Diluted magnetic semiconductors (DMS) have received strong attention due to their application in magnetooptics,1 spintronics,2 displays, and lasers.3 Recently, it has been realized that the magnetic exchange properties of Mn2+, Eu2+, and Co2+ in semiconductor nanocrystals (NCs) can be changed due to the quantum confinement effects.4 These DMS NCs can be used to investigate and manipulate a single spin (or a small number of spins) that is embedded in a semiconductor quantum dot.5 Although a number of nanoscaled DMS systems such as Cd1−xMnxTe,6 Zn1−xMnxSe,7 and Cd1−x−yMnx+ySe8 have been thoroughly studied, we have noted that the investigation of DMS NCs is still limited to II–VI and III–V semiconductor systems. Since its exciton Bohr radius is as large as 46 nm,9 nanometer-sized lead selenide (PbSe), as a IV–VI semiconductor, offers unique access to the regime of large quantum confinement that is hard to detect in either II–VI or III–V materials.10 Although monodisperse PbSe NCs have recently been synthesized11 and their optical properties have been studied,11,12 to our knowledge, an investigation of Mn-doped PbSe (Pb1−xMnxSe) NCs has not yet been reported. As strong sp−d exchange coupling exists between the localized moment of the Mn dopant and the band electrons of PbSe, Pb1−xMnxSe NCs may show unique properties which are different from those of the pure PbSe NCs13 and should be a promising material for spin applications. We have therefore focused our interest on the investigation of Pb1−xMnxSe NCs. In this communication, we report our recent success in the preparation and the analyses of this material. The challenge in this synthesis is to make sure that the Mn2+ ions are indeed incorporated into PbSe NCs. Due to the low quality of the Mn-doped sample when being prepared at room temperature2 and the problem of Mn segregation onto the particle surface even at high temperature8 when using regular acetate precursors (for Pb2+ and Mn2+), we have to alternatively employ a special prebonded Se−Mn complex in which the existing Se−Mn bond may assist in “dragging” the Mn2+ into the PbSe lattice. Previously, Mn2(μ-SeMe)2(CO)8 as an ideal Se−Mn-containing precursor has been selected by Mikulec et al.5 when successfully synthesizing Mn-doped CdSe NCs. We accordingly adopted their choice to use a small amount of Mn2(μ-SeMe)2(CO)8 as a source of Mn2+ and conduct the synthesis at high temperature to enhance the magnitude of the doping level and to minimize the degree of lattice mismatch. In a typical experiment, organometallic precursors [2 mg of Mn2(μ-SeMe)2(CO)8 (the preparation method was referred to ref 8), 0.5 mL of 1 M lead (II) 2-ethylhexanoate (Alfa Aesar) which was predissolved in trioctylphosphate (TOP, Aldrich, 90%), and 0.7 mL of Se-TOP solution (1 M for Se)] were premixed with an additional 3 mL of TOP. The mixed solution was rapidly injected into 20 g of trioctylphosphate oxide (TOPO, Aldrich, 90%) with 0.5 mL of oleic acid (Aldrich, 90%) which was heated to 260 °C under an argon stream on a Schlenk line. The hot mixture was vigorously agitated at 260 °C for 1−10 min to produce different average-sized crystals. The crystalline growth was subsequently terminated by cooling it to room-temperature once the dispersion reached the desired size. Pb1−xMnxSe NCs were separated from the multidisperse mixture by a size-selective precipitation, i.e. by centrifugation using a pair of solvents consisting of methanol and toluene. To efficiently eliminate those Mn ions which may physically be adsorbed on the surface of NCs, the as-prepared Pb1−xMnxSe NCs were subsequently immersed into pyridine for 3 days with the assistance of ultrasunics several times (5 min at each time) to perform the ligand exchange on the surface of the size-selected NCs.14 After the pyridine treatment, the Mn concentration in 10.5 nm NCs was examined by energy dispersive spectroscopy (EDS) and inductively coupled plasma (ICP). We found a strong linear dependence between the EDS or ICP results and input concentrations of the Mn precursor as illustrated in the Supporting Information (Figure S1), indicating the presence of Mn2+ inside PbSe NCs. The ICP/EDS values will be used for all the further investigations. Figure 1 shows a transmission electron microscopic (TEM) image of the sample Pb0.985Mn0.015Se, demonstrating a short-range close-packed pattern. The Mn concentration of this sample was determined to be 1.5 mol % (EDS), and the mean crystalline size was measured as 10.5 nm with a standard deviation δ ≈ 8%. To differentiate whether the doped Mn ions are on the surface or in the PbSe NCs, we first measured the lattice constant using X-ray diffraction (XRD). A plot of the lattice parameter (a) vs molar percentage of Mn2+ together with a typical TEM diffraction pattern is shown in Figure 2. The recorded XRD patterns are provided in Figure S2 (Supporting Information). All the detectable peaks are indexed to almost the same positions as those from a standard bulk15 and from cubic PbSe NCs,11 but the measured lattice constant is different. We applied Cohen’s method16 to estimate the average lattice constant (a) mainly from the three selected XRD peaks (111), (200), and (220). We found a lattice contraction after introduction of Mn ions. For example, a = 6.107 Å for our Pb0.998Mn0.012Se...
The broad curve is due to electron’s spin interactions. The broad curve and six lines of sharp splittings (Figure S4 in Supporting Information). The broad curve is observed since the sample size is smaller than the skin depth. The nuclear spin of Mn ions is \( \frac{\hbar}{2} \); therefore, six hyperfine splittings are observed in the EPR spectra. Hyperfine splitting spectra of various Mn-concentrations were obtained by a subtraction of spin—spin interaction after it was normalized (as shown in Figure 3b). This hyperfine structure shows the electron spin—nuclear spin interactions in an isolated Mn ion. As the Mn ion is affected by other Mn ions that are randomly distributed around it, the Mn—Mn interactions should result in a reduction of the electron spin—nuclear spin interactions in an individual Mn ion. We did observe that the intensity of the spin—nuclear interactions decreases with an increase of Mn concentration. The result confirms again that the Mn ions are embedded in the lattice of our PbSe NC samples.

In summary, we have, for the first time, synthesized Mn-doped PbSe NCs. The existence of Mn\(^{2+}\) inside the PbSe NCs has been clearly demonstrated by the X-ray diffraction, SQUID, and EPR characterizations. Further investigation on these DMS NCs is significant in the spin applications, such as quantum computing.

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Supporting Information Available: EDS/ICP results, XRD patterns, SQUID data and EPR spectra. These materials are available free of charge via the Internet at http://pubs.acs.org.

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