Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Boosting the growth and aggregation of sulfide nanoparticles via regulating heterogenous nucleation for enhanced sedimentation

Chunxue Li [a], Wenchao Zhang [ab], Jiahui Wu [a], Junqin Liu [a] , Han Wang [a], Qingzhu Li [ab], Liyuan Chai [ab], Qingwei Wang*[ab], Zhang Lin [ab]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, China

[b] Chinese National Engineering Research Center for Control and Treatment of Heavy Metal Pollution, Changsha 410083, China

*Corresponding author:

Qingwei Wang

Tel:15116211257

E-mail: qw_wang@csu.edu.cn

List of figures and tables

Fig.S1. Schematic diagram of experimental apparatus

Fig.S2. The size of CuS primary particles at 0g/L crystal seed dosage or 0rpm stirring rate.

Fig.S3. The CuS supernatant optical microscope picture (a)without stirring and seeding, (b)stirring and seeding.

Fig.S4. (a)The TEM and HR-TEM images, (b)The XRD patterns of CuS for none, only stirring, only seeding, stirring and seeding.

Fig.S5. TEM images of CuS particles at different volumes of seeds (a) without stirring, (b)stirring.

Fig.S6. TEM images of CuS nucleation growth (a)15min with stirring and (b) 30min without stirring.

Fig.S7. The optical micrographs of CuS of none, stirring only, seeding only, stirring and seeding.

Fig.S8. High-resolution XPS spectra of (a) none, (b) stirring only, (c) seeding only, (d) stirring and seeding.

Fig.S9. The contact angle of particles produced with and without stirring at the same crystal seed volume.

Fig.S10. Size of CuS particles produced at different H_2S concentrations as a function of time (a)stirring,(b)without stirring.

Table S1. Data used for calculation of total potential of interaction between hydrophobic particles.

Table S2. Calculation results of total potential of interaction between hydrophobic hematite particles.

Fig.S1

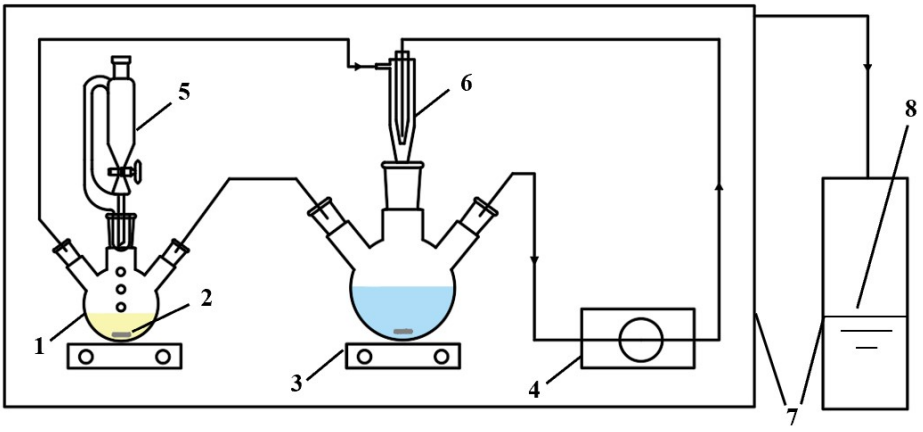

Fig.S1. Schematic diagram of experimental apparatus (1-Gas generating bottle; 2-Magnetic stirring sub; 3-Magnetic stirrer; 4-Peristaltic pump; 5-Separating funnel; 6-Reactor; 7-Exhaust gas adsorption device; 8-NaOH absorbing solution).

Fig.S2

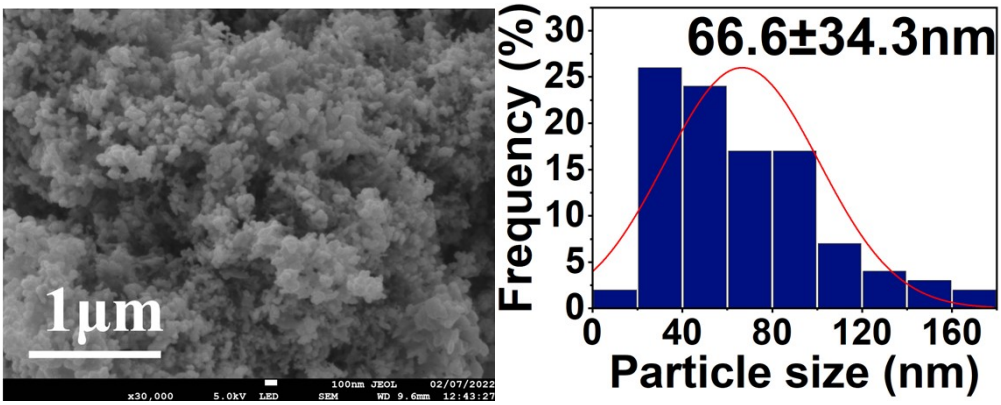

Fig.S2. The size of CuS primary particles at 0g/L crystal seed dosage or 0rpm stirring rate

Fig.S3

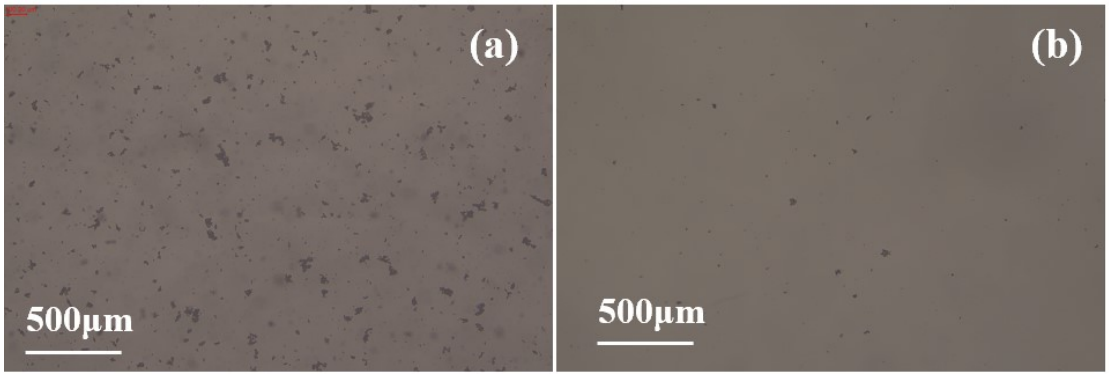

Fig.S3. The CuS supernatant optical microscope picture (a)without stirring and seeding, (b)stirring and seeding.

Fig.S4

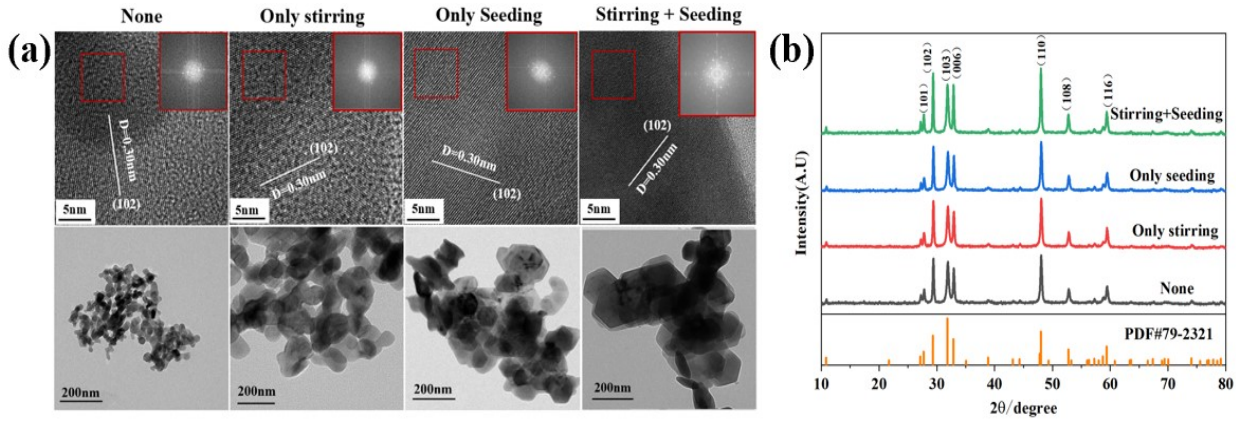

Fig.S4. (a)The TEM and HR-TEM images (b)The XRD patterns of CuS for none, only stirring, only seeding, stirring and seeding.

Fig.S5

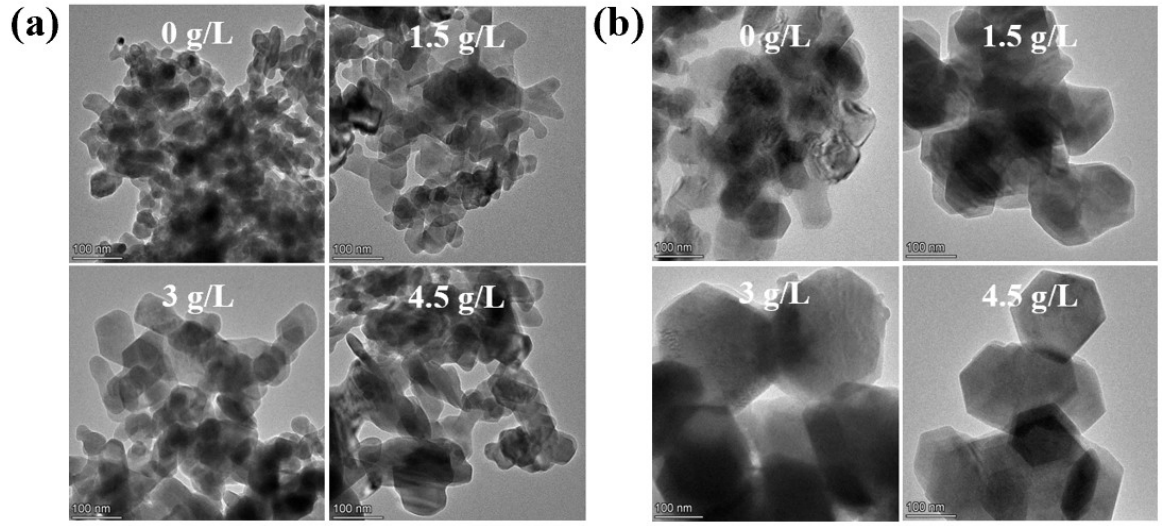

Fig.S5. TEM images of CuS particles at different volumes of seeds (a) without stirring, (b)stirring.

Fig.S6

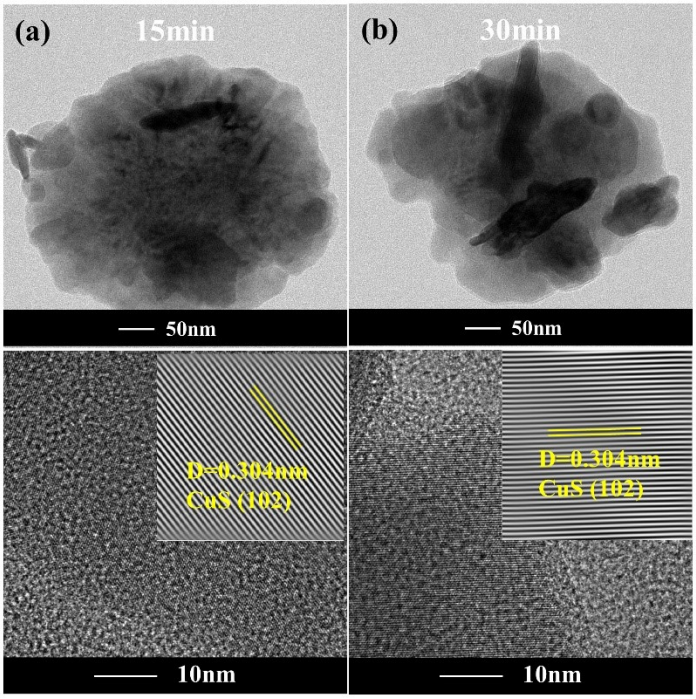

Fig.S6. TEM images of CuS nucleation growth (a)15min with stirring and (b) 30min without stirring.

Fig.S7

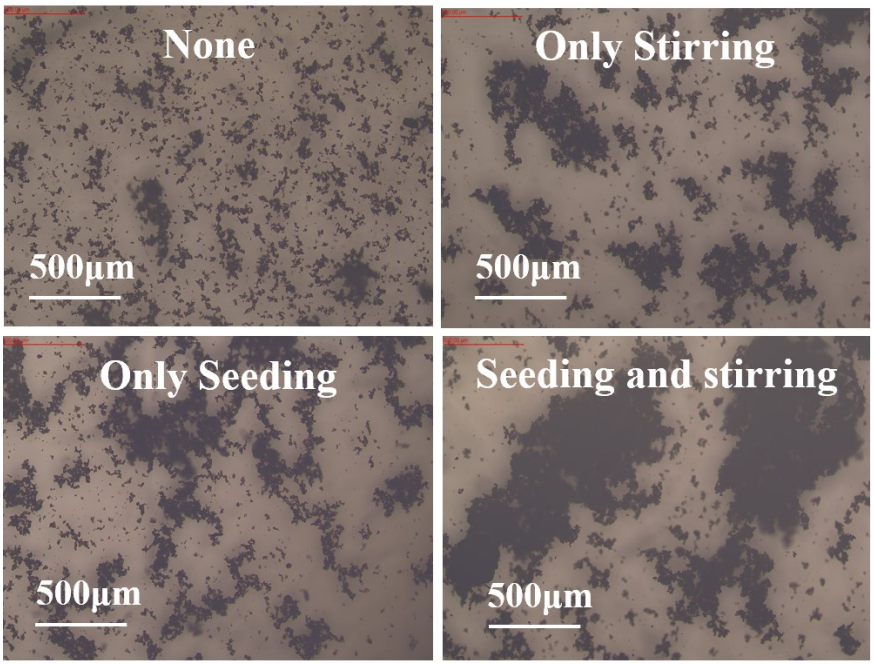

Fig.S7. The optical micrographs of CuS of none, stirring only, seeding only, stirring and seeding.

Fig.S8

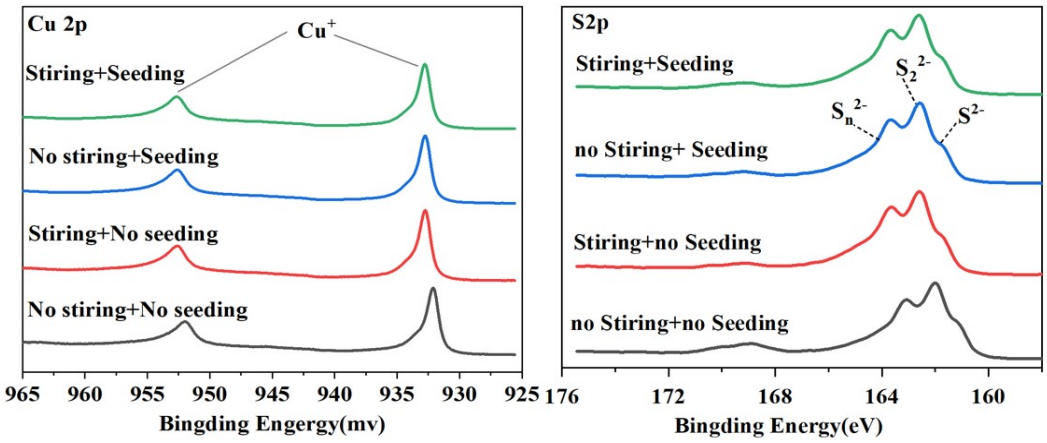

Fig.S8. High-resolution XPS spectra of (a) none, (b) stirring only, (c) seeding only, (d) stirring and seeding.

Fig.S9

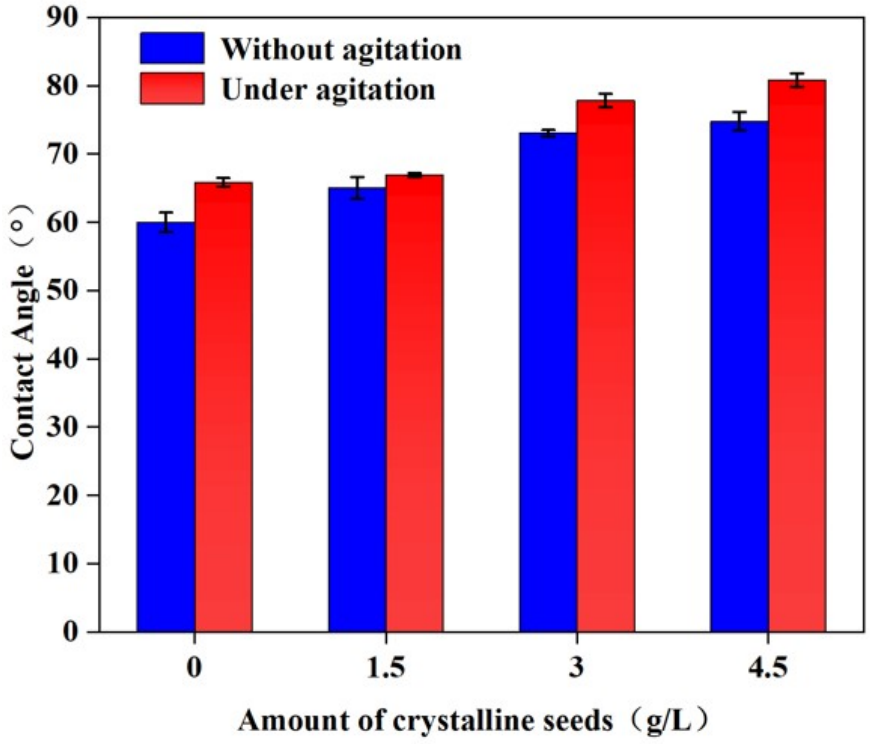

Fig.S9. The contact angle of particles produced with and without stirring at the same crystal seed volume.

Fig.S10

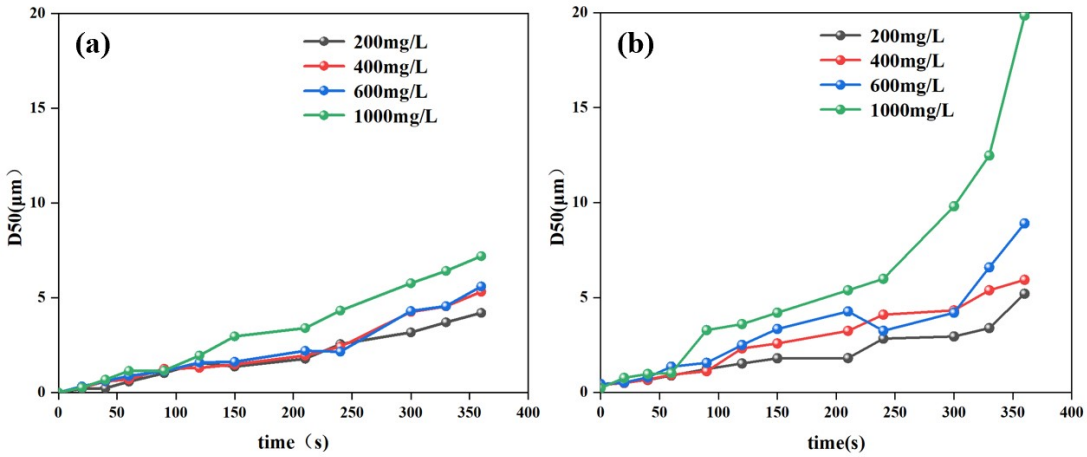

Fig.S10. Size of CuS particles produced at different H_2S concentrations as a function of time (a)stirring,(b)without stirring.

Calculation of total potential of interaction between hydrophobic particles

Based on the extended DLVO theory(Yin et al., 2011), the total interaction force between hydrophobic particles is calculated. (1)

$$U_T=U_A+U_R+U_{HI}$$

where U_T is the total potential of interaction between hydrophobic particles; U_A is van der Waals attractive potential; U_R is electric double layer repulsion interaction potential; U_{HI} is hydrophobic interaction potential;

For two spherical particles ,the van der Waals attractive potential between them is

$$U_A=\frac{Ar}{12H} \quad (2)$$

Where r is radius of the particle; A is Hamaker or the material characteristic constant; H is the shortest distance between particles. Eq.(2) is suitable for the case of the sizes of particle being much larger than their distance.

Hamaker constant is determintant for U_A and can be calculated by

$$A=\pi^2 c\rho^2=\pi^2\rho^2\frac{3\alpha_0^2 h_0 v}{4(4\pi\varepsilon_0)^2} \quad (3)$$

Where ρ is the density of the particles, kg/m^3; c is the dispersive interaction energy; α_0 is the atomic polarisation rate, c^2m^2/J; h_0 is Plank constant, 6.62×10^{-34}; ν is electronic rotation frequency.

For spherical particles, when the distance between the particles is greater than the thickness of the double layer of electricity, the repulsive interaction potential is

$$U_R = \frac{1}{2}\varepsilon r\Phi_0^2 \ln\left[\exp(-\kappa H)\right] \tag{4}$$

where r is radius of particles, m; k is Boltzmann constant, 1.38×10^{-23} J/K; Φ_0 is surface potential of particles, V; ε is permittivity of solution, F/m; κ is thickness of electric double layer, m^{-1}.

$$\kappa = \left(\frac{8\pi e^2 nZ^2}{\varepsilon kT}\right)^{1/2} \tag{5}$$

The empirical equation for the hydrophobic force is as follow(Pascoe and Doherty, 1997):

$$U_{HI} = -Crh_0 \exp\left(-\frac{H}{H_0}\right) \tag{6}$$

where C is constant, N/m, $C=2.51\times10^{-3}\,k_1$ (k_1 is hydrophobic coefficient, related to contact angle θ, $k_1 = \frac{\exp(\theta/100)-1}{e-1}$); H_0 is attenuation length, m.

Table S1. Data used for calculation of total potential of interaction between hydrophobic particles.

Parameter	Value
Absolute temperature/K	293
Hamaker constant, A/J	1.01×10^{-20}
Mean particle radius, r/m	2.72×10^{-6}
Zeta potential of particle surface, φ_0/V	-36.3×10^{-3}
Debye constant, κ/m^{-1}	3×10^{7}
Constant, $C/(N\cdot m^{-1})$	14.8×10^{-4}
Attenuation length, h_0/m	5.1×10^{-9}

Table S2. Calculation results of total potential of interaction between hydrophobic hematite particles.

H/nm	UA/ 10^{-19}J	UR/ 10^{-19}J	UHI/ 10^{-19}J	UT/ 10^{-19}J
1.0	-20.48	7.46	-168.75	-181.77
1.3	-15.59	7.42	-159.11	-167.28
2.0	-10.13	7.32	-138.49	-141.30
2.6	-7.78	7.21	-123.12	-123.69
4.0	-4.98	6.99	-93.56	-91.55
6.0	-3.37	6.68	-63.21	-59.9
10.0	-2.03	6.11	-28.86	-24.78
20.0	-1.01	4.82	-4.05	-0.24
30.0	-0.67	3.75	-0.57	2.51
50.0	-0.42	2.22	0.01	1.8
100.0	-0.20	0.53	0	0.33