Clusters and Lattices of Particles Stabilized by Dipolar Coupling

Artem Baskin, † Wai-Yip Lo, † and Petr Král †,‡,*

†Department of Chemistry and ‡Department of Physics, University of Illinois at Chicago, Illinois 60607, United States

In recent years, colloidal nanoparticles (NP) of different materials, 1,2 shapes, 3–6 and ligations 7–10 have been self-assembled into superlattices with many types of packing. 11–23 It is crucial to understand the principles underlying their self-assembly 24 to predict and control the structures formed. 25 The interparticle forces that lead to these structures originate in the bulk and surface characteristics of the colloidal NPs. 8,26–29 When the bulk forces dominate in the NP self-assembly, we might described them by averaged force-fields acting between the NPs. 22,30–35 Otherwise, we need to model the NPs atomistically and pay attention to their ligands. 36

Among the many prepared systems, clusters and lattices of NPs stabilized by coupled electric 31,35,37 and magnetic 38–41 dipoles have been observed. It turns out that the type of structures formed depends on the number of particles and the relative strength of the anisotropic dipole–dipole coupling and the isotropic van der Waals (vdW) coupling. If the relative strength of coupling is fixed and the number of particles is increased, the Stockmayer model predicts the formation of perfect icosahedra, entangled knots, linear chains, and planar rings. 42 On substrates, colloidal magnetic NPs (MNPs) at low densities were seen to form lines and rings, while at high densities, they form chains and bandlike aggregates. 43–46

The types of lattices stabilized should depend on the strength of dipolar coupling. At weak dipolar coupling, the vdW coupling dominates and leads to closed-packed fcc and hcp lattices. 23,33,47–49 As the strength of dipolar coupling increases, the dipoles can form ordered structures at room temperatures. 14,50 At large (dominant) dipolar coupling, the vdW coupling becomes irrelevant. Then, one should observe the formation of lattices with looser arrangement of NPs, such as simple hexagonal (sh) lattices of PbSe semiconducting NPs with electric dipoles 35 or nearly close-packed assemblies of Co nanocrystals and Rh₄H₂ atomic magnetic clusters. 14,51 The stabilization conditions of particle clusters might also depend on the substrate used for their deposition. 52 Various intricate spatial spin configurations were predicted to exist in ultrathin films, such as the presence of magnetic vortices. 53 The question is if such complex dipolar arrangements can also be prepared in NP systems.

In this work, we systematically investigate clusters and lattices stabilized by electric or magnetic dipolar coupling of their particle constituents. Despite the formal similarity of NPs with electric and magnetic coupling, the absence of magnetic charges make them rather different. 35,54 Typically, the self-assembly of colloidal NPs with electric dipoles can be largely influenced by screening in ionic solutions. On the other hand, magnetic dipolar interactions are relatively weak, but less

**ABSTRACT**

We model stabilization of clusters and lattices of spherical particles with dominant electric and magnetic dipolar coupling, and weak van der Waals coupling. Our analytical results demonstrate that dipolar coupling can stabilize nanoparticle clusters with planar, tubular, Möbius, and other arrangements. We also explain for which parameters the nanoparticles can form latices with fcc, hcp, sh, sc, and other types of packing. Although these results are valid at different scales, we illustrate that realistic magnetic and semiconducting nanoparticles need to have certain minimum sizes to stabilize at room temperature into nanostructures controlled by dipolar coupling.

**KEYWORDS:** clusters • dipolar coupling • stabilization • nanostructures

*Address correspondence to pkral@uic.edu.*

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spatially limited, due to lack of magnetic screening. MNPs can also have more complex coupling, since they interact at different length scales by dipole–dipole, magnetic anisotropy, and exchange mechanisms.\(^\text{25–58}\) The atomic exchange interaction acts at the length scale of 10 nm,\(^\text{43,59}\) which is about the size of MPs for which this coupling matters.\(^\text{60}\) The magnetic anisotropy and the MNP-shape are also important factors guiding the self-assembly.\(^\text{59}\) However, magnetic anisotropy is of less relevance for freely rotating MPs. Thus, dipolar coupling dominates in the formation of structures with 10–100 nm MNPs,\(^\text{62–67}\) with rich potential applications.\(^\text{58}\)

**METHODS**

We will calculate the energies of assembled particles with dipolar coupling in different clusters and lattices. The dipole–dipole interaction energy between the \(i\) and \(j\) particles located at the \(\mathbf{x}_i\) and \(\mathbf{x}_j\) positions, and having the dipoles \(\mathbf{\mu}_i\) and \(\mathbf{\mu}_j\), respectively, is

\[
W_{ij} = -\frac{\mu_i \cdot \mu_j}{|\mathbf{x}_i - \mathbf{x}_j|^3} = \lambda_{\text{m}(e)} w_{ij}
\]

where \(\mathbf{n}_{ij}\) is a unit vector in the \(\mathbf{x}_j - \mathbf{x}_i\) direction. We can rewrite \(W_{ij}\) as a product of the unitless geometric factor, \(w_{ij}\), and the effective magnetic and electric dipole–dipole interaction strengths, \(\lambda_m = \mu_0 \alpha^2 / (4\pi d^3)\) and \(\lambda_e = \mu_0^2 / (4\pi \epsilon_0 d^3)\), respectively. Here, \(\mu_0\) is the magnetic permeability of vacuum, \(\epsilon_0\) is dielectric constant for vacuum, and \(d\) is the particle diameter.

The dipole moment of a spherical particle with homogeneous magnetization \(m\) per unit volume or \(\rho\) electric dipolar density are given by

\[
\mu_m = \frac{\pi}{6} d^3 m, \quad \mu_e = \frac{\pi}{6} d^3 \rho
\]

In our energy calculations, we will use the local dipole approximation, where we replace the material by point dipoles of the size \(\epsilon_{\text{m}(e)}\), located in the particle center. If its size scales as \(d \rightarrow \alpha d\), the binding energy scales as \(W \rightarrow \alpha^2 W\). This allows us to estimate the minimal size of the particles that form systems stable at room temperatures.

In the following, we consider different dipolar and lattice arrangements with \(N\) particles and calculate their total binding energies

\[
E_{\text{tot}} = \sum_{i < j} W_{ij} = \sum_{i < j} \lambda_{\text{m}(e)} \epsilon
\]

We find the relative stability of different particle assemblies by evaluating the average energy factor per particle, \(\bar{\epsilon}\).

The model in eq 3 describes anisotropic dipole–dipole coupling between spherical particles. When the dipolar coupling is strong, such as in Co nanocrystals\(^\text{14}\) and ionic colloidal microparticles,\(^\text{69}\) this coupling alone can determine the lattice structure. If other interparticle coupling mechanisms are relevant they can be added in the model as well.\(^\text{36}\) Here, we estimate the effect of isotropic vdW interactions between the spherical particles using the formula\(^\text{32,70}\)

\[
W_{ij}^{\text{vdW}} = -\left(\frac{A}{12d_{ij}(1 + d_{ij}/4R)} + \frac{1}{1 + d_{ij}/R + d_{ij}^2/4R^2}\right) + 2 \ln \left(\frac{d_{ij}(1 + d_{ij}/4R)}{(1 + d_{ij}/R + d_{ij}^2/4R^2)}\right)
\]

Here, \(R\) is the particle radius, \(d_{ij}\) is the distance between the \(i\)th and \(j\)th nanoparticles, and \(A\) is the Hamaker constant.

At finite temperatures, the stability of different particle arrangements (phases) is determined by their free energies. To find out which of the (two) possible phases is more stable at a given temperature \(T\) and pressure \(P\), we can evaluate the change of the Gibbs free energy associated with the transition between the arrangements, \(\Delta G = \Delta U + \Delta PV - TAS\), where \(U\) is the potential energy (\(E\) in eq 3), \(V\) is the volume, and \(S\) is the entropy of each arrangement.

**RESULTS AND DISCUSSION**

**Planar Arrangements of Dipolar Particles.** Recently, superlattices of spherical colloidal PbSe NPs were observed to form loose sh packing on conductive substrates, and explained by vertical antiferroelectric dipolar ordering.\(^\text{35}\) However, the proposed dipolar organizations may not be the most stable. Moreover, other dipolar planar structures might allow stabilization of NPs with different lattice arrangements. We study planar systems with different dipolar and lattice structures, compare their energies using eq 3, and check their stabilization with large magnetic particles (see Figure 7).

Magnetic structures with closed fluxes, such as rings and other more complex arrangements, tend to be highly stable.\(^\text{50,54,59,71,72}\) Therefore, we will investigate first planar clusters and lattices with closed fluxes. In Figure 1 (top), we show closed-flux clusters which contain \(M\) circumspheres of dipoles oriented along a tangent to the circumsphere. The central dipole points up or down. Even though, we do not optimize the dipole orientations, the closed flux guarantees that their orientations are almost correct (for plaques of 2 and higher circumspheres the dipoles should not be exactly tangential). The clusters have a nonzero quadrupole moment and belong to the \(6/mmm\) magnetic group symmetry.

Upon evaluation of the energy factor \(\bar{\epsilon}\) for the clusters in Figure 1 (top), we found that it is almost independent of \(M\) and approaches \(\bar{\epsilon} \rightarrow -2.7\). In an infinite chain of NPs with a head-to-tail orientation of
Clusters in Figure 1 (top) are stable at room temperature, function. It is useful to estimate at which sizes of NP the size of the plaques. When the number of circumcircles they tend to be further away and form the lattice, while if they are oriented in the opposite way, layers, they tend to get closer and form the to evaluate the asymptotic dependence of \( \varepsilon(N) = -2(\zeta(3) - (\zeta(2)/6N)) \rightarrow -2.404 \), where \( \zeta(k) \) is the zeta function. It is useful to estimate at which sizes of NP the clusters in Figure 1 (top) are stable at room temperature, i.e., \( \Lambda \varepsilon \approx 10 \) KT. For the saturation magnetization of \( m_s = 425 \) kA m\(^{-1}\) in cobalt ferrite MNPs, we obtain \( d_{\text{ext}} = 13.31, 11.97, 11.55 \) nm, while for CdSe NPs with the uniform dipolar density \( \rho_s = 3.265 \times 10^{-3} \) C m\(^{-2}\), we get \( d_{\text{ext}} = 9.61, 8.62, 8.34 \) nm (\( M = 1, 3, \infty \)).

**Multilayers of Honeycomb Plaques.** Next, we study multilayers of coupled honeycomb plaques. In Figure 2, we show two stable arrangements of honeycomb plaques placed on the top of each other. The total dipole–dipole interaction energies per particle of these clusters are summarized in Table 1. It is very interesting that when the dipole are oriented in the same way within the layers, they tend to get closer and form the hcp (fcc) lattice, while if they are oriented in the opposite way, they tend to be further away and form the sh lattice. Moreover, the stability of these clusters depends on the size of the plaques. When the number of circumcircles exceeds 4, the hcp lattice becomes more stable than the sh lattice. This dipole organization might explain the experimentally observed lattices.

It is also of interest to find out when the looser sh structure, stabilized here by the anisotropic dipole–dipole coupling, becomes destabilized by the isotropic vdW coupling between the particles to the extent that the structure switches to the hcp lattice arrangement. We briefly study the transition between the hcp and sh configurations in the double layer of honeycomb plaques (\( M = 1, 3 \)) with the opposite direction of dipoles in each layer. We combine eqs 3–4 to evaluate the total energy of the two arrangements as a function of the particle radius \( R \) and the saturation magnetization \( m_s \) (strength of dipolar coupling). We use this energy (\( U \)) to evaluate the difference of the Gibbs free energy of the two phases, \( \Delta G \), where their entropy is approximated by the values obtained in bulk lattices (see below) and the pressure term \( P \Delta V \) is neglected.

In Figure 3, we present the phase diagram of the two plaques calculated from \( \Delta G \), where the vdW coupling is characterized by the average Hamaker constant (metals) of \( A = 2.38 \) eV. At zero temperature, the hcp configuration dominates (lower \( E \)) when the particle radius \( R \) or magnetization \( m_s \), are small, whereas the sh configuration prevails elsewhere. At larger plaques, the hcp arrangement becomes stable at larger \( R \) and \( m_s \). To roughly simulate the presence of surfactants on the particles, we also show by the dashed lines the results obtained for looser structures, where the distance between adjacent spherical particles is 1 nm. At higher temperatures, the larger entropy of the hcp configuration becomes significant, causing the phase transition to shift toward particles with larger \( R \) and \( m_s \) (larger coupling).

In our calculation of \( \Delta G_{\text{sh-hcp}} \), we have estimated the entropy for the sh and hcp arrangements using the known bulk values (per particle) in hard sphere and side views are given.

<table>
<thead>
<tr>
<th>Layers orientation</th>
<th>circ: 1 (7)</th>
<th>circ: 2(19)</th>
<th>circ: 3(37)</th>
<th>circ: 4(61)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sh</td>
<td>-1.76</td>
<td>-2.28</td>
<td>-2.46</td>
<td>-2.53</td>
</tr>
<tr>
<td>opp.</td>
<td>-1.98</td>
<td>-1.81</td>
<td>-2.63</td>
<td>-2.41</td>
</tr>
<tr>
<td>sh</td>
<td>-1.85</td>
<td>-1.98</td>
<td>-2.44</td>
<td>-2.45</td>
</tr>
<tr>
<td>opp.</td>
<td>-2.08</td>
<td>-1.77</td>
<td>-2.65</td>
<td>-2.46</td>
</tr>
<tr>
<td>sh</td>
<td>-1.88</td>
<td>-2.02</td>
<td>-2.38</td>
<td>-2.66</td>
</tr>
<tr>
<td>opp.</td>
<td>-2.13</td>
<td>-1.79</td>
<td>-2.46</td>
<td>-2.66</td>
</tr>
</tbody>
</table>

*Note: The top row horizontally arranged numbers show the circumcircles (circ.) in these clusters. The first column numbers (1–4) give the number of layers and the mutual dipole orientation in the neighboring layers. The bold numbers show dipole orientations with minimal energies.*
polarizable substrate AV shifts toward larger the saturation magnetization, \(/C_0^2 AV_{sh}\). (Electric) Horizontal (AH) and Circular ferromagnetic (Electric) Vertical (AV), Antiferromagnetic comb Plaques with Different Orientation of Dipoles: Anti-

From Figure 3, we can starting at temperature is raised to the minimum separation of 1 nm (surfactants). When the temperature is raised to \(T = 298\) K, the hcp/sh phase boundary shifts toward larger \(m_s\) and \(R_{NP}\) (stronger coupling), since the hcp configuration has a larger entropy.

**Figure 3.** The phase diagram for magnetic NPs with a bulk vdw coupling plotted as a function of the NP-radius, \(R_{NP}\), and the saturation magnetization, \(m_s\). The NPs are arranged in two plaques with \(M = 1\) and 3 circumferences and opposite orientations of dipole moments, which are positioned on the top of each other in the hcp and sh configurations. The solid lines represent the hcp/sh phase boundary of touching NPs, while the dashed lines give the phase boundary for NPs with the minimum separation of 1 nm (surfactants). When the temperature is raised to \(T = 298\) K, the hcp/sh phase boundary shifts toward larger \(m_s\) and \(R_{NP}\) (stronger coupling), since the hcp configuration has a larger entropy.

**Figure 4.** The potential energy per particle, \(\tilde{\varepsilon}\), in a double layer of honeycomb plaques of different sizes, rotated one with respect the other by the angle of \(\alpha\); \(M = 1\) (up), \(M = 2\) (middle), \(M = 3\) (bottom). The \(\alpha = 0\) angle corresponds to the sh configuration. Solid and dashed curves correspond to the opposite and the same orientations of dipoles, respectively.

**Table 2.** The Energy Factors Per Particle, \(\bar{\varepsilon}\), in Honeycomb Plaques with Different Orientation of Dipoles: Antiferromagnetic(Electric) Vertical (AV), Antiferromagnetic (Electric) Horizontal (AH) and Circular

<table>
<thead>
<tr>
<th>layers</th>
<th>circ. (K)</th>
<th>2(19)</th>
<th>3(37)</th>
<th>4(61)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AV</td>
<td>−0.57</td>
<td>−0.69</td>
<td>−0.75</td>
</tr>
<tr>
<td></td>
<td>AH</td>
<td>−1.26</td>
<td>−1.59</td>
<td>−1.72</td>
</tr>
<tr>
<td>2</td>
<td>AV,sh</td>
<td>−1.46</td>
<td>−1.54</td>
<td>−1.59</td>
</tr>
<tr>
<td></td>
<td>AV,hcp</td>
<td>−1.06</td>
<td>−1.15</td>
<td>−1.21</td>
</tr>
<tr>
<td></td>
<td>AH,sh</td>
<td>−1.49</td>
<td>−1.75</td>
<td>−1.86</td>
</tr>
<tr>
<td>polarizable substrate</td>
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<td>−1.54</td>
<td>−1.59</td>
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<tr>
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<td>AH</td>
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<td>−1.86</td>
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<tr>
<td></td>
<td>circular</td>
<td>−1.99</td>
<td>−2.41</td>
<td>−2.55</td>
</tr>
</tbody>
</table>

\(\bar{\varepsilon}\) and \(\tilde{\varepsilon}\) double-layers with the sh and hcp lattices are considered. Bold numbers show the dipole orientations with a minimal energy.

crystals\(^{76-79}\) and replacing for simplicity \(\Delta S_{sh-hcp} \approx \Delta S_{fcc-hcp} \approx 0.001\) k per particle. Using the enthalpy differences obtained in our systems, \(\Delta H_{fcc-hcp}\), and starting at \(T = 0\) K in the sh phase in the phase diagram from Figure 3, we can find the critical NP size that would keep the system in this phase at a given temperature. At room temperature, the NPs with \(m_s = 425\) kA m\(^{-1}\) must have the diameter \(d > 5.2, 5.8\) nm for the plaques \(M = 1, 3\), respectively, to prevent the transition to the more entropic hcp arrangement. For \(d = 10\) nm, the enthalpy is already 10 times larger than the entropic term. If the vdw coupling is neglected, we can find that the critical size of NPs scales with temperature as \(d_{\text{min}} \approx T^{1/2}\).

We can extend the stability analysis to systems with honeycomb plaques of antiferromagnetic (electric), vertical (AV), and horizontal (AH) orientation of dipoles, shown in Figure 1 (bottom).\(^{35}\) Our results in Table 2 show that these dipolar open-flux arrangements are less stable than those discussed above; that is, the total energy per particle is \(\bar{\varepsilon}_{sh} > \bar{\varepsilon}_{AV}\). Similar situation holds for a double layer. We tested both sh and hcp lattices and found that the AH sh configuration is the most stable, while the AH hcp configuration is not stable.

We also calculate the energies of these clusters on an ideally polarizable substrate. Although the circular orientation of dipoles provides the largest coupling energy per particle, the AV structures gives the strongest binding to the substrate, as found experimentally.\(^{35}\) Even though the clusters with circular orientation of dipoles stabilized on the surface have the largest total binding energy per particle, we need to deposit them on the substrate already assembled, since individual NPs deposited on the surface prefer the vertical orientation. Therefore, controlling the kinetics of self-assembly is important for the design of materials with tailored properties. The kinetics depends on the substrate polarizability, the speed of solvent evaporation, the speed of particle aggregation, and other factors. Strong NP attraction to the substrate may prevent relaxation of the formed structures, resulting in malformed aggregates.\(^{14,80}\)

It is of interest to investigate how the energies of the double-layer systems change when the layers are rotated and translated with respect to each other. We examine first two identical honeycomb plaques with the same or opposite dipole circulations in the sh configurations, and rotate them around the central particle. In Figure 4, we present the obtained potential...
energy profiles for different sizes of plaques. As the plaques rotate, they acquire intermediate states between sh and hcp lattices, some of which are locally stable. These configurations can be identified with the formation of the Moire pattern.\textsuperscript{81}

Next, we explore the potential energy profile as a function of a mutual shift of the two plaques. In Figure 5 (top and bottom), we visualize these profiles for two different systems. The first one is formed by two identical plaques ($M = 1$, Figure 1 (top)) sitting on the top of each other, oriented in the same way, and mutually shifted in the common plane, while the distance between the plaques is constant. In the second system, the sizes of the two plaques are different ($M = 1$ and $M = 3$). The four insets show the potential energy when the plaques with the same (right) and opposite (left) circulations are shifted one with respect to the other (the coordinates are plotted in the units of the particle diameter).

When the vertical axis of both plaques coincide, the plaques are in the sh configuration, corresponding to the $(0,0)$ center of coordinates in Figures 5a–d. This center is the most stable point for the opposite orientations of dipoles (left). For the same dipole orientation (right), the most stable configurations lie on the circle with the radius of $r = 1/\sqrt{3}$, where we can find hcp (fcc) arrangements, except of the slightly larger distance between the plaques. Once we leave the area close to the $(0,0)$ center, a number of small local minima can be
observed, depending on the system size. The magnetic vortices in both plaques break the translational symmetry of these systems at any plaque size.

**Planar Lattices Built from Particle Plaques.** We continue to study periodic systems assembled from the above plaques. In Figure 6a,b, we show two plaques in two stable configurations, with the same and opposite circulations of dipoles at the particle boundaries as in Figure 2, respectively. In Table 3, we give the binding energies between plaques per particle at the boundary for two plaques of different sizes and dipole orientations (for example, the \( M = 3 \) plaques have eight particles at their boundary); the same and opposite orientations of dipoles in neighboring plaques favor different boundaries. As the plaques become larger, the binding energy per particle at the boundary should saturate.

We also extend this plaque binding to lattices. In Figure 6c,d, we show the lattices formed of \( M = 1 \) and \( M = 3 \) hexagonal plaques having the same (s) and opposite (o) circulations. When the magnetic fluxes circulate in the same direction, the plaque is the elementary cell of the 2D crystal. In this case, the s-type junctions allow the formation of structures without vacancies. On the other hand, when the plaques are connected with the o-type junctions, as in Figure 6e,f, their magnetic fluxes circulate in alternating directions, so the elementary cell is formed by four neighboring plaques, the same-type junctions. The o-type junctions lead to lattices with (periodic) vacancies. One can also imagine 2D lattices with combined s and o-types of junctions. Some of them can tend to form partially corrugated lattices.

**Tubular Arrangements of Dipolar Particles.** Particles with dipolar coupling can also form various tubular structures, which can be assembled into lattices. Typically, tubular structures can form rings, where the dipoles circulate around the circumference. Again, these rings can be connected with the s and o-type junctions, as shown in Figure 7a,b. The dipoles circulate in the directions shown in Figure 7j.

Other more exotic structures can also be formed. For example, we can assemble chiral tubular structures of dipolar particles, observed experimentally. These helices can have different pitch, which can be equal integer numbers for the s-type junctions, as shown in Figure 7f,k, and even numbers for the o-type junctions, as shown in Figure 7g. The s-type tubular structures have nonzero fluxes oriented along their axes, proportional to the pitch, while the o-type structures have almost zero fluxes. One can even form knots based on a right-handed or a left-handed Möbius strip with the s and o-type junctions, as depicted in Figure 7c. The dipolar particles might also be stabilized to form conical structures, as illustrated in Figure 7d. The dipoles circulate in a uniform direction spirally around the cone, similar to that of the close-packed chiral nanotube.

Apart from planar and tubular structures, other stable structures can be assembled from dipolar particles. In Figure 7e, we show a simple cubic crystallite. Within each layer of the lattice, the dipoles in each chain are antiparallel to the neighboring chains, as well as to those in the layers above or below it. The stabilization takes part in similar way as in the structures discussed before. In Figure 7h, we also show a hollow icosahedral structure, which is formed by hexagons and pentagons, with closed magnetic fluxes. The direction of dipole circulation in each face is the same, which makes the structure chiral.

**CONCLUSIONS**

We have described a rich spectrum of clusters and lattices that can be stabilized from particles with electric and magnetic dipole–dipole coupling. The dipolar coupling between large particles should be strong enough to control both their dipolar and lattice structures. We show in a phase diagram the effect of interparticle vdW coupling and entropic effects associated with different lattice arrangements at finite temperatures. The obtained results can provide guidance for the self-assembly of unique structures at different scales, but their formation might require a careful control of the particle kinetics. The assembled particles can have applications as new materials for electronics, magnetism, and optics.

**Conflict of Interest:** The authors declare no competing financial interest.

**REFERENCES AND NOTES**
