2$ and (**b**) $S_3$; the inset is corresponding pore size distribution curves.

The surface area and pore size were measured through the Barett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) measurement methods (Quantachrome NOVA 4200e). The BET surface areas of $S_2$ and $S_3$ were 37.7 and 41.3 $m^2\ g^{-1}$, respectively (Figure S3). The pore size distribution curves in the inset of Figure S3 revealed that S2 and S3 had a narrow pore-size distribution, and the mesoporous existed in two sample judged by the distribution center size of 3.8 nm and 3.6 nm [12].

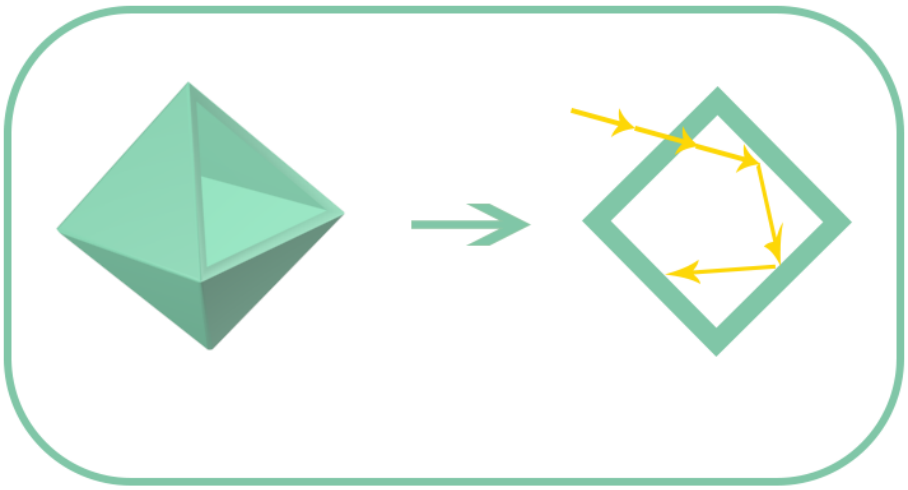

**Figure S5.** Schematic illustration of light reflections and refractions in $S_2$.

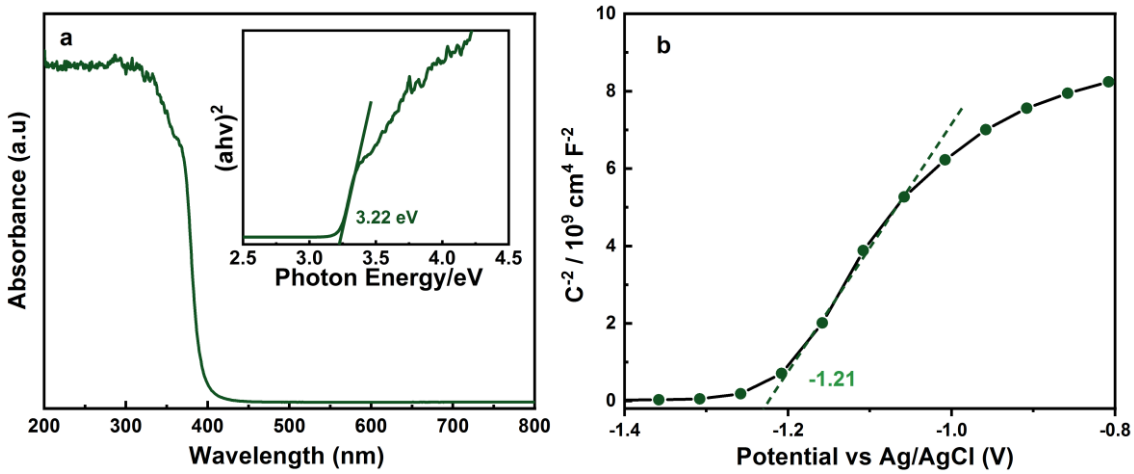


**Figure S6.** $ZnSnO_3$ nanosheets: (**a**) UV-vis absorption spectra; (**b**) Mott-Schottky plots; Inset of (a): the corresponding Tauc's curves.

Based on the results of Figure S5, the $E_g$ of the $ZnSnO_3$ nanosheet was estimated to be around 3.22 eV, and the $E_{fb}$ was calculated to be -1.21 V (vs. Ag/AgCl, pH=7). Then, the conduction band (CB) potentials could be determined to be -0.99V (vs NHE, pH=7). According to the formula ($E_{VB} = E_{CB} + E_g$), the valence band (VB) potential of the $ZnSnO_3$ nanosheet was calculated to be 2.23 V.

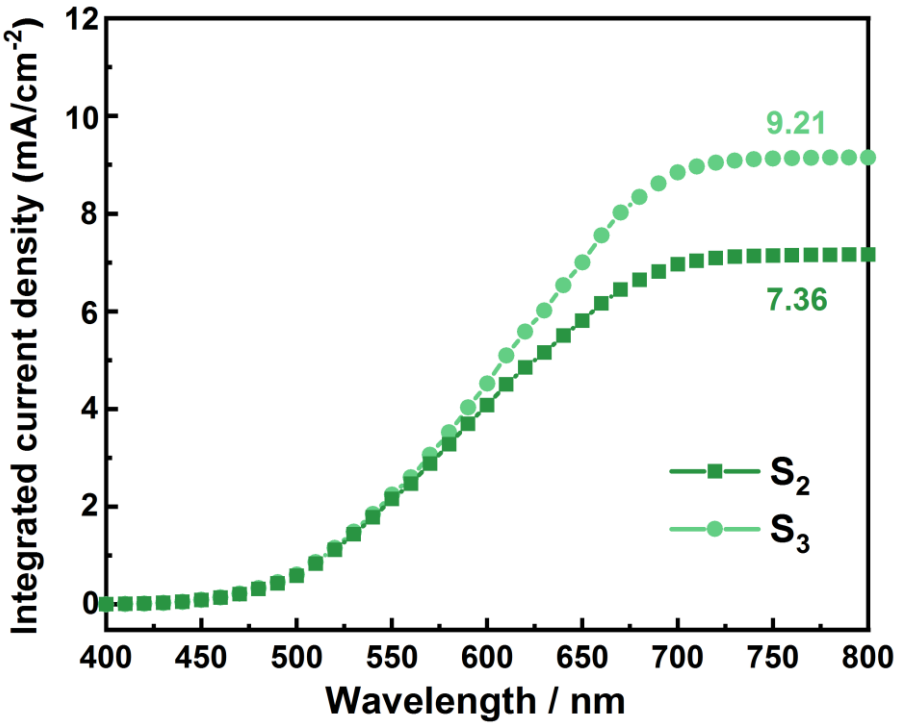


**Figure S7.** The estimated current density by integrating the IPCE spectrum.

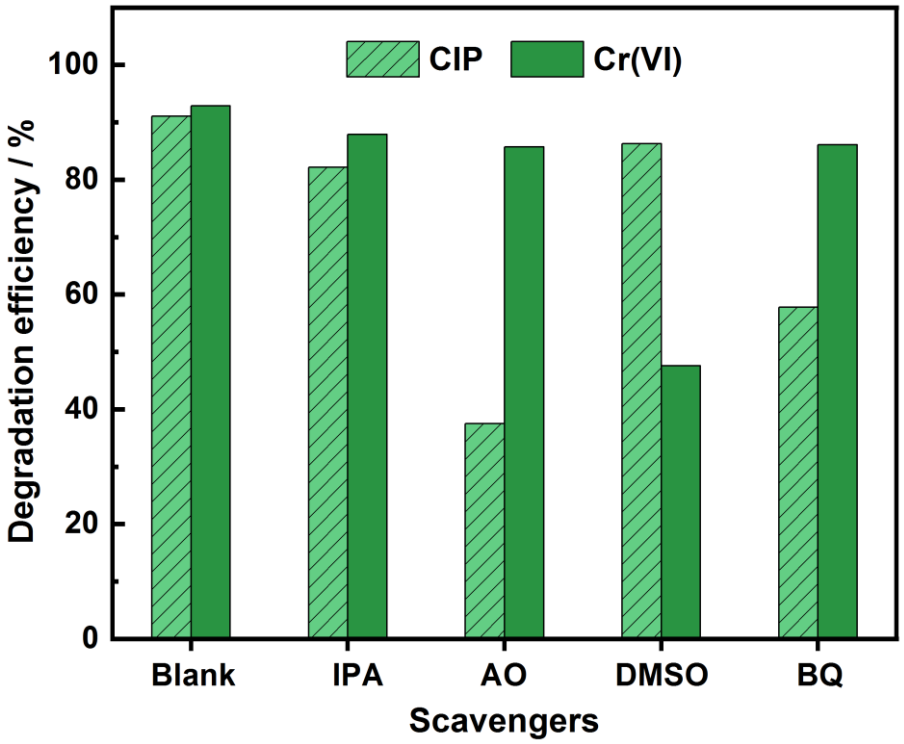


**Figure S8.** Controlling experiments using different radical scavengers for the removal of CIP and Cr(VI).

**Table S1.** The calculated results of the samples about band gap energy ($E_g$), flat band potential ($E_{fb}$), $E_{CB}$ and $E_{VB}$.

| Samples | Eg (eV) | $E_{fb}$ (*vs* Ag/AgCl) | $E_{CB}$ (*vs* NHE) | $E_{VB}$ (*vs* NHE) |
|---|---|---|---|---|
| **$S_1$** | 3.83 | -1.15 | -0.93 | 2.90 |
| **$S_2$** | 3.59 | -1.15 | -0.93 | 2.66 |
| **$S_3$** | 3.43 | -1.29 | -1.07 | 2.36 |
| **$ZnSnO_3$ nanosheet** | 3.22 | -1.21 | -0.99 | 2.23 |

**Table S2.** Detailed photovoltaic parameters of solid $Zn_2SnO_4$-based DSSCs with film thicknesses of 10 μm and various dye-loading times.

| Time | $V_{oc}$ (mV) | $J_{sc}$ (mA $cm^{-2}$) | FF | η (%) |
|---|---|---|---|---|
| **2** hours | 637 ± 9 | 3.77 ± 0.11 | 67.84 ± 1 | 1.63 ± 0.07 |
| **4** hours | 643 ± 7 | 4.82 ± 0.07 | 68.12 ± 1 | 2.11 ± 0.05 |
| **6** hours | 644 ±10 | 5.32 ± 0.11 | 68.71 ± 1 | 2.35 ± 0.11 |
| **8** hours | 643 ± 8 | 4.29 ± 0.14 | 66.33 ± 1 | 1.83 ± 0.10 |

**Table S3.** Detailed photovoltaic parameters of DSSCs based on the $Zn_2SnO_4$ photoanode with different film thicknesses.

| Film thickness | $V_{oc}$ (mV) | $J_{sc}$ (mA $cm^{-2}$) | FF | η (%) |
|---|---|---|---|---|
| **6 μm** | 651 ± 9 | 4.17 ± 0.09 | 70.03 ± 1 | 1.90 ± 0.08 |
| **9 μm** | 646 ±11 | 4.91 ± 0.13 | 68.71 ± 1 | 2.18 ± 0.09 |
| **12 μm** | 643 ± 10 | 5.65 ± 0.16 | 68.79 ± 1 | 2.49 ± 0.12 |
| **15 μm** | 639 ± 12 | 4.36 ± 0.17 | 65.93 ± 1 | 1.83 ± 0.11 |
| **18 μm** | 576 ±10 | 3.25 ± 0.15 | 63.12 ± 1 | 1.18 ± 0.07 |

**Table S4.** Detailed photovoltaic parameters of $ZnSnO_3/Zn_2SnO_4$-based DSSCs with film thicknesses of 12 μm and various dye-loading times.

| Time | $V_{oc}$ (mV) | $J_{sc}$ (mA $cm^{-2}$) | FF | η (%) |
|---|---|---|---|---|
| **3** hours | 660±4 | 7.13±0.09 | 67.13±1 | 3.16±0.07 |
| **4** hours | 663±2 | 9.39±0.20 | 69.58±1 | 4.31±0.15 |
| **5** hours | 661±3 | 8.22±0.13 | 67.18±1 | 3.65±0.09 |
| **6** hours | 657±5 | 7.06±0.15 | 65.23±1 | 3.03±0.08 |

**Table S5.** Comparison of the photovoltaic performance of $ZnSnO_3/Zn_2SnO_4$ hollow octahedrons against previously reported DSSCs.

| Samples | $V_{oc}$ (V) | $J_{sc}$ (mA $cm^{-2}$) | FF | η (%) | Ref. |
|---|---|---|---|---|---|
| $Ba^{2+}$/ $Zn_2SnO_4$ | 0.679 | 9.83 | 0.739 | 4.94 | [41] |
| Ag/$Zn_2SnO_4$ | 0.76 | 3.83 | 0.55 | 1.618 | [42] |
| Au/$Zn_2SnO_4$/$SnO_2$ | 0.60 | 5.88 | 57.7% | 2.04 | [43] |
| MgO/$Zn_2SnO_4$ | 0.66 | 8.59 | 0.51 | 2.90 | [44] |
| ZnO/$Zn_2SnO_4$ | 0.61 | 17.8 | 0.31 | 3.36 | [45] |
| $ZnSnO_3/Zn_2SnO_4$ | 0.66 | 9.39 | 69.58% | 4.31 | This work |

**Table S6.** The fitting results about photocatalytic removal of the pollutants over the different samples.

| Samples | System | Pollutants | Fitting formula | $k$ | $R^2$ |
|---|---|---|---|---|---|
| **$S_2$** | single | CIP | Y=0.00931X-0.05523 | 0.010 | 0.9817 |
| **$S_3$** | single | CIP | Y= 0.02561X-0.02426 | 0.026 | 0.9835 |
| **$S_2$** | single | Cr(VI) | $Y=0.00435X-1.764*10^{-4}$ | 0.004 | 0.9821 |
| **$S_3$** | single | Cr(VI) | Y= 0.01011X-0.11242 | 0.010 | 0.9833 |
| **$S_3$** | co-existing | CIP | Y=0.03298X-0.12417 | 0.032 | 0.9813 |
| | co-existing | Cr(VI) | Y=0.01678X-0.11827 | 0.017 | 0.9807 |