Fix some $s > 0$. Because the exponential function is monotonically increasing, the event

$$X_1 + \cdots + X_n \geq na$$

is identical to the event

$$\exp\{s(X_1 + \cdots + X_n)\} \geq e^{sna}.$$

Therefore,

$$\begin{aligned}
\mathbf{P}(X_1 + \cdots + X_n \geq na) &= \mathbf{P}\big(\exp\{s(X_1 + \cdots + X_n)\} \geq e^{sna}\big) \\
&\leq \mathbf{E}\big[\exp\{s(X_1 + \cdots + X_n)\}\big]/e^{sna} \\
&= \big(\mathbf{E}[e^{sX_1}]\big)^n/e^{sna} \\
&= \big((e^s + e^{-s})/2\big)^n/e^{sna}
\end{aligned}$$

The first inequality above is obtained by applying the Markov inequality $\mathbf{P}(Z \geq a) \leq \mathbf{E}[Z]/a$ to the nonnegative random variable $Z = \exp\{s(X_1 + \cdots + X_n)\}$. The next equality holds because the random variables X_i are independent and identically distributed, which implies that the random variables e^{sX_i} are also independent and identically distributed. The last equality follows from the expected value rule and the assumption that X_1 is equally likely to be -1 or 1.

We now bound from above the term $(e^s + e^{-s})/2$. Using the infinite Taylor series for e^s and for e^{-s}, we have

$$\begin{aligned}
\frac{1}{2}(e^s + e^{-s}) &= \frac{1}{2}\sum_{i=0}^{\infty}\frac{s^i}{i!} + \frac{1}{2}\sum_{i=0}^{\infty}\frac{(-s)^i}{i!} \\
&= \sum_{i=0}^{\infty}\frac{s^{2i}}{(2i)!} \\
&\leq \sum_{i=0}^{\infty}\frac{s^{2i}}{i! \cdot 2^i} \\
&= \sum_{i=0}^{\infty}\frac{(s^2/2)^i}{i!} \\
&= e^{s^2/2}.
\end{aligned}$$

In the above, the second equality is obtained because for odd i, $s^i + (-s)^i = 0$. The inequality that follows holds because for $i = 0$, the fact $0! = 1$ implies that the denominator terms $(2i)!$ and $i!2^i$ are both equal to 1, while for $i \geq 1$,

$$(2i)! = i! \cdot (i+1) \cdots (2i) \geq i! \cdot 2^i,$$

since there are i terms from $i+1$ to $2i$, each of which is greater than or equal to 2. The next equality is just a regrouping of terms. The last equality is the Taylor series expansion of the exponential function, applied to $e^{s^2/2}$.

Combining the above inequality with our earlier conclusions, we obtain

$$\mathbf{P}(X_1 + \cdots + X_n \geq na) \leq \left(\frac{e^{s^2/2}}{e^{sa}} \right)^n = e^{n(s^2/2 - sa)}.$$

By setting s equal to a, we obtain the desired upper bound, $e^{-na^2/s}$.