mostly aseismic in this experiment (Fig. 3B). Micro-earthquakes are triggered only when the estimated size of the slip zone exceeds the pressurized zone (Fig. 3C), suggesting that they occur off the pressurized zone. However, they might occur within the sliding zone or be triggered off the sliding area by static stress increase. Aftershocks might relate to afterslip in a similar way (23).

The ratio of the shear stress to the effective normal stress increases from about 0.4 to about 0.8 and indicates a friction between 0.6 and 0.8 once slip becomes notable (fig. S4). Qualitatively, this evolution correlates with slip rate better than with slip. The data suggest a logarithmically varying, rate-dependent friction, as frequently observed in laboratory measurements of rock friction (24) or derived from studies of afterslip following large earthquakes (23, 25). We tested such a law based on a simple one-dimensional model (16). The model, which involves only two adjustable parameters, qualitatively fits the observations well (Fig. 3D). We determine the friction  $\mu_0 = 0.67$ (+/–0.05) at a reference velocity of  $v_0$  = 0.1  $\mu m/s,$ with a rate dependency of  $a = \frac{\partial \mu}{\partial \ln v} = 0.0447$  (±0.005). We also tested rate-and-state friction laws (16) but found that the improvement was irrelevant in view of the uncertainties of the measurements. The friction coefficient increases to about 0.7 for slip rates of 1 to 20  $\mu$ m/s. Similar values have been measured in the laboratory on faults formed in limestone and at comparable sliding rates (26-28). These laboratory experiments also show a rate-strengthening behavior at temperatures less than 100°C but a rate dependency at steady-state typically one order of magnitude lower than the value we obtained.

The aseismic behavior triggered by the fluid injection in this experiment is apparently due to an intrinsically rate-strengthening behavior, rather than to conditional stable creep of a rateweakening fault. However, the seismicity, which was probably triggered outside the pressurized zone, requires some areas to allow earthquake nucleation, hence weakening during deformation. This observation is an indication that the frictional properties are likely heterogeneous, as supported by the observations of the main slip surface that displays gouge-rich zones and slickensided areas cutting solid rock (Fig. 1C). During the injection, the effective behavior is rate-strengthening. This behavior is possibly due to the fault zone being rate-strengthening on average, with the gougerich zones being possibly more rate-strengthening than the zones where the fault cuts solid rock (27) or because the rate-weakening asperities are brought to conditional stability by the increase in pore pressure. This interpretation could explain why seismicity is observed only when the crack radius has become larger than the radius of the pressurized zone. Our results prove unambiguously that fluid injection can trigger primarily aseismic slip, with seismicity induced as a secondary effect. This is observed in the context of our experiment, which is characterized by a particularly low effective normal stress. Thus, our results may be of particular relevance to seismic activity triggered at shallow depth by humaninduced injections and shallow aseismic slip. Mechanism observed in this experiment could also be of relevance to explain natural processes at greater depth, such as deep afterslip, slow-slip events, and tremors.

#### **REFERENCES AND NOTES**

- C. B. Raleigh, J. H. Healy, J. D. Bredehoeft, Science 191,
- 1230–1237 (1976).
- 2. W. L. Ellsworth, Science 341, 1225942 (2013).
- C. Nicholson, R. L. Wesson, Pure Appl. Geophys. 139, 561–578 (1992).
- F. H. Cornet, H. Helm, H. Poitrenaud, A. Etchecopar, Pure Appl. Geophys. 150, 563–583 (1997).
- C. Nicholson, R. L. Wesson, Earthquake hazard associated with deep well injection: A report to the U.S. Environmental Protection Agency. U.S. Geol. Surv. Bull. 1951 (1990); http://pubs.usgs.gov/bul/1951/report.pdf.
- 6. E. Majer et al., Geothermics 36, 185-222 (2007).
- M. K. Hubbert, W. W. Rubey, Geol. Soc. Am. Bull. 79, 115–166 (1959).
- 8. H. Noda, N. Lapusta, Nature 493, 518-521 (2013).
- 9. P. Segall, J. Rice, J. Geophys. Res. 100, 22155-22171
- (1995).
- 10. C. Scholz, Nature 391, 37-42 (1998).
- 11. S. Bourouis, P. Bernard, Geophys. J. Int. 169, 723–732 (2007).
- M. Zoback, A. Kohli, I. Das, M. McClure, The importance of slow slip on faults during hydraulic fracturing stimulation of shale gas reservoirs, SPE 155476, Society of Petroleum Engineers, Americas Unconventional Resources Conference, Pittsburgh, PA, 5 to 7 June 2012.
- 13. Y. Guglielmi et al., Rock Mech. Rock Eng. 47, 303-311 (2014).
- 14. Laboratoire Souterrain à Bas Bruit, www.lsbb.eu
- P. Jeanne, Y. Guglielmi, J. Lamarche, F. Cappa, L. Marie, J. Struct. Geol. 44, 93–109 (2012).
- Materials and methods are available as supplementary materials on *Science* Online.
- B. C. Haimson, F. H. Cornet, Int. J. Rock Mech. Min. Sci. 40, 1011–1020 (2003).
- 18. I. Das, M. Zoback, Leading Edge (Tulsa Okla.) 30, 778–786 (2011).
- 19. J. Rutqvist, O. Stephansson, Hydrol. J. 11, 7-40 (2003).

- F. Cappa, Y. Guglielmi, J. Virieux, *Geophys. Res. Lett.* 34, L05301 (2007).
- F. Cappa, J. Rutqvist, Int. J. Greenh. Gas Control 5, 336–346 (2011).
- O. Scotti, F. H. Cornet, Int. J. Rock Mech. Min. Sci. Geomech. Abstr. 31, 347–358 (1994).
- 23. H. Perfettini, J. P. Avouac, J. Geophys. Res. 109, B02304 (2004).
- C. Marone, Annu. Rev. Earth Planet. Sci. 26, 643–696 (1998).
  C. Marone, C. Scholtz, R. Bilham, J. Geophys. Res. 96 (B5),
- 25. C. Marone, C. Scholtz, R. E 8441–8452 (1991).
- T. Tesei, C. Collettini, M. R. Barchi, B. M. Carpenter, G. Di Stefano, *Earth Planet. Sci. Lett.* **408**, 307–318 (2014).
- B. M. Carpenter, M. M. Scuderi, C. Collettini, C. Marone, J. Geophys. Res. Solid Earth 119, 9062–9076 (2014).
- B. A. Verberne, C. R. He, C. J. Spiers, Bull. Seismol. Soc. Am. 100 (5B), 2767–2790 (2010).

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#### SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/348/6240/1224/suppl/DC1 Materials and Methods Figs. S1 to S6 References (29–32) Database S1

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### NANOMATERIALS

## A tunable library of substituted thiourea precursors to metal sulfide nanocrystals

Mark P. Hendricks, Michael P. Campos, Gregory T. Cleveland, Ilan Jen-La Plante, Jonathan S. Owen\*

Controlling the size of colloidal nanocrystals is essential to optimizing their performance in optoelectronic devices, catalysis, and imaging applications. Traditional synthetic methods control size by terminating the growth, an approach that limits the reaction yield and causes batch-to-batch variability. Herein we report a library of thioureas whose substitution pattern tunes their conversion reactivity over more than five orders of magnitude and demonstrate that faster thiourea conversion kinetics increases the extent of crystal nucleation. Tunable kinetics thereby allows the nanocrystal concentration to be adjusted and a desired crystal size to be prepared at full conversion. Controlled precursor reactivity and quantitative conversion improve the batch-tobatch consistency of the final nanocrystal size at industrially relevant reaction scales.

he tunable electronic properties of nanometer scale crystals have inspired many synthetic methods that control crystal size and shape with extraordinary fidelity. Modern metal chalcogenide quantum dots, in particular, can be synthesized with a size that varies by less than a layer of surface atoms across the distribution. This precise control is afforded by the homogeneous nucleation and growth mechanism first described by LaMer and Dinegar to follow a three-phase sequence shown in Fig. 1A (1). In this mechanism, nucleation only occurs during a brief period of time when crystal monomers ([ME]<sub>i</sub>) reach a so-called "critical concentration." Modern syntheses achieve these conditions by using nanocrystal precursors that slowly convert to crystal monomers at a rate that limits the crystallization steps (Fig. 1B) (2–4). The precursor conversion reaction kinetics, therefore, plays a central role in the nucleation and growth process. In particular, the rate of monomer supply to the crystallization medium during nucleation determines the number of nanocrystals produced (3, 5-8). Moreover, if conversion kinetics can be precisely tuned, the number of nanocrystals can be used to control the size at full conversion.

The most widely used sulfide precursors include bis(trimethylsilyl) sulfide [(TMS)<sub>2</sub>S], phosphine sulfides (R<sub>3</sub>P=S, where R indicates an alkyl or aryl group), and hydrogen sulfide produced by heating elemental sulfur in alkane or amine solvents (9). Depending on the conditions of the crystallization, a precursor is selected that provides the necessary rate of monomer supply. For example, (TMS)<sub>2</sub>S typically reacts rapidly with metal salts, allowing it to be used near room temperature; however, the rapid reactivity can lead to mixing limitations during the injection step that hinder the reaction scale. R<sub>3</sub>P=S derivatives, on the other hand, typically react sluggishly until ~300°C and produce low reaction yields. Although reactions of elemental sulfur with alkanes and amines are more versatile and can be used at intermediate temperatures, their conversion reactions follow ill-defined radical pathways that are difficult to control and sensitive to the presence of impurities. Further, sulfurcontaining by-products contribute to batch-to-batch variability and have detrimental effects on nanocrystal properties. Recently, several phosphine chalcogenides and dichalcogenides have been investigated whose conversion kinetics depends on the organic substituents (10, 11). These compounds show promise for tuning nanocrystal size and shape, but few are commercially available and others require involved, multistep syntheses.

We report a library of inexpensive and airstable substituted thioureas whose conversion reactivity can be finely tuned over many orders of magnitude by adjusting the organic substituents (Fig. 2). The widely tunable reactivity allows an optimum chalcogen precursor to be matched with the reactivity of a metal complex at a desired reaction temperature. By controlling the monomer supply kinetics, we adjusted the extent of nucleation in syntheses of lead sulfide, cadmium sulfide, zinc sulfide, and copper sulfide nanocrystals and reliably prepared a desired size with a narrow size distribution and in quantitative vield.

Multigram quantities of air-stable *N,N*<sup>-</sup> disubstituted and *N,N,N*<sup>-</sup>trisubstituted thioureas are obtained in quantitative yields via a one-step "click" reaction between inexpensive, commercially available substituted isothiocyanates and

The thiourea conversion reactivity depends on the number of substituents and their electronic and steric properties. The rate decreases as the number of substituents increases: Tetrasubstituted thioureas convert most slowly, followed by trisubstituted and then disubstituted derivatives. Thus, the substitution pattern can be used to optimize monomer supply kinetics at the desired crystallization temperature. For example, monodisperse lead sulfide nanocrystals can be synthesized from lead oleate and reactive disubstituted thioureas at temperatures from 90° to 150°C (Fig. 2D). However, monodisperse CdS nanocrystals require higher temperature conditions (150° to 250°C), where disubstituted thioureas convert at a rate that is limited by mixing during the injection. Instead, less-reactive N,N,N'- trialkylthioureas (9 to 11) or N,N,N',N'tetramethylthiourea (12) were found to have the appropriate conversion reactivity (fig. S1). Monodisperse zinc sulfide nanocrystals could also be obtained, but only at high temperatures (≥240°C) (fig. S2). However, the lower reactivity of zinc oleate compared with cadmium oleate allows more-reactive disubstituted thioureas to be used. In each case, the conversion reactivity could be optimized to induce nucleation shortly after injection at the temperature needed to obtain narrow size distributions. In this manner, a wide variety of metal sulfides could be synthesizedincluding photoluminescent core-shell nanocrystals (CdSe/CdS/ZnS), plasmonic nanocrystals (Cu<sub>2-x</sub>S), catalyst materials (NiS), complex compound semiconductors (CuZnSnS<sub>4</sub>), and one-dimensional (1D) and 2D anisotropic nanostructures (CdS nanorods, SnS nanosheets)-across a diverse set of growth media, including amine, carboxylate, and phosphonate surfactant mixtures (figs. S3 to S10).

In addition to matching the demands of the crystallization and co-reactants, tunable monomer supply can control the number of nanocrystals and thereby define a desired size after 100% yield is reached. We demonstrate this principle by optimizing an inexpensive synthesis of lead sulfide nanocrystals with diameters from 2.5 to 7.2 nm [wavelength  $\lambda_{max}(1S_e - 1S_h) = 850$  to 1800 nm, full width at half maximum (FWHM) = 30 to 160 meV] on multigram scales and in quantitative yield [as determined by the final absorbance at  $\lambda = 400$  nm, where the extinction is proportional to the concentration of lead sulfide formula units within nanocrystals (12)] (Fig. 2D and fig. S11). To ensure highly reproducible reactivity, 100-g batches of pure, hydroxide-free lead oleate were prepared by dissolving lead oxide in trifluoroacetic anhydride solution and neutralizing the lead trifluoroacetate product with oleic acid and triethylamine (Fig. 2B and fig. S12). N,N'- disubstituted thioureas (1 to 8) react with lead oleate at temperatures at or below 150°C, providing access to colloidal PbS nanocrystals with linewidths of the 1S<sub>e</sub> - 1S<sub>b</sub> absorption that are among the narrowest reported, including at sizes relevant for PbS solar cells (13, 14). Concentrated conditions also proved accessible, allowing up to 6 g of nanocrystals to be prepared in 150 ml of solvent with a high degree of reproducibility. Figure 2E shows the results of nine syntheses conducted using N,N'-diphenylthiourea (2) and six syntheses conducted using N-dodecyl-N'phenylthiourea (3d) that produce between 0.2 and 6 g of nanocrystals. Within one set of conditions, a final size and size distribution are reliably obtained (Fig. 2E and fig. S13). Moreover, little change in the final size and size distribution is observed as the scale, concentration, and stoichiometry are varied (10 to 150 ml, 25 to 100 mM, 1.2:1 to 3:1 Pb:S) (Fig. 2E and fig. S13). The reproducibility and monodispersity are unusual given the high nanocrystal concentrations (up to 0.12 mM). illustrating the reliability and homogeneity provided by well-defined lead and thiourea precursors.

To determine the relationship between conversion reactivity and the final size, we monitored the kinetics of lead sulfide formation in situ by tracking the absorbance at  $\lambda = 400$  nm. Lead sulfide formation approaches 100% yield within a few minutes and can be approximated by a single exponential process (fig. S15), from which rate constants [ $k_{obs}(\mathbf{1})$  to  $k_{obs}(\mathbf{8})$  (s<sup>-1</sup>)] are extracted. By normalizing  $k_{obs}(\mathbf{1})$  through  $k_{obs}(\mathbf{8})$  to the rate constant of the slowest precursor [ $k_{obs}(\mathbf{8})$ ], we determined relative first-order rate constants



**Fig. 1. The mechanism of precursor-limited homogeneous nucleation and growth of colloidal metal chalcogenide nanocrystals.** (**A**) The time evolution of the monomer concentration as described by LaMer and Dinegar, where monomer supersaturation (I) precedes crystal nucleation (II) and is followed by growth (III). (**B**) Metal and chalcogen precursors (MX<sub>2</sub>, ER<sub>2</sub>) react and supply monomers ([ME]<sub>i</sub>) to the growth medium at a rate that limits the crystallization.

Department of Chemistry, Columbia University, New York, NY 10027, USA. \*Corresponding author. E-mail: jso2115@columbia.edu

primary or secondary amines (Fig. 2A). Based on the number of commercially available starting materials, we estimate that  $10^3$  to  $10^4$  structures can be accessed in a single step. In most cases, the electrophilicity of isothiocyanates makes the reaction with amines rapid at room temperature, allowing *N*,*N*-diaryl; *N*,*N*-dialkyl; mixed *N*-alkyl-*N*'-aryl; and *N*,*N*,*N*'-trialkylthiourea structures to be prepared (**1** to **11**).



tion spectra of PbS nanocrystals synthesized using substituted thioureas: 1 and 2 (95°C); 3b, c, d, and f (120°C); 6 and 8 (150°C). a.u., arbitrary units. (E) Results of a reproducibility study showing the nanocrystal diameter and relative size distribution of three reactions for two different precursors (2 and 3d). The varying shades of dot color represent differing reaction scale, concentration, or amount of excess lead oleate used in the reaction. See fig. S14 for detailed reaction conditions.

15

1.0

A						<b>B</b>	
$\begin{array}{c} & & \mathbf{k_{rel}} \\ \mathbf{R}_{1:N} \stackrel{N}{\to} \mathbf{R}_2 + \mathrm{Pb(oleate)}_2 \stackrel{k_{rel}}{\longrightarrow} [\mathrm{PbS}]_{\mathrm{NC}} \\ & & \mathbf{C} \end{array}$					Vield [PbS], 2 80 40 40	F <sub>3</sub> C ( <b>3b</b> ) - Cl ( <b>3c</b> ) -	
_		R <sub>1</sub>	R <sub>2</sub>	T(°C)	k <sub>rel</sub>	× 20	H (3d) — Me (3e) —
	1	3,5-CF <sub>3</sub> -Ph	Ph	90	4000	0	MeO ( <b>3f</b> ) —
	2	Ph	Ph	90	1100	0	0 5 10
	3a	<i>p</i> -CN-Ph	C <sub>12</sub> H <sub>25</sub>	120	200	D	Time (min)
	3b	<i>p</i> −CF <sub>3</sub> −Ph	$C_{12}H_{25}$	90, 120	91	-1.0	<u>7</u>
	3c	<i>p</i> -Cl-Ph	$C_{12}H_{25}$	120	45		
	3d	Ph	$C_{12}H_{25}$	120	21	1.5	
	3e	<i>p</i> -Me-Ph	$C_{12}H_{25}$	120	16	<i>k</i> <sub>obs</sub>	6
	3f	<i>p</i> -OMe-Ph	$C_{12}H_{25}$	120, 150	11	)gol	
	5	<i>t</i> -butyl	$C_{12}H_{25}$	150	19	-2.0	
	6	<i>i</i> -propyl	$C_{12}H_{25}$	150	2.6		5
	7	cyclohexyl	$C_{12}H_{25}$	150	2.3	-2.5	<b>↓,∕,</b>
-	8	hexyl	$C_{12}H_{25}$	150	1	-1	.0 -0.5 0.0 0.5 Hammett σ

Fig. 3. The reaction of disubstituted thioureas with lead oleate in hexadecane and diphenyl ether follows single exponential kinetics, allowing the conversion rate constants to be quantitatively compared. (A) Schematic of PbS formation reaction used to measure conversion kinetics at 90° to 150°C. (B) Kinetics of lead sulfide formation as measured in situ by the absorbance at  $\lambda = 400$  nm. (C) Effect of thiourea substitution pattern on the relative thiourea conversion rate constants [ $k_{rel}(1)$  to  $k_{rel}(8)$ , e.g.,  $k_{rel}(7) = k(7)/k(8)$ ]. The wide range of reactivity requires that kinetics are measured at multiple temperatures. To account for the temperature dependence of the conversion rate constant, **3b** and **3f** were measured at two temperatures, and the change in rate constant was used to normalize the relative rate constants of the respective temperatures {e.g.,  $k_{rel}(3b) = [k(3b)^{120°C}/k(8)^{150°C}] \times [k(3f)^{150°C}]$ . (D) Hammett plot illustrating the well-defined relationship between the electronic structure of the thiourea and the rate of lead sulfide formation.

 $[k_{\rm rel}(1)$  to  $k_{\rm rel}(8)]$  across a range of temperatures (90° to 150°C), allowing the reactivity to be quantitatively compared over more than three orders of magnitude (Fig. 3C). These measurements show a well-defined dependence of the conversion reactivity on the thiourea structure that is defined by the substituents.

Within the disubstituted thiourea derivatives, the conversion rate constants decrease over three orders of magnitude upon replacing electron-withdrawing aryl substituents with alkyl substituents. Thus, N,N-diarylthioureas such as N-(3.5,-bis-trifluoromethylphenyl)-N'-phenylthiourea (1) convert most rapidly, whereas N,N'-di-nalkylthioureas (8) react 4000-fold more slowly. Similar reactivity trends were found with cadmium oleate (fig. S16). Mixed N-alkyl-N'-aryl variants showed intermediate reactivity toward lead oleate that can be finely adjusted by appending electron withdrawing or donating substituents on the aromatic ring. The conversion rate constants of para-substituted N-p-X-phenyl-N'-ndodecylthioureas (3a to 3f, where X = CN, CF3, Cl, H, Me, MeO) increase by a factor of 20 as the para-substituent becomes increasingly electron withdrawing. The logarithms of the observed firstorder rate constants are plotted versus the Hammett sigma parameter of the para-substituent in Fig. 3D (15). A linear relationship is observed, demonstrating the well-behaved dependence of conversion kinetics on the thiourea acidity.

A large positive slope ( $\rho = 1.3$ ) indicates a buildup of negative charge during the conversion reaction. These results can be explained by rate-limiting deprotonation of the thiourea or nucleophilic attack on the thiocarbonyl carbon. Conversion of **3d** is faster in the presence of tri-*n*-butylamine and slower when oleic acid



Fig. 4. Increasing thiourea conversion reactivity produces a higher nanocrystal concentration and a smaller final nanocrystal diameter. (A) Nanocrystal concentration and final diameter plotted versus the rate constant of lead sulfide formation  $(k_{obs})$  for **3a** to **3f** ([Nanocrystal]<sub>t</sub>  $\propto$  [PbS]<sub>t</sub>/ $(r_t^3)$ , where *t* is time and *r* is the nanocrystal radius at time *t*). (**B** to **D**) Transmission electron micrographs of PbS nanocrystals synthesized under reaction conditions used for kinetics experiments (**3a**, **3d**, and **3f**).

is present, both of which suggest that deprotonation of the thiourea precedes the formation of lead sulfide. Deprotonation of thiourea in water is known to speed its hydrolysis to cyanamide (16). Increasing steric bulk of the thiourea substituents also speeds the rate of conversion (5 to 8); the increased bulk may accelerate elimination of lead sulfide from an intermediate lead thioureate complex formed by deprotonation of a lead-bound thiourea. Although detailed work is required to determine the precise conversion mechanism, these observations highlight the importance of the microscopic steps leading to the rate-determining precursor conversion step, which vary depending on the surfactants used as well as the nature of the metal co-reactant.

The nanocrystal concentrations obtained from **3a** to **3f** are plotted versus  $k_{obs}$  in Fig. 4A, where an eightfold increase in the conversion rate leads to a fourfold increase in the nanocrystal concentration. The finely tuned monomer supply kinetics controls the extent of nucleation, because the rate of Ostwald ripening is negligibly slow under these conditions (Fig. 4A and fig. S17). A similar dependence is observed in studies of zinc sulfide, copper sulfide, nickel sulfide, and cadmium sulfide nanocrystals (figs. S2, S4, S5, and S16). Tuning the precursor reactivity can also be used to finely control the aspect ratio of CdS nanorods; thioureas of decreasing reactivity (3f, 9, and 12) lead to a systematic increase in the volume and rod aspect ratio, a trend that results from the lower nanocrystal concentration produced by slower conversion kinetics (figs. S7 to S9) (17).

Previous experimental and theoretical work on cadmium selenide and silver halides reported a similar correlation between the concentration of nanocrystals and the precursor conversion rate during nucleation (*3*, *5–7*, *18*). The correlation results from a nucleation process that continues until the collective consumption of monomers by growing nuclei exceeds monomer production by precursor conversion. At this point, the concentration of nuclei is sufficiently high to cause the supersaturation to drop and the nucleation process to end. A "critical" dependence of the nucleation rate on monomer supersaturation, like the one predicted by classical nucleation theory, is expected to produce a linear relationship between the nanocrystal concentration and the precursor conversion rate during nucleation (5,  $\delta$ ). However, a subcritical dependence can be observed in Fig. 4A that will require more accurate models of nucleation to explain. Nonetheless, the smooth correlation between precursor conversion rate and nanocrystal concentration can be used to predictably obtain a desired nanocrystal size.

Controlling the final size with the precursor reaction rate rather than modifying the crystallization medium (e.g., reaction temperature, solvent, and surfactant concentration), or limiting the conversion, greatly simplifies the nanocrystal composition because both the starting materials as well as the reaction by-products can bind the nanocrystals (19). Although the thiourea conversion by-products were not found to bind the nanocrystals in this case (fig. S18), cadmium and lead oleate precursors are known to reversibly bind and passivate nanocrystal surfaces, and their coverage may depend on the concentration of these complexes remaining after conversion (20).

Tuning size with precursor reactivity and running reactions to full conversion allows the final ratio of lead sulfide product and unconverted lead oleate to be determined by the amounts of reactants used. This advance enables a standard purification procedure to be optimized to reproducibly control the final oleate ligand shell and nanocrystal stoichiometry. Moreover, by using preformed lead oleate, syntheses run at or below 120°C can be conducted in low-boiling solvents like 1-octene that are conveniently distilled under vacuum after completion of the synthesis. This reduces the volume of solvent used during the isolation and facilitates large-scale reactions. For example, nanocrystals with a 3.4-nm diameter were synthesized on a 3-g scale from a 1.5:1 lead oleate-to-2 mixture and isolated with 5.7 oleates per square nanometer of surface area, from which we estimate a Pb:S ratio of 1.26. Larger nanocrystals (6.5 nm) with a lower surface area-tovolume ratio were synthesized on a 6-g scale with a lower lead oleate-to-3d ratio (1.2:1) and isolated with 2.9 oleates nm<sup>-2</sup>, from which we estimate a Pb:S ratio of 1.07 (fig. S18). In both cases, the purification is greatly simplified compared with methods where the conversion is limited. Rather than removing a large excess of unreacted metal precursor-a process that is complicated by the polymeric structures and low solubilities of zinc, cadmium, and lead carboxylates, phosphonates, and halides-a desired amount of remaining metal precursor can be chosen by the starting metal-to-sulfur ratio. Thus, obtaining a desired size at complete conversion is an important step toward reproducibly defining the surface structure and optoelectronic properties at large reaction scales.

Tailoring precursor reactivity will greatly advance our ability to rationally design highperformance materials and to relate atomic structure to nanocrystal function. In particular, highly reproducible syntheses of PbS nanocrystals with narrow size distributions and well-defined surface chemistry can advance the systematic development of solution-processed nanocrystal photovoltaics. Tunable sulfide precursors will also advance the synthesis of complex metal chalcogenide alloys and heterostructures used in solid-state lighting and luminescent displays. More broadly, these results highlight the value of rationally controlling the nanocrystal synthesis mechanism to obtain a desired nanocrystal product in high yields and with a high degree of batch-to-batch consistency.

#### **REFERENCES AND NOTES**

- 1. V. K. LaMer, R. H. Dinegar, J. Am. Chem. Soc. 72, 4847–4854 (1950).
- H. Liu, J. S. Owen, A. P. Alivisatos, J. Am. Chem. Soc. 129, 305–312 (2007).
- J. S. Owen, E. M. Chan, H. Liu, A. P. Alivisatos, J. Am. Chem. Soc. 132, 18206–18213 (2010).
- M. P. Hendricks, B. M. Cossairt, J. S. Owen, ACS Nano 6, 10054–10062 (2012).
  - T. Sugimoto, F. Shiba, T. Sekiguchi, H. Itoh, Colloids Surf. A Physicochem. Eng. Asp. 164, 183–203 (2000).
  - T. Sugimoto, F. Shiba, Colloids Surf. A Physicochem. Eng. Asp. 164, 205–215 (2000).
  - 7. S. Abe, R. K. Čapek, B. De Geyter, Z. Hens, ACS Nano 6, 42-53 (2012).

- J. Y. Rempel, M. G. Bawendi, K. F. Jensen, J. Am. Chem. Soc. 131, 4479–4489 (2009).
- R. García-Rodríguez, M. P. Hendricks, B. M. Cossairt, H. Liu, J. S. Owen, *Chem. Mater.* 25, 1233–1249 (2013).
- T. P. A. Ruberu *et al.*, *ACS Nano* 6, 5348–5359 (2012).
  Y. Guo, S. R. Alvarado, J. D. Barclay, J. Vela, *ACS Nano* 7, 0000 (2002).
- 3616-3626 (2013).
- 12. I. Moreels *et al.*, *ACS Nano* **3**, 3023–3030 (2009). 13. M. C. Weidman, M. E. Beck, R. S. Hoffman, F. Prins,
- W. A. Tisdale, ACS Nano 8, 6363–6371 (2014).
- C.-H. M. Chuang, P. R. Brown, V. Bulović, M. G. Bawendi, Nat Mater. 13, 796–801 (2014).
- 15. C. D. Ritchie, W. F. Sager, Prog. Phys. Org. Chem. 2, 323–400 (1964).
- G. Marcotrigiano, G. Peyronel, R. Battistuzzi, J. Chem. Soc. Perkin Trans. 2 1972, 1539 (1972).
- 17. F. Wang, W. Buhro, J. Am. Chem. Soc. 134, 5369-5380 (2012).
- 18. G. G. Yordanov, C. D. Dushkin, E. Adachi, Colloids Surf.
- A Physicochem. Eng. Asp. 316, 37-45 (2008).

**ELECTROCHEMISTRY** 

D. Zherebetskyy et al., Science 344, 1380–1384 (2014).
 N. C. Anderson, M. P. Hendricks, J. J. Choi, J. S. Owen,

J. Am. Chem. Soc. 135, 18536–18548 (2013).

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#### SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/348/6240/1226/suppl/DC1 Materials and Methods Figs. S1 to S20 References (*21–27*)

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# High-performance transition metal-doped Pt<sub>3</sub>Ni octahedra for oxygen reduction reaction

### Xiaoqing Huang,<sup>1,2\*†</sup> Zipeng Zhao,<sup>1,2\*</sup> Liang Cao,<sup>3</sup> Yu Chen,<sup>1,2</sup> Enbo Zhu,<sup>1,2</sup> Zhaoyang Lin,<sup>4</sup> Mufan Li,<sup>4</sup> Aiming Yan,<sup>5,6,7</sup> Alex Zettl,<sup>5,6,7</sup> Y. Morris Wang,<sup>8</sup> Xiangfeng Duan,<sup>2,4</sup> Tim Mueller,<sup>9</sup><sup>‡</sup> Yu Huang<sup>1,2</sup><sup>‡</sup>

Bimetallic platinum-nickel (Pt-Ni) nanostructures represent an emerging class of electrocatalysts for oxygen reduction reaction (ORR) in fuel cells, but practical applications have been limited by catalytic activity and durability. We surface-doped  $Pt_3Ni$  octahedra supported on carbon with transition metals, termed *M*-Pt\_3Ni/C, where *M* is vanadium, chromium, manganese, iron, cobalt, molybdenum (Mo), tungsten, or rhenium. The Mo-Pt\_3Ni/C showed the best ORR performance, with a specific activity of 10.3 mA/cm<sup>2</sup> and mass activity of 6.98 A/mg<sub>Pt</sub>, which are 81- and 73-fold enhancements compared with the commercial Pt/C catalyst (0.127 mA/cm<sup>2</sup> and 0.096 A/mg<sub>Pt</sub>). Theoretical calculations suggest that Mo prefers subsurface positions near the particle edges in vacuum and surface vertex/edge sites in oxidizing conditions, where it enhances both the performance and the stability of the Pt<sub>3</sub>Ni catalyst.

roton-exchange membrane (PEM) fuel cells use reactions between the fuel (such as hydrogen or alcohols) at the anode and the oxidant (molecular oxygen) at the cathode (1-3). Both cathode and anode reactions need catalysts to lower their electrochemical overpotential for high-voltage output, and so far, platinum (Pt) has been the universal choice (4-6). To fully realize the commercial viability of fuel cells, the following challenges, which may not be strictly independent of one another, need to be simultaneously addressed: the high cost of Pt, the sluggish kinetics of the oxygen reduction reaction (ORR), and the low durability of the catalysts (7-11).

Alloying Pt with a secondary metal reduces the usage of scarce Pt metal while at the same time improving performance as compared with that of pure Pt on mass activity (*12–15*), which has led to the development of active and durable Pt-based electrocatalysts with a wide range of compositions (*16–20*). However, although studies

so far have led to a considerable increase in ORR activity, the champion activity as observed on bulk  $Pt_3Ni(111)$  surface has not been matched in nanocatalyts (21–25), indicating room for further improvement. At the same time, one noted major limitation of Pt-Ni nanostructures is their low durability. The Ni element in these nanostructures leaches away gradually under detrimental corrosive ORR conditions, resulting in rapid performance losses (23–27). Thus, synthesizing Pt-based nanostructures with simultaneously high catalytic activity and durability remains an important open challenge (28).

Because surface and near-surface features of a catalyst have a strong influence on its catalytic performance, we adopted a surface engineering strategy to further explore and enhance the performance of  $Pt_3Ni(111)$  nanocatalysts. We specifically focused our efforts on  $Pt_3Ni$ -based nanocatalysts because the bulk extended  $Pt_3Ni(111)$  surface has been shown to be one of the most efficient catalytic surfaces for the ORR. On the basis of the

control over dopant incorporation of various transition metals onto the surface of dispersive and octahedral Pt<sub>3</sub>Ni/C (termed as *M*-Pt<sub>3</sub>Ni/C, where M = V, Cr, Mn, Fe, Co, Mo, W, or Re), we have developed ORR catalysts that exhibit both high activity and stability. In particular, our Mo-Pt<sub>3</sub>Ni/C catalyst has high specific activity (10.3 mA/cm<sup>2</sup>), high mass activity (6.98 A/mg<sub>Pt</sub>), and substantially improved stability for 8000 potential cycles.

We prepared highly dispersed Pt<sub>3</sub>Ni octahedra on commercial carbon black by means of an efficient one-pot approach without using any bulky capping agents, which used platinum(II) acetylacetonate [Pt(acac)2] and nickel(II) acetylacetonate [Ni(acac)<sub>2</sub>] as metal precursors, carbon black as support, N.N-dimethylformamide (DMF) as solvent and reducing agent, and benzoic acid as the structure-directing agent (fig. S1A). The surface doping for the Pt<sub>3</sub>Ni/C catalyst was initiated by the addition of dopant precursors,  $Mo(CO)_6$ , together with Pt(acac)<sub>2</sub> and Ni(acac)<sub>2</sub> into a suspension of Pt<sub>3</sub>Ni/C in DMF, and the subsequent reaction at 170°C for 48 hours (fig. S1B). The transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images of the Pt<sub>3</sub>Ni/C and Mo-Pt<sub>3</sub>Ni/C catalysts (Fig. 1, A and B, and fig. S2) revealed highly dispersive octahedral nanocrystals (NCs) in both samples, which were substantially uniform in size, averaging  $4.2 \pm 0.2$  nm in

<sup>1</sup>Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095, USA. <sup>2</sup>California NanoSystems Institute (CNSI), University of California, Los Angeles, CA 90095, USA. <sup>3</sup>Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218, USA. <sup>4</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, USA. <sup>5</sup>Department of Physics and Center of Integrated Nanomechanical Systems, University of California, Berkeley, CA 94720, USA. <sup>6</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. <sup>7</sup>Kavli Energy NanoSciences Institute at the University of California, Berkeley, and the Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. <sup>8</sup>Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory (LLNL), Livermore, CA 94550, USA. <sup>9</sup>Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, USA. \*These authors contributed equally to this work. †Present address: College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 215123 Suzhou, China. ‡Corresponding author. E-mail: tmueller@jhu.edu (T.M.); yhuang@seas.ucla.edu (Y.H.)



## A tunable library of substituted thiourea precursors to metal sulfide nanocrystals Mark P. Hendricks et al. Science 348, 1226 (2015);

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