Intercalation of alkali metals into the galleries of layered materials modifies a broad range of physical and chemical properties while also enabling their exfoliation, dispersion and functionalization; these are key steps towards many practical applications of mono- and few-layered systems. However, alkali metal intercalation (and subsequent processing) has been considered impractical for layered insulators because charge transfer into materials with large bandgaps is usually unfavorable. Here we describe a straightforward molten-metal-assisted approach that produces grams of potassium-intercalated hBN. First-principles calculations suggest that the intercalation occurs by coordination of K atoms with nitrogen vacancies which then 'pillar' the hBN layers, facilitating the infiltration of K into the hBN galleries from the edges of hBN particles, along with partial charge transfer from K to hBN layers. The K-intercalated hBN material is easily exfoliated and dispersed in tetrahydrofuran as single/few-layer crystalline hBN nanosheets or as surfactant-free aqueous dispersions when transferred to water. Furthermore, the reaction of the negatively charged hBN nanosheets with transition metal salts yields nanocomposite materials comprising of metal or metal oxide nanoparticles anchored on hBN (Pt(Np)/hBN) which exhibit exceptional catalytic properties, and overperforms when compared to commercial Pt/C.