

Introduction

- Sulfate radical ($SO_4^{\cdot-}$) based advanced oxidation processes are an effective treatment method for the degradation of organic pollutants in water.
- Different classes of compounds have been explored as catalysts for the activation of persulfate (PS) for the generation of sulfate radicals such as transition metal ions and metal oxides e.g. iron-based compounds such as zerovalent iron (ZVI), iron oxide/hydroxides, sulphides; carbon-based materials e.g activated carbon, graphene/graphene oxide etc.
- There is however limited studies on copper-based compounds as catalysts for persulfate activation
- The aim of this study is to evaluate the persulfate-activation activity of different stoichiometric phases of copper antimony sulphides (CAS).

Aim

Objectives

- The objectives of the study include:
- achieve selective synthesis of different phases of CAS
 - characterise the synthesized CAS
 - evaluate the persulfate-activation activity of the CAS phases for tetracycline degradation.

Methods

- The co-thermolysis of single source precursors in high boiling liquids was employed for CAS synthesis
- Dithiocarbamate metal complexes of copper (CuL) and antimony (SbL) were prepared by mixing the pre-prepared ligand with corresponding metal salt as shown in fig 1a.
- The obtained metal complexes were dissolved in high boiling solvent and thermolyzed under N_2 to obtained CAS nanoparticles as shown in fig 1b.
- Selective synthesis of three different phases of CAS: $CuSbS_2$, Cu_3SbS_4 and $Cu_{12}Sb_4S_{13}$ was achieved by varying precursor ratio, temperature and solvent.
- Persulfate activation activity of the obtained CAS phases was evaluated for tetracycline degradataion (10 mg/L) using 10 mg of CAS and 1mM of PS

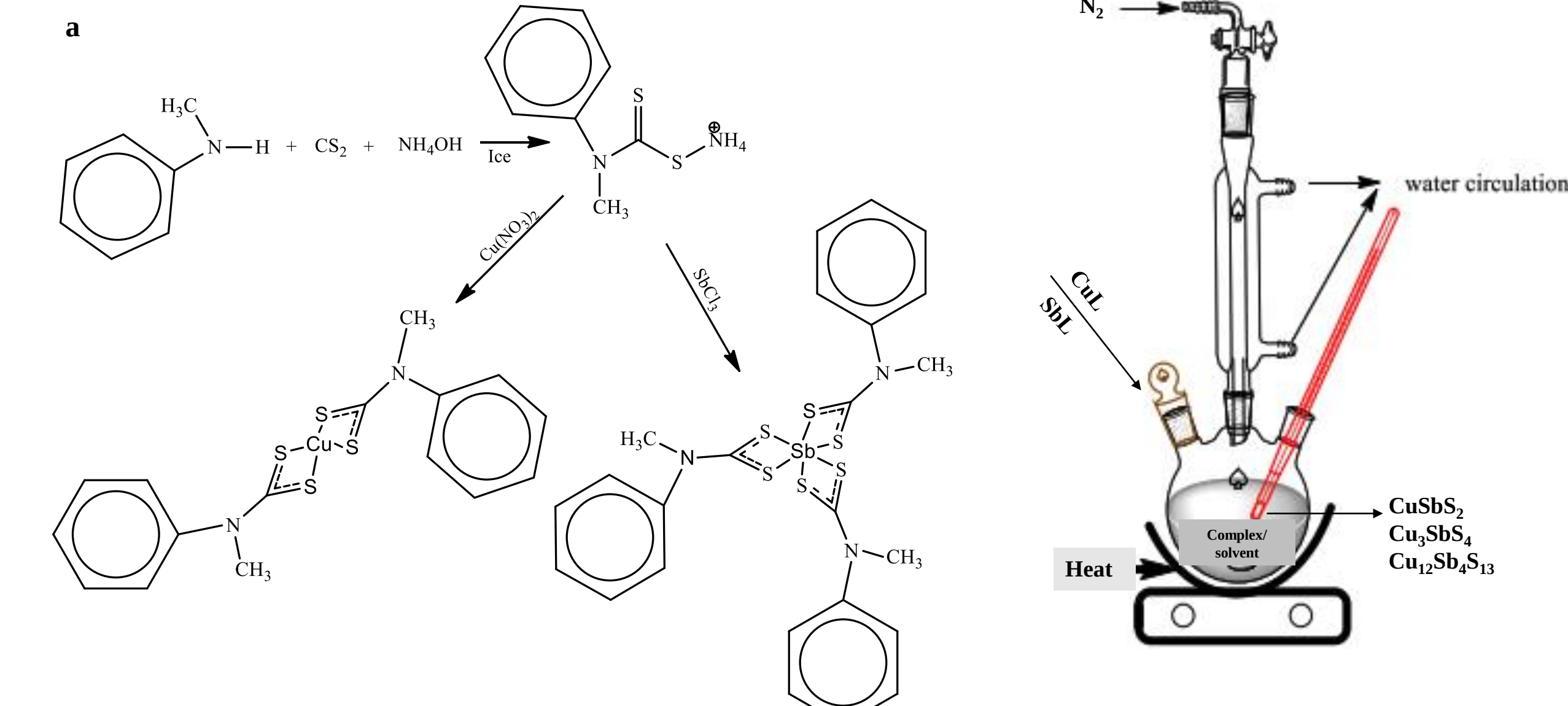


Fig. 1: (a) Synthetic scheme for copper and antimony dithiocarbamate metal complexes (b) Thermolysis set up for the synthesis of CAS phases

Results and Discussion

- Three different stoichiometric phases of CAS were achieved by varying process parameters such as reaction temperature, precursor ratio and solvent
- Thermolysis of CuL and SbL at precursor ratio of 1:1 at 280 °C gave the $CuSbS_2$ pure phase in oleylamine
 - Structural properties
 - Crystal properties: Orthorhombic phase; space group pbmn (No 62); lattice parameter: a= 6.00 Å, b = 3.78 Å, c = 14.495Å
 - Crystallite size: using the Scherrer equation the crystallite size of the nanoparticle was calculated to be 222.98 nm

- Morphology
- The $CuSbS_2$ nanoparticles were agglomerated and Oval shaped

- Optical properties
- Intense absorption into the NIR region with absorption onset at about 300 nm. The calculated energy Band gap was 1.5 eV

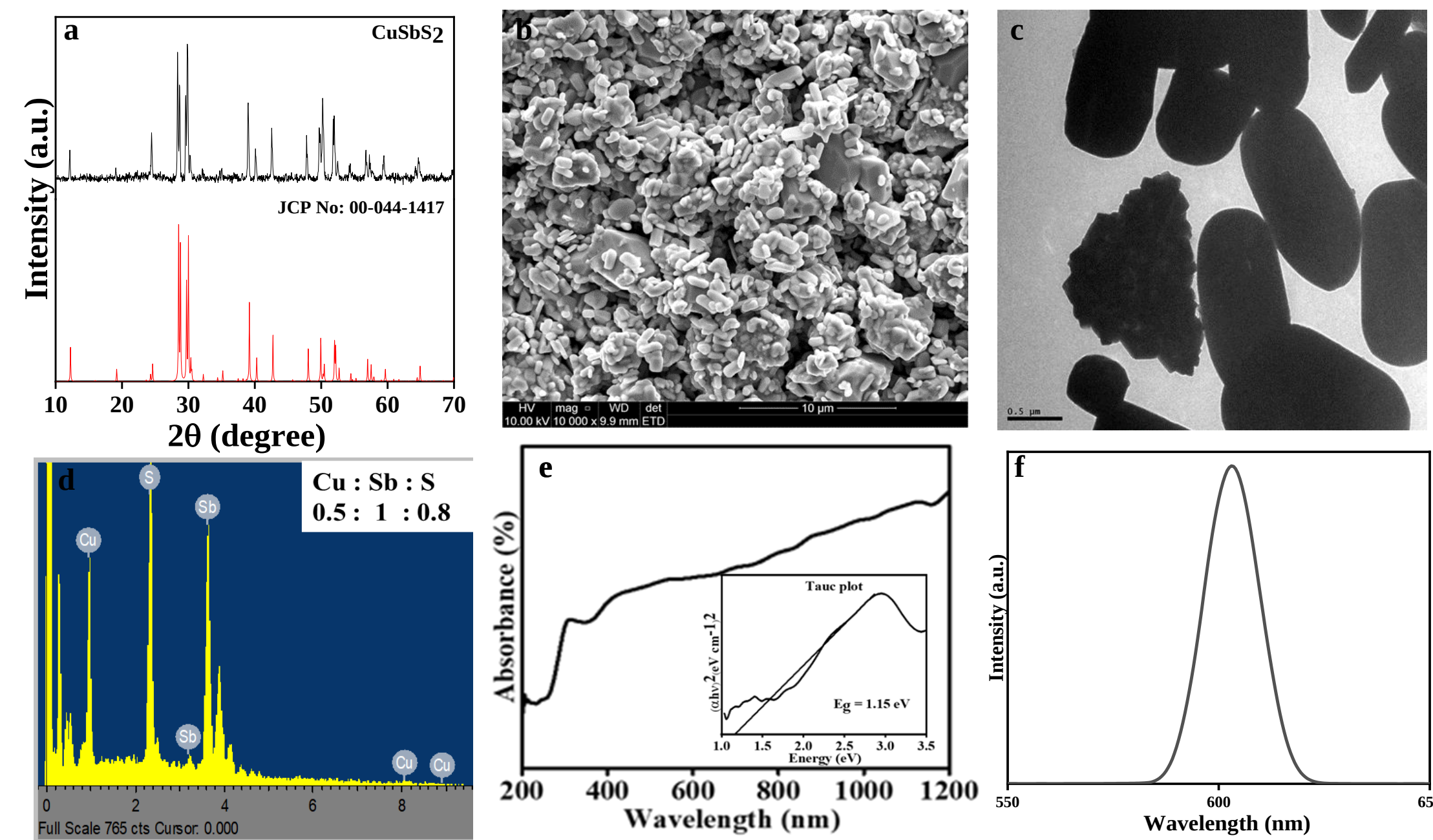


Fig 2. (a) XRD spectra (b) SEM (c) TEM (d) EDX (e) UV-Vis spectra (inset: Tauc plot) and (f) PL spectra of $CuSbS_2$

- The synthesis of Cu_3SbS_4 was achieved by thermolyzing the Cu and Sb ligand in stoichiometric ratio at 220 °C in oleylamine.
- Fig. 3 shows the XRD, SEM, TEM, EDX, absorption and emission spectra of the obtained nanoparticle
- Structural properties of Cu_3SbS_4
 - Crystal properties: the body-centered tetragonal Cu_3SbS_4 (JCPDS No 35-0581, space group 1-42m, lattice parameters: a = b = 5.38 Å, c = 10.76 Å)
 - Crystallite size: using the Scherrer equation the crystallite size of the nanoparticle was calculated to be 12.4 ± 1.7 nm
- Morphology
- The Cu_3SbS_4 nanoparticles were agglomerated and irregular round shaped
- Optical properties
- Intense absorption into the NIR region with absorption phenomenon centred at about 300 and 500 nm. The calculated energy band gap was 1.38 eV

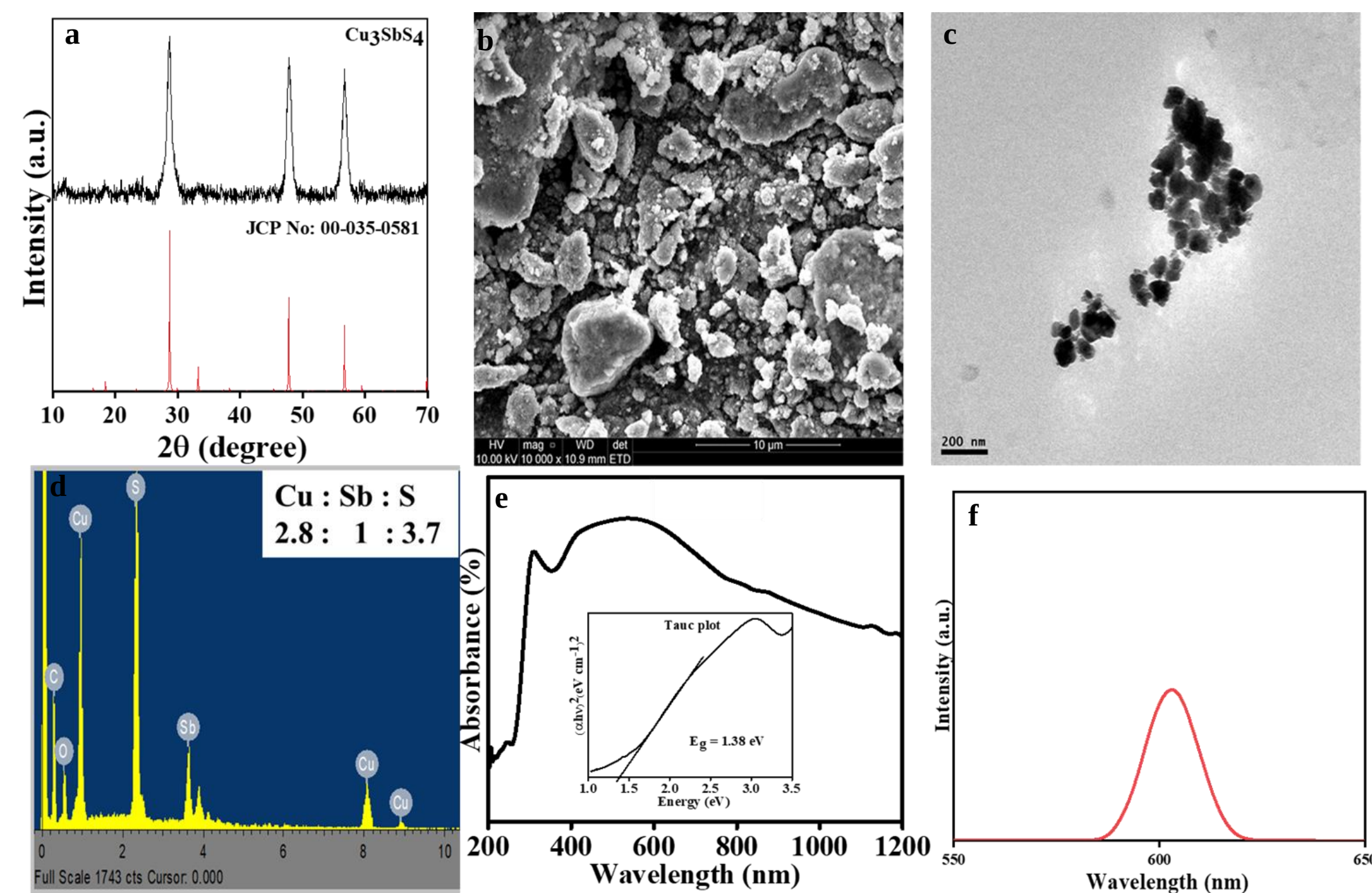


Fig 3. (a) XRD spectra (b) SEM (c) TEM (d) EDX (e) UV-Vis spectra (inset: Tauc plot) and (f) PL spectra of Cu_3SbS_4

- The synthesis of $Cu_{12}Sb_4S_{13}$ was achieved by thermolyzing CuL and SbL in stoichiometric ratio at 220 °C in 1:1 mixture of oleylamine and DDT
- Fig. 4 shows the XRD, SEM, TEM, EDX, absorption and emission spectra of the obtained nanoparticle
- Structural properties of Cu_3SbS_4
 - Crystal properties: body-centered cubic $Cu_{12}Sb_4S_{13}$ (JCPDs No 00-024-1318 space group 1-43m lattice parameters: a = b = c = 10.32 Å)
 - Crystallite size: using the Scherrer equation the crystallite size of the nanoparticle was calculated to be 49.5 ± 4.9 nm
- Morphology
- The $Cu_{12}Sb_4S_{13}$ nanoparticles were agglomerated and round shaped
- Optical properties
- Intense absorption into the NIR region with absorption onset at about 300 and 400 nm. The calculated energy Band gap was 1.38 eV

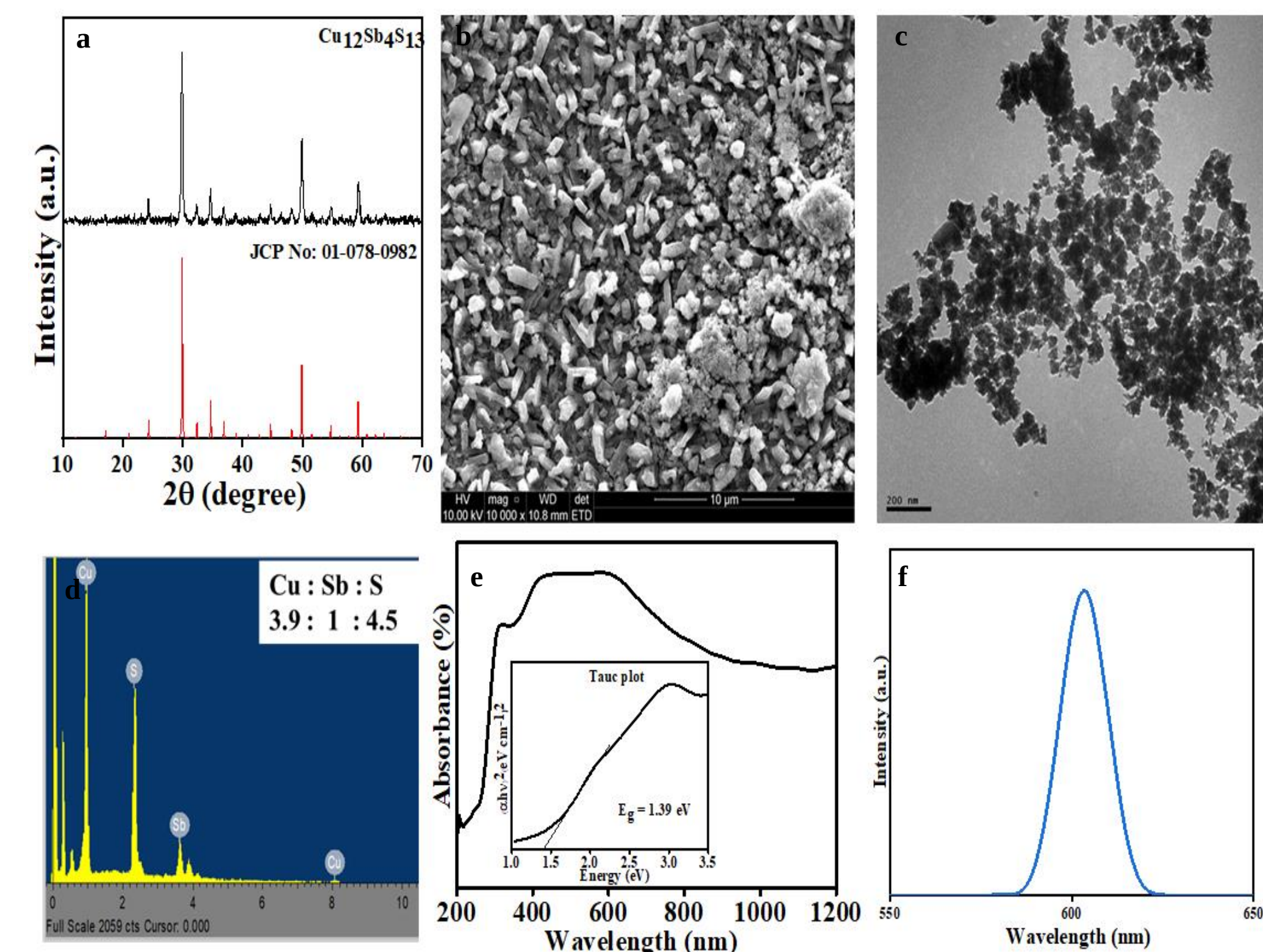


Fig 4. (a) XRD spectra (b) SEM (c) TEM (d) EDX (e) UV-Vis spectra (inset: Tauc plot) and (f) PL spectra of $Cu_{12}Sb_4S_{13}$

Evaluation of persulfate-activation activity

The catalytic activity of the obtained CAS stoichiometric phases were evaluated for their persulfate activation activity

- At pH of 4, Cu_3SbS_4 and $Cu_{12}Sb_4S_{13}$ showed comparable PS activation resulting in TCE degradation efficiency of 55.6 and 54.6% respectively (fig. 5a)
- $CuSbS_2$ and PS alone achieved degradation efficiency of 26.1 and 12 % respectively.
- Degradation rate constant for TCE degradation was 7.1×10^{-4} , 3.0×10^{-4} , 7.5×10^{-3} and $7.2 \times 10^{-3} \text{ min}^{-1}$ for PS alone, $CuSbS_2$, Cu_3SbS_4 and $Cu_{12}Sb_4S_{13}$ respectively (fig. 5b)
- Effect of pH on the degradation process using Cu_3SbS_4 , showed an increase in degradation efficiency at neutral pH compare to acidic and basic pH (fig. 5c)
- Radical scavenging experiment, showed the degradation proceeded via the action of radical species, compare to non-radical processes which involves electron transfer (fig. 5d)
- It can thus be confirmed that the Cu_3SbS_4 phase showed the highest persulfate activation activity, which is pH dependent and proceeded via the radical process.

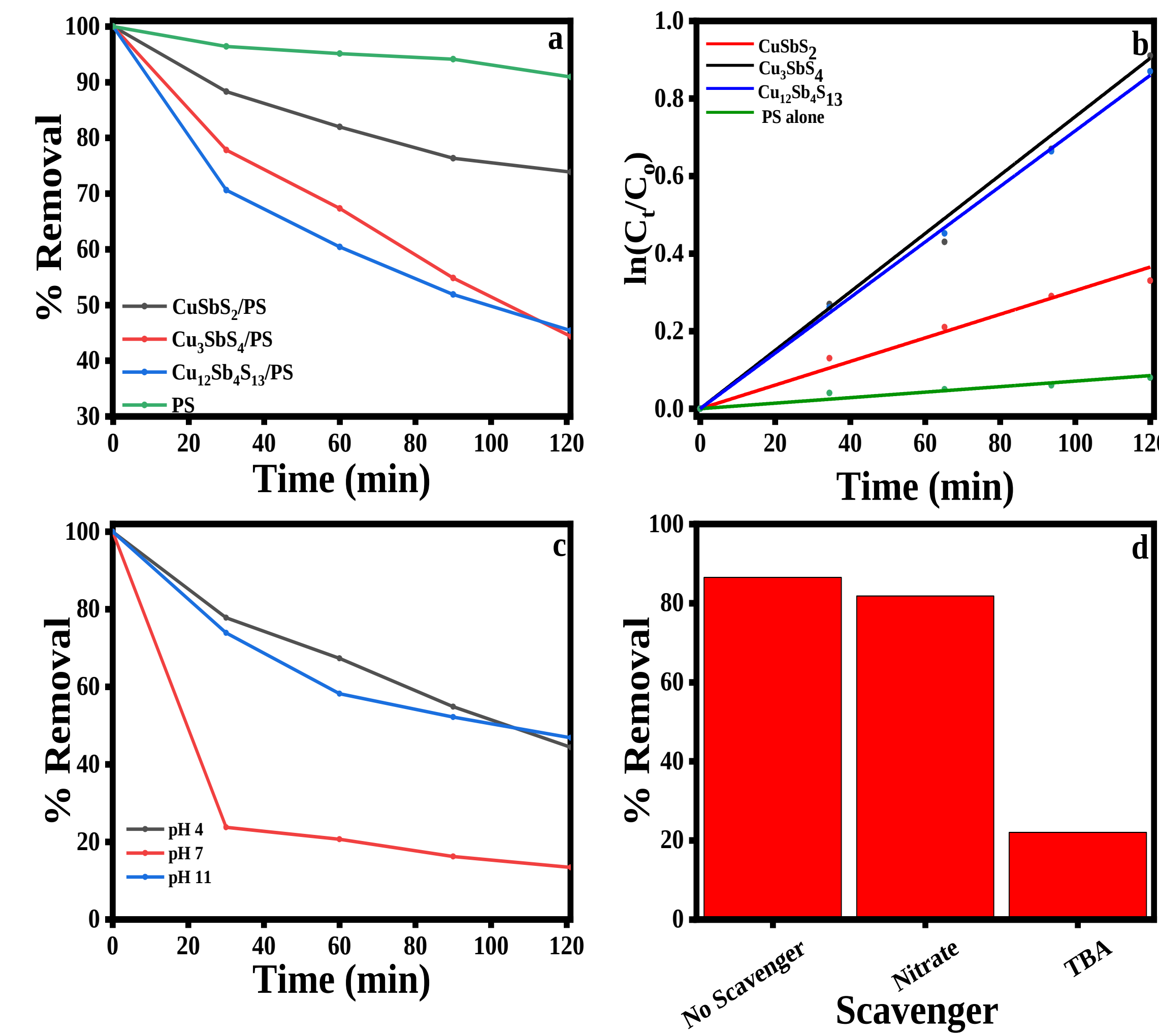


Fig. 18: Persulfate activation activity of CAS stoichiometries for the degradation of tetracycline: (a) TCE degradation profile (b) kinetic plot for the degradation process (c) Effect of pH on degradation activity (d) Radical scavenging experiment

Conclusion

Three different stoichiometric phases of copper antimony sulphide: $CuSbS_2$, Cu_3SbS_4 and $Cu_{12}Sb_4S_{13}$ were prepared by the solvothermal co-thermolysis process. Selective synthesis of the stoichiometric phases was achieved by varying process parameters such as precursor ratio, solvent and reaction temperature. Evaluation of the activity of the phases for persulfate activation for tetracycline degradation, showed that Cu_3SbS_4 phase showed the highest activity of persulfate activation. The process was observed to be highly effective at neutral pH compare to acidic or basic pH and the process proceeded via the radical generation pathway.

References

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