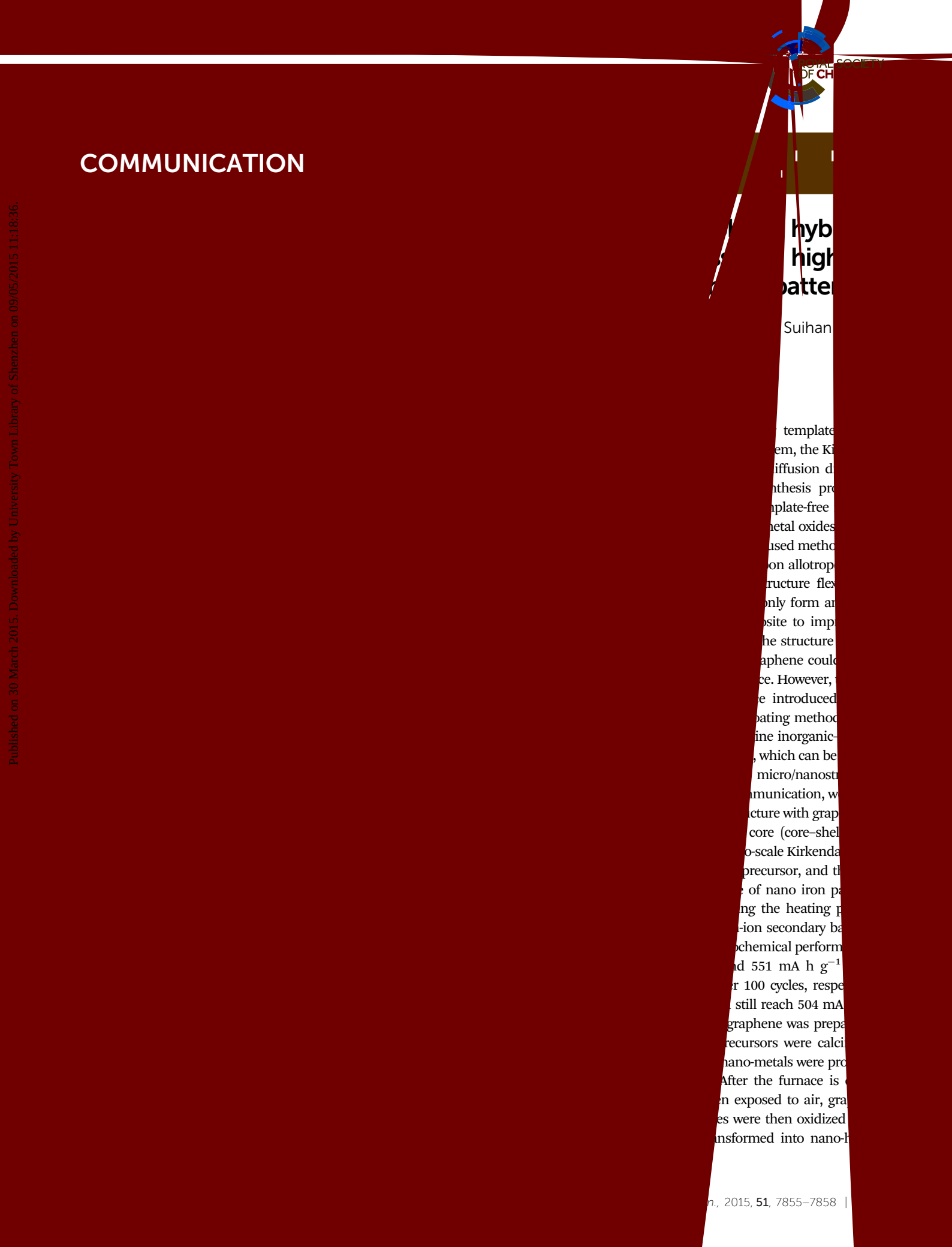
COMMUNICATION



γ

Fig. S4a (ESI†), and the three elements distribute uniformly in this hybrid. The BET specific surface area of the nano-hollow γ-Fe_2O_3@graphene is 203.24 m^2 g^{-1}. It is apparent that the specific surface areas of the mesoporous Fe_2O_3 are much larger than the solid core Fe_2O_3. Such higher surface areas can be attributed to the novel core–shell and nano-hollow structure.

Previous literature also reported that nano-hollow Fe_2O_3 can be obtained by direct decomposition of prussian blue particles. For example, Hu *et al.* first synthesized hollow PB precursors and then sintered them at 250 °C in air to get γ-Fe_2O_3 with hollow structures;[20] Zhang *et al.* first used the prepared PB to react with NaOH solution with different concentrations at room temperature to get $Fe(OH)_3$

In contrast, the capacity of the α-Fe_2O_3 electrode drops heavily during the cycles in our work (400 mA h g^{-1} after 100 cycles at the current rate of 1 C, Fig. S7a, ESI†) and in ref. 22*a*.

The cycling capacity of γ-Fe_2O_3@graphene is about 1050 mA h g^{-1} at 0.1 C (Fig. S9, ESI†), and γ-Fe_2O_3 can contribute 835.81 mA h g^{-1} (83% in weight). The left part could be ascribed to the capacitance from the carbon (graphene and amorphous carbon, 17% in weight in this composite), which is estimated to be 1260 mA h g^{-1}. In fact, we can divide the discharge capacity into two parts by 0.8 V (Fig. S7b, ESI†) and plot the capacity for the two parts with the increasing cycle number in Fig. S9 (ESI†). The capacity above 0.8 V denotes the capacity within the discharge platform, and the capacity below 0.8 V denotes the capacity for the tails in the discharge curve. We can see that the capacity above 0.8 V is on the way down, the capacity below 0.8 V is on the rise with the increasing cycle number. In order to explain this phenomenon, we did a CV test at different rates (Fig. 3d). Assuming that the current obeys a power-law relationship ($i = av^b$), where a and b are adjustable values.[26] If the value of b is equal to 0.5, then we can say that the current is controlled by semi-infinite diffusion. If b is equal to 1, it reflects a capacitive process. Here we got the b-value of 0.98 through fitting the logarithmic relationship of the sweep rate and current at 0.35 V (inset in Fig. 3d), demonstrating that capacitance plays an important role at low voltage (0.8–0.1 V) during the discharge process. We attribute this large contribution from capacitance to the graphene shells around the nano-hollow γ-Fe_2O_3@graphene particles and the huge specific surface areas.

In summary, the nano-hollow γ-Fe_2O_3@graphene with a core–shell structure has been synthesized through the Kirkendall process at room temperature. When used as anode material for LIBs, this hybrid demonstrated a remarkable electrochemical performance: a high reversible capacity of 1095, 833, and 551 mA h g^{-1} at the current rates of 0.1 C, 1 C, and 2 C after 100 cycles, respectively. When evaluated at 10 C, the capacity still can reach 504 mA h g^{-1}. This remarkable performance can be attributed to the novel nano-hollow and core–shell structure and the structure stability of γ-Fe_2O_3 ((400) peak exists all the time). At the same time, the huge contribution of capacitance is verified, which could be ascribed to the huge specific surface area and the tightly coated graphene layers. This synthetic route is simple, low-cost, eco-friendly, and especially combines Li storage with capacitance in energy storage. It enables the modified γ-Fe_2O_3 to be a promising anode material for advanced LIBs.

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